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Key Points:

- We present over 2000 measurements of methane and nitrous oxide concentrations from water column profiles and rivers across the North American Arctic Ocean
- The Bering and Chukchi Seas are dominant source regions for nitrous oxide, whereas methane production occurs primarily in the Chukchi and Beaufort Seas
- The North American Arctic Ocean currently has a negligible impact on the global methane and nitrous oxide budgets, based on annual sea-air flux calculations
Abstract

Between 2015–2018, we collected ~2000 measurements of methane (CH₄) and nitrous oxide (N₂O) concentrations in the North American Arctic Ocean during summer and early fall from water column profiles. We also obtained 25 measurements of CH₄ and N₂O concentrations in rivers along the Northwest Passage and Ellesmere Island in mid-summer 2017–2019. Our results show that N₂O is generated in the highly productive Bering and Chukchi Seas and transported northeastward, producing a persistent subsurface N₂O peak in the Beaufort Sea. The Chukchi and Beaufort Sea sediments are a significant source of CH₄ to the water column. These sedimentary sources and associated water column consumption display significant spatial gradients and interannual variability. CH₄ isotope data demonstrate the importance of CH₄ oxidation across the study region. We find that rivers are not a significant source of CH₄ or N₂O to the Arctic Ocean at the time of year sampled. The estimated annual sea-air flux across the study region (2.3 million km²) had a median (interquartile range) of 0.009 (0.002, 0.023) Tg CH₄ y⁻¹ and −0.003 (−0.013, 0.010) Tg N y⁻¹. These results suggest that the North American Arctic Ocean currently plays a negligible role in global CH₄ and N₂O budgets. Our expansive dataset, with observations at many repeat stations, provides a synopsis of present-day Arctic CH₄ and N₂O distributions and their range of variability, as well as a benchmark against which future climate-dependent changes can be evaluated.

Plain Language Summary

Methane (CH₄) and nitrous oxide (N₂O) are powerful greenhouse gases in the atmosphere, and N₂O contributes to depletion of the stratospheric ozone layer. The concentrations of these gases in the atmosphere are increasing due to human activities. Rapid warming could change Arctic emissions of CH₄ and N₂O. To date, most Arctic studies of CH₄ and N₂O have focused on small geographic regions and/or have not involved repeat observations. This limits our understanding of variability across time and space. We collected ~2000 measurements of CH₄ and N₂O across the North American Arctic Ocean between 2015 and 2018 in summer and early fall, including many observations repeated across multiple years. We also collected river measurements between 2017 and 2019. Our results show that N₂O is produced in the Bering and Chukchi Seas and transported eastward into the Beaufort Sea. The Chukchi and Beaufort Sea sediments are a considerable source of CH₄ to the water column. These sedimentary sources and the associated water column consumption display significant variability over time and space. We find that rivers are not a substantial source of CH₄ or N₂O to the Arctic Ocean in mid-summer. The calculated rate of ocean CH₄ and N₂O emission to the atmosphere suggests that North American Arctic Ocean currently plays a very minor role in the atmospheric concentrations of these two gases. By providing CH₄ and N₂O observations across the North American Arctic from 2015–2019, this study serves as a benchmark against which future changes can be evaluated.

1 Introduction

Climate change is rapidly impacting Arctic regions, where marine and terrestrial systems are currently warming at least two times faster than the global average (Cohen et al., 2014). Changes to the Arctic environment, including reductions in sea ice cover, thawing permafrost,
and altered hydrological cycles (Blunden & Arndt, 2019), may result in climate feedbacks through impacts on biogeochemical cycling and atmospheric emissions of the potent greenhouse gases methane (CH$_4$) and nitrous oxide (N$_2$O) (James et al., 2016). In addition to contributing to global warming, N$_2$O is currently the most significant ozone-depleting substance being emitted to the atmosphere (Ravishankara et al., 2009).

Some previous work has suggested that ocean warming could lead to the destabilization of subsea CH$_4$ hydrates, as well as subsea and terrestrial permafrost, but potential CH$_4$ emissions due to these processes remain highly uncertain (Archer et al., 2009; James et al., 2016; Lenton et al., 2008). Many studies have also shown elevated CH$_4$ concentrations in bottom waters and surface sediments of some Arctic shelf regions (Coffin et al., 2013; Fenwick et al., 2017; Myhre et al., 2016; Sparrow et al., 2018). However, these studies have reported a wide range of sea-air CH$_4$ flux estimates, suggesting significant variability in seafloor release rates and subsequent water column oxidation. Furthermore, the potential impact of increasing freshwater discharge (from rivers and groundwater) on CH$_4$ emissions is currently poorly understood (Lamarche-Gagnon et al., 2019; Manning et al., 2020). To date, most studies of Arctic Ocean CH$_4$ distributions have focused on a single region and/or have lacked repeat observations across multiple years (Lapham et al., 2017; Rogener et al., 2020), making extrapolations of fluxes to broader spatial and temporal scales challenging.

As with CH$_4$, the importance of the Arctic Ocean in the global N$_2$O budget is currently poorly constrained, with some regions likely acting as N$_2$O sinks and others as net sources (Fenwick et al., 2017; Yang et al., 2020; Zhan et al., 2021; Zhang et al., 2015). Thawing terrestrial permafrost may act as a net source of N$_2$O to the atmosphere, but there is no consensus on whether thawing subsea permafrost will be a net source or sink of N$_2$O (Voigt et al., 2017b; Voigt et al., 2017a). Oceanic N$_2$O production and consumption rates are controlled by a wide range of biogeochemical processes, e.g. nitrification and denitrification (Bange et al., 2010; Codispoti, 2010), and are likely to be impacted by ongoing Arctic change. Some studies have reported significant N$_2$O supersaturation can occur in the Bering and Chukchi Seas (Hirota et al., 2009; Toyoda et al., 2021; Zhan et al., 2021). Fewer published N$_2$O data exist in other North American Arctic Ocean regions, including the Northwest Passage, and Baffin Bay (Kitidis et al., 2010; Zhang et al., 2015).

Fenwick et al. (2017) presented CH$_4$ and N$_2$O concentration profiles from ~50 stations across the North American Arctic Ocean during 2015. Their observations presented the first three-dimensional picture of CH$_4$ and N$_2$O across a ~10,000 km transect of the North American Arctic. Here we combine the existing 2015 dataset with new oceanographic observations from 2016–2018 to investigate broader patterns of spatial and interannual variability in the distributions and sea-air fluxes of these gases. We also use measurements of the isotopic composition of CH$_4$ (δ$^{13}$C-CH$_4$) to investigate CH$_4$ sources and sinks in the water column and provide an updated treatment of sea-air fluxes that accounts for time-variability in both wind speed and sea ice coverage. Finally, we present CH$_4$ and N$_2$O measurements from 19 Arctic rivers to investigate the potential summertime impact of rivers on the distribution of these gases in the Arctic Ocean.

Our study region spans a broad range of hydrographic and biological regimes (section 3.1), including both high and low productivity waters, as well as shelf and slope regions of strong and weak sedimentary CH$_4$ sources. With these observations, we are able, for the first time, to characterize the persistent patterns of subsurface N$_2$O supersaturation in the Beaufort
Sea shelf and slope (observed in all four years of observations), and contrast these with the strong interannual variability of N$_2$O in the shallow Bering and Chukchi Seas. We also demonstrate strong spatial gradients and inter-annual variability in subsurface CH$_4$ distributions in the Chukchi and Beaufort Seas associated with variability in seafloor release and water column consumption. Our new multi-year dataset, based on measurements conducted in a single laboratory, enables confidence the identification of inter-annual variability. These new ocean and river measurements also provide an important benchmark of current CH$_4$ and N$_2$O distributions in the North American Arctic, enabling the detection of future changes under a rapidly warming climate.

2 Methods, data and calculations

2.1 Research expeditions

We collected oceanographic samples during annual research expeditions on three Canadian icebreakers between 2015 and 2018, during summer and early fall (early July to mid-October; see Table S1 for sampling dates). The Bering and Chukchi Sea samples came from the Distributed Biological Observatory (DBO) program conducted on the CCGS *Sir Wilfrid Laurier* (Grebmeier et al., 2019) in July of each year, while the Beaufort Sea samples primarily came from the Joint Ocean Ice Study (JOIS) program conducted on the CCGS *Louis S. St-Laurent* in September–October. These research programs involve annually repeated stations and transects. Samples from the Northwest Passage (Canadian Arctic Archipelago) primarily came from the ArcticNet and GEOTRACES sampling programs conducted on the CCGS *Amundsen* between July to September. Additional sampling from the CCGS *Amundsen* was conducted in Baffin Bay (2015, 2017, and 2018), the eastern Beaufort Sea (2016), and Hudson Bay, James Bay and Foxe Basin (2017). The research programs, priorities, and cruise tracks on the CCGS *Amundsen* vary from year to year, so the sampling stations are less consistent than those of the DBO and JOIS programs.

The full dataset includes a total of 220 water column profiles and 1977 measurements collected between 2015 and 2018. We sampled 129 unique stations, with 17, 12, 16, and 84 stations sampled in four, three, two and one years, respectively (Figure 1). Additionally, we collected 25 measurements from rivers discharging into the North American Arctic Ocean during CCGS *Amundsen* expeditions between 2017 and 2019 (19 rivers were sampled in one year and three rivers were sampled in two years). River sites were accessed via helicopter and samples were collected at a single location near the mouth of each river. The data collected from oceanographic stations during the 2019 CCGS *Amundsen* cruise will be published separately.
Figure 1. Map showing the locations of Arctic ocean sampling stations. The solid black line designates a transect connecting many of the stations and/or repeat hydrography lines. The along-transect distance is indicated in 1000 km intervals from west to east. Colored diamonds, circles, triangles, and squares represent stations sampled one, two, three, or four times, respectively. White triangles represent off-transect stations (typically >200 km from the transect line) that were only sampled in one year. Data from the off-transect stations are not presented in this paper, but are included in the accompanying dataset. Dashed black lines indicate the boundaries between different oceanic regions/seas, defined based on the International Hydrographic Organization (1953).

To focus our analysis of regional and temporal trends in the dataset, we defined a nearly 8000 km-long transect line (starting in the Bering Sea) that intersected many of the repeat stations (Figure 1). For analyses based on along-transect distance, station locations were interpolated to the nearest point on the transect. Data from stations located more than 200 km from the transect, as well as measurements collected directly over a hydrocarbon seep at Scott Inlet (northeastern coast of Baffin Island, 155 km from the transect), are not discussed in this manuscript. The Scott Inlet CH$_4$ data are described in Cramm et al. (2021). These off-transect stations (14 out of 129 stations, indicated by white triangles in Figure 1) were only sampled in one of the four years and cannot be used to investigate interannual variability in gas distributions. In accordance with the principles of findable, accessible, interoperable and reusable (FAIR) data (Wilkinson et al., 2016), all station locations are shown in Figure 1, and all data have been archived in the open access repositories PANGAEA and MEMENTO (see Open Data section).

2.2 Sample collection and analysis

CH$_4$ and N$_2$O samples were collected from Niskin bottles into glass serum vials (60 mL for concentration and 200 mL for CH$_4$ isotopic composition) and sealed with butyl rubber stoppers and aluminum crimp seals. Before sealing, saturated mercuric chloride solution was added as a preservative to each sample (50 or 100 μL for 60 mL samples, and 200 μL for 200 mL
samples). Preserved samples were stored in the dark and analyzed in the laboratory within four months of sample collection.

In 2017, 2018, and 2019, CH$_4$ and N$_2$O samples were collected from rivers in the Canadian Arctic Archipelago. Sampling sites were chosen based on their proximity to the cruise track, and reflected the wide range of geological variability within the region (Alkire et al., 2017). All sampling sites were accessed by helicopter. River water was collected using Tygon tubing secured to an extendable pole and connected to a peristaltic pump on shore. A hand-held probe (Oakton Con5 or Cole-Parmer C100) was used to measure sample temperature and conductivity in freshly collected samples. The river water depth at the sampling location was typically less than 1 m. The elevation difference between the peristaltic pump head and the water intake was always less than 1 m to prevent sample degassing due to vertical suction. Gas samples were collected in glass serum vials and treated as described above for seawater depth profile measurements.

Gas concentrations were measured using a purge and trap system coupled to a gas chromatograph-mass spectrometer (Capelle et al., 2015). Calibration was performed during every run using a Praxair certified standard (5% accuracy for CH$_4$ and N$_2$O), which was diluted with helium to prepare working standards of varying concentration. The Praxair standards were validated against an international standard prepared by NOAA and found to be equivalent to the certified values within the uncertainty of the test (~5%). As part of every run, air-equilibrated water samples were analyzed as an additional quality control measure. For concentration measurements, duplicate samples were analyzed, and the precision (standard deviation) is reported. For the entire dataset, the average standard deviation was 0.5 nmol kg$^{-1}$ for both gases, representing 10% and 3% mean relative standard deviation for CH$_4$ and N$_2$O, respectively.

In the 2018 dataset, measured N$_2$O concentrations in air-equilibrated water samples were 9 to 13% lower than the expected concentrations, and the N$_2$O concentrations measured on deep water samples (where little interannual variability is expected) displayed a similar offset. The offset may have been due to deactivation of the Nafion tube used to dry the sample, an issue which was identified after the analysis was complete. To correct for this offset, samples collected on the CCGS Amundsen, CCGS Sir Wilfrid Laurier, and CCGS Louis S. St-Laurent cruises in 2018 were increased by 9.1, 13.4, and 13.2%, respectively, which is the mean offset observed for the air-equilibrated water samples analyzed along with the samples for each cruise. After applying this correction, deep water N$_2$O measurements at repeat stations were consistent across all four years. The measured CH$_4$ concentrations in air-equilibrated water samples from 2018 did not have a systematic offset, and therefore the 2018 CH$_4$ concentrations were not adjusted.

Methane isotopic measurements ($\delta^{13}$C-CH$_4$) were conducted at the Alfred Wegener Institute using a Finnigan Delta XP Plus mass spectrometer following the method of Damm et al. (2015). The samples were pre-concentrated through a purge and trap system (Finnigan PreCon Trace Gas Pre-Concentrator). Methane carbon isotope ratios are reported as $\delta^{13}$C-CH$_4$ = $^{13}$R$_{sample}/^{13}$R$_{std}$ − 1, where $^{13}$R is the ratio of $^{13}$C/$^{12}$C in the sample or standard, respectively, and the standard is Vienna Pee Dee Belemnite (VPDB). A CO$_2$ reference gas (Air Liquide) was inserted via the reference gas port in each acquisition to correct for effects that occur in the mass spectrometer ion source. The isotope ratios of all peaks were calculated against this CO$_2$ working
standard and then referenced to VPDB. For most depths, only a single sample was analyzed, but the typical reproducibility derived from duplicates by this method is 1–1.5%.

All CTD rosette hydrographic data from each cruise has been archived with metadata documenting the calibration procedures, including the shipboard analysis of salinity samples with a salinometer and oxygen samples by Winkler titration (see Data Availability Statement).

2.3 Sea-air flux calculations

Sea-air fluxes of CH₄ and N₂O integrated over the mixed layer residence time of each gas were calculated, incorporating variability in wind speed, sea ice cover, and sea level atmospheric pressure. This approach contrasts with some previous studies based on Arctic Ocean seawater measurements that have calculated sea-air fluxes of CH₄ and N₂O using either instantaneous wind speeds (Heo et al., 2021; Hirota et al., 2009; Zhan et al., 2017), or wind speeds averaged over a fixed amount of time, e.g., one month (Li et al., 2017; Lorenson et al., 2016). As gas exchange is a nonlinear function of wind speed, high wind speeds have a disproportionately large impact on the total sea-air flux. As described in Supporting Text S1, the majority of gas transfer velocities we derived from instantaneous or monthly-averaged wind speeds were systematically biased low compared to mixed layer residence time-weighted sea-air fluxes (Wanninkhof et al., 2002, 2009). In addition, sea ice decreases the effective gas transfer velocity, and it is thus necessary to incorporate ice cover variability prior to sampling to accurately calculate the time-weighted sea-air flux (Ji et al., 2019; Ouyang et al., 2021).

Sea-air flux calculations were performed using the CCMP V2.0 ocean vector wind speed analysis product, which provides data every 6 hours with 0.25° x 0.25° resolution (https://www.remss.com, Atlas et al. (2011)). Sea ice concentration products with daily frequency and 10 km resolution from the EUMETSAT Ocean and Sea Ice Satellite Application Facility (https://osi-saf.eumetsat.int). Sea ice concentration product AMSR-2 (identifier OSI-408) was used in 2017–2018 and SSMIS (identifier OSI-401-b) was used in 2015–2016 (as product AMSR-2 was not available). Sea level atmospheric pressure data (6-hour temporal and 2.5° x 2.5° spatial resolution) were obtained from the NCEP/NCAR reanalysis product, which is provided by the NOAA-ESRL Physical Sciences Laboratory (https://psl.noaa.gov/data/gridded).

The gas transfer velocity integrated over the residence time of the gas in the mixed layer was calculated based on equations 5–7 of Teeter et al. (2018), which modify equation 6 of Reuer et al. (2007).

\[
k = \frac{\sum_{t=1}^{n} f_{open,t} k_t \omega_t}{\sum_{t=1}^{n} \omega_t} \tag{1}
\]

\[
\omega_n = 1, \quad \omega_{t+1} = (1 - f_{t+1}) \tag{2}
\]

\[
f_{i} = \frac{k_i \Delta t}{MLD}, \quad k_i \Delta t < MLD \tag{3}
\]

Here \(k\) is the gas transfer velocity calculated with the equation of Ho et al. (2006) with Schmidt numbers for CH₄ following Jähne et al. (1987) and N₂O following Wanninkhof (2014), based on
the work of Hayduk and Laudie (1974) and Wilke and Chang (1955). In equations 1–3, \( t \) is the time step, with \( t = n \) representing the most recent gas transfer velocity, and \( t = 1 \) the first measurement (60 days prior to the measurement date). The variable \( f_i \) is the fraction of the mixed layer ventilated at index \( i \), \( \omega_i \) is the weighting coefficient at index \( i \), MLD is the mixed layer depth, and \( \Delta t \) is the time interval between each index (6 h). To account for the effect of sea ice on gas exchange, the fraction of open water, \( f_{\text{open}} \) was incorporated into the method of Teeter et al. (2018), as shown in equation 1. We assumed that the gas transfer velocity scales linearly as a function of the fraction of open water (Butterworth & Miller, 2016; Manning et al., 2019).

Sea-air gas flux was calculated as

\[
F = k([C]_{\text{meas}} - [C]_{\text{eq}}). \tag{4}
\]

Here \([C]_{\text{meas}}\) and \([C]_{\text{eq}}\) are the measured and equilibrium gas concentrations, respectively, with positive values indicating a net sea to air flux (i.e., ocean outgassing). Equilibrium concentrations were calculated from the measured temperature and salinity following Wiesenburg and Guinasso (1979) for \( \text{CH}_4 \) and Weiss and Price (1980) for \( \text{N}_2\text{O} \). The atmospheric concentration for each gas was estimated based on the mean monthly flask measurements reported for Barrow, Alaska by the NOAA Earth System Research Laboratory Global Monitoring Division for June-October in each year (Dlugokencky et al., 1994; Hall et al., 2007). Dry concentrations were 328.25, 329.14, 330.11, and 330.96 ppb for \( \text{N}_2\text{O} \) and 1919.64, 1933.67, 1934.92, and 1933.50 ppb for \( \text{CH}_4 \) in 2015, 2016, 2017, and 2018, respectively (Dlugokencky et al., 2020b, 2020a). These dry atmospheric concentrations were adjusted to local sea level pressure using the mean sea level pressure from the 30 days prior to each measurement and adjusted to wet concentrations by assuming 100% relative humidity.

The mixed layer depth was defined based on a potential density difference criterion of 0.125 kg m\(^{-3}\) relative to the density at 5 m depth, using CTD profiles binned to 1 m. The mixed layer depth was set to a minimum value of 5 m.

To estimate annual sea-air fluxes and the contribution of our study region to the global budgets of \( \text{CH}_4 \) and \( \text{N}_2\text{O} \), seasonal variability in the gas transfer velocity, driven by changes in sea ice cover and wind speeds was incorporated into the calculations. The average sea-air flux was calculated over the calendar year in which the sample was collected, using 12 months of wind speed, sea ice fraction, and sea level pressure data at the sampling location. Since only one observation per year was available, we assumed a constant gas saturation anomaly (i.e., \([C]_{\text{meas}} - [C]_{\text{eq}}\) at each location over the 12-month period. We calculated fluxes for each of the five ocean regions (Bering Sea, Chukchi Sea, Beaufort Sea, Northwest Passage, and Baffin Bay/Davis Strait) by taking the median or average of all fluxes in each region within 200 km of the transect line (see section 2.1, Figure S1, and Table S2). Due to the sparse sampling, variability in stations sampled each year, and significant interannual variability among the stations, we did not perform any spatial or temporal interpolation when upscaling the fluxes to each region. We calculated the area of each ocean region using the ETOPO1 1 Arc-Minute Global Relief Model, including all locations with a seafloor depth of at least 1 m (Amante & Eakins, 2009). Although these annual flux estimates have uncertainty due to the lack of seasonally-resolved measurements and the limited number of observations, they are useful for comparison with other Arctic studies that have also estimated annual \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) fluxes based on instantaneous measurements (Hirota et
al., 2009; Thornton et al., 2016, 2020), as well as with global emissions estimates (Ciais et al., 2013; Saunois et al., 2020; Yang et al., 2020).

Further details on the calculation methodology for the regional fluxes and the impact of the time weighting approach on the calculated sea-air fluxes are provided in the Supporting Information.

3 Regional trends

3.1 Circulation and biogeochemistry in the North American Arctic Ocean

To aid in the interpretation of our datasets, we summarize some key characteristics of Arctic Ocean circulation and productivity regimes (Mclaughlin et al., 2006; Timmermans & Marshall, 2020). The Arctic Ocean is primarily salinity-stratified, with a strong halocline inhibiting convection, thereby enabling the formation of sea ice in winter (Carmack, 2007; Padman, 1995; Rudels, 2015). Freshwater inputs driving this stratification are provided via river discharge, precipitation, and inflow of Pacific-derived water through the Bering Strait (Carmack et al., 2016; Haine et al., 2015). Liquid freshwater storage in the Arctic Ocean has significantly increased over the past 40 years and is expected to increase in the future due to increased supply from these sources, as well as reductions in sea ice volume (Carmack et al., 2016; Haine et al., 2015).

In addition to representing a significant freshwater source to the Arctic Ocean, Pacific-derived waters also contain elevated nutrients, which support high rates of biological productivity in the northern Bering and Chukchi Seas (Grebmeier et al., 2006). A component of the dense and nutrient-rich Pacific-derived water flowing into the Chukchi Sea is transported eastward into the southern Beaufort Sea as a shelf break jet (von Appen & Pickart, 2012; Brugler et al., 2014), providing a subsurface source of nutrients to this region. High productivity conditions can lead to the production of N₂O through water column and sedimentary nitrification and incomplete sedimentary denitrification, and the production of CH₄ from sedimentary methanogenesis during organic matter decomposition (Bange et al., 2010; Valentine, 2011). In contrast to the Bering and Chukchi Seas, the Beaufort Sea is generally considered oligotrophic (Bergeron & Tremblay, 2014; Carmack et al., 2004).

Complex circulation patterns within the Northwest Passage (Canadian Arctic Archipelago) result from the interaction of topographic constrictions, tidal flows, and significant freshwater inputs from rivers and sea ice melt (Mclaughlin et al., 2006). These circulation patterns regulate the transport of water masses formed in the Bering/Chukchi Seas that contain unique biogeochemical signatures. In near-surface waters, there is net eastward transport toward Baffin Bay, a marginal sea located between Baffin Island and Greenland (Mclaughlin et al., 2006). At depth, westward transport of warmer, saltier Atlantic-derived waters occurs within the Northwest Passage, but the presence of sills such as Barrow Strait (average depth 175 m) effectively limits the lateral transport of these waters into the Beaufort Sea (Mclaughlin et al., 2006). Atlantic-derived waters primarily enter the central Arctic Ocean via Fram Strait, between Greenland and Svalbard, Norway (Rudels, 2015). This dense Atlantic water is not found on the
shallow Bering and Chukchi shelves, but is present throughout much of the remainder of the North American Arctic Ocean.

In Baffin Bay, surface flows are cyclonic. Northward inflow of water occurs along the Greenland shelf via the West Greenland Current (Arctic origin), and West Greenland Slope Current (North Atlantic origin). Southward outflow occurs via the Baffin Island Current, including near-surface waters from the Northwest Passage, waters from the northern archipelago (Smith Sound), and recirculation of the inflowing waters (Curry et al., 2011; Münchow et al., 2015). The exchange and ventilation of the deep and bottom waters in Baffin Bay are restricted by a sill at Davis Strait, which marks the boundary between Baffin Bay and the Labrador Sea, as well as sills within the Canadian Arctic Archipelago (Barrow Strait and Smith Sound) (Top et al., 1980; Wallace, 1985). High primary productivity has been reported in the North Water Polynya region of northern Baffin Bay, although productivity may have decreased in recent years due to increased stratification (Bergeron & Tremblay, 2014; Tremblay et al., 2002).

Prior studies have used a variety of definitions and names for the water masses present in the North American Arctic Ocean (Brugler et al., 2014; Danielson et al., 2017; Gong & Pickart, 2015; Pickart et al., 2016). In this manuscript, we focus on the eastward transport of Pacific-derived, nutrient-rich water masses. We follow the definitions of Danielson et al. (2017) where the Bering-Chukchi Winter Water is defined by temperatures between −2 and 0 °C and practical salinity between 30 and 33.5, and the Bering-Chukchi Summer Water (BCSW) is defined by temperatures between 0 and 7 °C and practical salinity between 30 and 33.5. The BCWW forms during cooling and brine rejection in winter and the BCSW primarily consists of BCWW that has subsequently warmed. A portion of the dense BCWW and BCSW is transported eastward to the Beaufort Sea along the shelf break and upper slope (von Appen & Pickart, 2012; Brugler et al., 2014; Rudels, 2015).

### 3.2 Regional profiles of CH₄ and N₂O

Figure 2 displays the median depth profiles of N₂O and CH₄ from each region, with all four years of data pooled based on potential density anomaly (σ₀), with a bin size of 0.4 kg m⁻³. Median CH₄ concentrations at all density surfaces in the Bering Sea ranged from 3.3 to 5.6 nmol kg⁻¹. In the Chukchi Sea, we observed an increase in CH₄ concentrations in the densest waters, with peak median concentrations of 11.1 nmol kg⁻¹ at a potential density anomaly (σ₀) of 26.2 kg m⁻³. The Beaufort Sea displayed a CH₄ peak at intermediate density surfaces (median concentrations were ~9.5 nmol kg⁻¹ from 24.8 to 26.0 kg m⁻³), but significant variability existed within each density surface. The elevated CH₄ concentrations and large variability in subsurface waters of the Chukchi and Beaufort Seas likely reflect the release of CH₄ from sedimentary organic matter diagenesis, as well as spatially-heterogeneous sedimentary hydrate and permafrost deposits throughout parts of the Beaufort Sea and eastern Chukchi Sea (Coffin et al., 2013; Ruppel et al., 2016). The Northwest Passage had relatively low CH₄ concentrations throughout the water column (median concentrations ranging from 3.2 to 8.3 nmol kg⁻¹), reflecting the limited sedimentary sources. In Baffin Bay and Davis Strait, the median CH₄ concentrations ranged from 1.3 to 5.1 nmol kg⁻¹. The CH₄ undersaturation observed in the stagnant deep waters of Baffin Bay reflects in situ oxidation, as well as lower atmospheric concentrations at the time of ventilation (Punshon et al., 2014).
Figure 2. Median profiles of CH₄ (a-e) and N₂O (f-j) from each region. Observations were binned into 0.4 kg m⁻³ potential density bins. The median concentration for each bin is shown with a black line, the 0.25–0.75 quantile range (interquartile range) in dark blue, and the 0.05–0.95 quantile range in light blue. The grey bar indicates the potential density anomaly (σϴ) range from 25.5 to 26.9 kg m⁻³, which represents the densest waters of the BCWW and BCSW (outlined in red on Figure 3).

In the Bering and Chukchi Seas, N₂O concentrations were highest in the densest waters. In the Bering Sea, the potential density surface 25.8 kg m⁻³ had a median N₂O concentration of 16.6 nmol kg⁻¹ (interquartile range 16.2 to 17.0 nmol kg⁻¹) and in Chukchi Sea, the potential density surface 26.2 kg m⁻³ had a median N₂O concentration of 18.9 nmol kg⁻¹ (interquartile range 16.8 to 19.8 nmol kg⁻¹). The high annual primary production and relatively low zooplankton grazing lead to substantial export of organic matter to the seafloor and active benthic ecosystems and remineralization (Campbell et al., 2009; Grebmeier et al., 2006; Sherr et al., 2009). Previous studies have suggested that the elevated N₂O concentrations observed in this region likely reflect production via incomplete denitrification in the sediments and/or nitrification in the water column or sediments (Fenwick et al., 2017; Hirota et al., 2009; Toyoda et al., 2021). The peak N₂O concentrations occur within the densest waters of the BCSW and BCWW and reflect supersaturation relative to atmospheric equilibrium (~16 nmol kg⁻¹).

Maximum N₂O concentrations in the Beaufort Sea were associated with a potential density anomaly of 26.6 kg m⁻³ and showed remarkable consistency across the four-year dataset (median concentration 18.1 nmol kg⁻¹, interquartile range 17.8 to 18.6 nmol kg⁻¹). N₂O concentrations decreased in deeper waters of the Beaufort Sea, with a median concentration of 13.2 nmol kg⁻¹ and in the densest waters sampled (σϴ = 28.2 kg m⁻³). This value is undersaturated relative to the present-day equilibrium concentration of ~16 nmol kg⁻¹, but close to equilibrium concentrations at the time of ventilation several hundred years ago, i.e. ~13 nmol
kg$^{-1}$ at 270 ppb N$_2$O (Druffel et al., 2017; Macdonald & Carmack, 1991; MacFarling Meure et al., 2006; Östlund et al., 1987). In the Northwest Passage, Baffin Bay and Davis Strait, N$_2$O concentrations were relatively homogeneous throughout the water column (median concentrations 14.0 to 16.6 nmol kg$^{-1}$), apart from the deep waters (>1200 m depth) in stagnant Baffin Bay where N$_2$O concentrations increased to ~20 nmol kg$^{-1}$. This deep N$_2$O excess is generated locally via sedimentary denitrification (Lehmann et al., 2019).

The overall distribution of N$_2$O across our survey region was thus characterized by production in the Bering and Chukchi Seas, eastward subsurface transport of this N$_2$O supersaturation into the Beaufort Sea and significantly attenuation of the N$_2$O supersaturation within the Northwest Passage. This attenuation likely reflects the mixing and dilution of Pacific-derived waters with Atlantic waters associated with the narrow channels and shallow sills within the Northwest Passage.

### 3.3 CH$_4$ and N$_2$O signatures of different water masses based on salinity, temperature and O$_2$ analysis

We characterized regional trends in CH$_4$ and N$_2$O distributions within discrete water masses using temperature-salinity plots, and by evaluating the relationship between N$_2$O saturation anomaly and apparent oxygen utilization (Figure 3). The saturation anomaly is reported as $\Delta N_2O = [N_2O]_{meas} - [N_2O]_{eq}$ (in nmol kg$^{-1}$) or $\Delta N_2O = ([N_2O]_{meas} - [N_2O]_{eq}) / [N_2O]_{eq} \times 100\%$ (in percent). Apparent oxygen utilization (AOU) is an estimate of the amount of O$_2$ consumed by respiration and is calculated as $AOU = [O_2]_{eq} - [O_2]_{meas}$. Because nitrification generates N$_2$O and consumes O$_2$, water column nitrification can generate a positive correlation between AOU and N$_2$O (Yoshinari, 1976).

The highest concentrations of CH$_4$ occurred in the Chukchi and Beaufort Seas (maximum concentration of 53 nmol kg$^{-1}$, as compared to atmospheric equilibrium of ~4 nmol kg$^{-1}$). Elevated CH$_4$ concentrations in the Chukchi and Beaufort Seas frequently occurred in the subsurface, and were likely associated with sedimentary sources (including seafloor CH$_4$ seeps, subseafloor permafrost, and CH$_4$ hydrates, etc.), as suggested in previous studies (Coffin et al., 2013; Kvenvolden et al., 1993; Lapham et al., 2017; Li et al., 2017; Lorenson et al., 2016; Matveeva et al., 2015; Sparrow et al., 2018). In addition, high CH$_4$ concentrations also occurred across a wide range of density surfaces and depths, suggesting the importance of mixing and circulation in transporting sedimentary CH$_4$ signatures. However, most of the samples with the highest CH$_4$ concentrations had temperature/salinity properties consistent with the BCWW and BCSW.

CH$_4$ concentrations in the Bering Sea, Northwest Passage and Baffin Bay were comparatively low; all samples had concentrations ≤15 nmol kg$^{-1}$, except for measurements from station 177 off Baffin Island near Cape Dyer (683 m bottom depth), which displayed peak CH$_4$ concentrations of 38 nmol kg$^{-1}$ at 247 m depth (salinity 33.5 PSS and potential temperature ~0.85 °C, Figure 3e). Seafloor CH$_4$ seeps in the Cape Dyer region have been previously reported (Punshon et al., 2014, 2019), and the peak CH$_4$ concentration occurring at mid-depth suggests the sample collection occurred offshore of the seeps.
Figure 3. Relationship between CH$_4$, N$_2$O, and water mass properties of different regions (see Figure 1 for regional boundaries). Temperature/salinity plots (a–j) showing the CH$_4$ and N$_2$O concentrations of water masses, and ΔN$_2$O versus apparent oxygen utilization plots (k–o) showing the potential density anomaly of different water masses. On (a–j), the dashed lines represent the potential density anomaly ($\sigma_0$, kg/m$^3$) and the upper and lower black rectangles denote the temperature/salinity properties of the BCSW and BCWW, respectively. The red lines indicate the potential density anomaly range 25.5 to 26.9 kg m$^{-3}$ that is highlighted on Figures 2, 5, and 7. On panel (m), the regression line for all Beaufort Sea samples with $\sigma_0 \leq$ 26.9 kg m$^{-3}$ is shown with a black dashed line. Note panels (k–n) use a different AOU range than panel (o).

In the Bering, Chukchi and Beaufort Seas, samples with the highest N$_2$O concentrations were typically associated with the BCWW as well as the coldest, most saline waters of the BCSW (potential density anomaly 25.5 to 26.9 kg m$^{-3}$). This observation is consistent with trends reported observed in 2015 (Fenwick et al., 2017). The magnitude of the supersaturation of N$_2$O within the BCWW was similar in the Chukchi and Beaufort Seas. This N$_2$O supersaturation was partially attenuated in the Northwest Passage and strongly attenuated in Baffin Bay and Davis Strait, where the influence of higher-salinity Atlantic Water becomes substantial.

Data from the shallow Bering and Chukchi Seas showed no consistent relationship between ΔN$_2$O and AOU ($r^2$ values for a linear regression between the two parameters were 0.05 and 0.04 in the Bering and Chukchi Seas, respectively). The lack of a correlation between N$_2$O and O$_2$ could be interpreted as evidence that water column nitrification is not the dominant...
source of N$_2$O in these regions (Nevison et al., 2003; Yoshinari, 1976). However, because the whole water column is ventilated annually, physical dynamics may act to erase the biogeochemical signature of nitrification on the O$_2$ and N$_2$O distributions. For example, Reeve et al. (2019) found that water column ventilation in the Chukchi Sea leads to a negative bias in fixed N losses estimated from N$_2$/Ar as compared to estimates from nutrient ratios (N:P), which are not affected by ventilation.

In the Beaufort Sea, there was a weakly positive correlation between $\Delta$N$_2$O and AOU at $\sigma_\theta \leq 26.9$ kg m$^{-3}$ ($r^2 = 0.40, p < 0.0001$). This relationship reflects mixing between the surface waters, which were near equilibrium, and subsurface waters from the Beaufort/Chukchi Seas (BCWW/BCSW). In the dense Atlantic Water of the Beaufort Sea ($\sigma_\theta > 26.9$ kg m$^{-3}$, salinity > 33.5 PSS), N$_2$O concentrations were undersaturated, reflecting the lower atmospheric concentrations at the time of ventilation of these water masses, i.e. 270 ppb compared to present-day values of 330 ppb (Druffel et al., 2017; MacFarling Meure et al., 2006). Within the Northwest Passage, $\Delta$N$_2$O was consistently close to 0 and showed no relationship with AOU ($r^2 = 0.0001$).

In Baffin Bay and Davis Strait there was a weakly positive correlation between $\Delta$N$_2$O and AOU across the entire dataset ($r^2 = 0.21, p < 0.0001$). However, this correlation was primarily driven by the $\Delta$N$_2$O and AOU increase in the deep waters of Baffin Bay below ~1000 m (Figure 3j, $\sigma_\theta \sim 27.7$ kg m$^{-3}$ potential temperature ~0 °C and salinity ~34.5 PSS; Figure 3o, AOU > 140 μmol kg$^{-1}$) and was not present throughout the region. The $\Delta$N$_2$O/AOU correlation in deep Baffin Bay is likely not a nitrification signature. Lehmann et al. (2019) used N$_2$O isotopomer data to demonstrate that the excess N$_2$O in deep Baffin Bay was generated by incomplete sedimentary denitrification and upward diffusion, whereas the AOU signature was driven by aerobic respiration in the water column.

### 3.4 CH$_4$ and N$_2$O in rivers

Although the Arctic Ocean represents less than 1% of total ocean volume, it receives over 10% of global river discharge, and this strongly seasonal discharge is increasing due to global warming (Blunden & Arndt, 2019; Peterson, 2002). The sparse measurements of CH$_4$ and N$_2$O in Arctic rivers make it difficult to quantify current and predict future impacts of rivers on current Arctic Ocean greenhouse gas budgets.

We collected 25 river CH$_4$ and N$_2$O measurements from 19 different rivers between 2017–2019 (three rivers were sampled in both 2017 and 2018), at latitudes ranging from 68 to 80 °N (Figure 4). Sampling occurred between 31 July and 26 August each year. Overall, the results indicate that rivers were not a significant source of CH$_4$ or N$_2$O to the North American Arctic Ocean at this time of year. For example, the median river CH$_4$ concentration was 7 nmol kg$^{-1}$ and 12 of 25 measurements were within 2 nmol kg$^{-1}$ of equilibrium. Additionally, 15 of the 25 measurements were undersaturated in N$_2$O (concentration range 12–19 nmol kg$^{-1}$, median 15 nmol kg$^{-1}$). All samples from Ellesmere Island were supersaturated in N$_2$O and rivers south of Lancaster Sound were undersaturated or near equilibrium in N$_2$O. The origin of the N$_2$O undersaturation is not known and could reflect physically or biologically-induced N$_2$O undersaturation in melting ice and snow, denitrification consuming N$_2$O in sediments, and/or
temperature changes that occur faster than the re-equilibration timescale (Quick et al., 2019; Randall et al., 2012).

CH$_4$ concentrations displayed significant variability across rivers, but no consistent regional trends. For example, the highest observed CH$_4$ concentration, 76 ± 4 nmol kg$^{-1}$, was found from a stream on the surface of marine-terminating Eugenie Glacier on Ellesmere Island, and the second highest CH$_4$ concentration, 24 ± 2 nmol kg$^{-1}$, occurred in the Tingmeak River on mainland North America (Figure 4). Other studies have reported similarly elevated CH$_4$ levels in glacial rivers and air in Greenland (Christiansen & Jørgensen, 2018; Lamarche-Gagnon et al., 2019). Seasonally-resolved measurements from a small river in the North American Arctic demonstrated a strong seasonality in riverine concentrations of CH$_4$ (but not N$_2$O), with the highest concentrations occurring during the early melt season (Manning et al., 2020). Our measurements in late July to late August may thus not reflect peak annual concentrations of CH$_4$ in Arctic rivers. Observations of both gas concentrations and river discharge throughout the discharge season are needed to better constrain annual greenhouse gas emissions from Arctic rivers.

![Figure 4](image)

Figure 4. River measurements of gas saturation anomalies (a) ΔCH$_4$ and (b) ΔN$_2$O, from samples collected between 2017–2019. Three rivers, indicated with a * symbol, were sampled in both 2017 and 2018. The position of the 2018 samples was shifted inshore on the map to reduce overlap. All rivers had ΔCH$_4$ ≤ 20 nmol kg$^{-1}$, except one river from Ellesmere Island, indicated with a # symbol on (a), which had ΔCH$_4$ = 72 nmol kg$^{-1}$.

4 Interannual variability in CH$_4$ and N$_2$O distributions and sea-air fluxes

Our sampling program across four consecutive years enabled us to examine interannual trends in CH$_4$ and N$_2$O distributions. We first discuss CH$_4$ (sections 4.1–4.4) and then N$_2$O
distributions (sections 4.4–4.7), and then consider the sea-air fluxes (section 4.8).

### 4.1 CH$_4$ variability at repeat stations along the transect between the Bering Sea and Northwest Passage

Across all years and sampling depths, mean and median CH$_4$ concentrations were consistently close to atmospheric equilibrium in the Bering Sea (mean 5.0 and median 4.6 nmol kg$^{-1}$) and the Northwest Passage (mean 5.2 and median 4.6 nmol kg$^{-1}$). In contrast, CH$_4$ distributions displayed strong interannual variability and a wider range in concentrations in the Chukchi and Beaufort Seas, likely due to temporal variability in sedimentary CH$_4$ sources, as well as heterogeneous production and consumption of CH$_4$ within the water column (Coffin et al., 2013; Damm et al., 2005, 2015; Fenwick et al., 2017; Kitidis et al., 2010).

Figure 5 shows concentration profiles at six representative stations that were sampled in all four years. Many of the stations with the greatest interannual variability in CH$_4$ were located in the Beaufort Sea along the continental shelf and slope (see also section 4.2), much of which lies within the gas hydrate stability zone (Lorenson et al., 2016). CH$_4$ profiles from the Beaufort Sea frequently displayed one or more subsurface maxima. For example, at station BL4, in all four years, there was a subsurface CH$_4$ peak at 50–70 m depth ($\sigma_\Theta = 24.7–25.8$ kg m$^{-3}$), but the peak CH$_4$ concentration varied from 9.5–26.2 nmol kg$^{-1}$ (Figure 5d). In 2017 and 2018 there was a second, deeper, CH$_4$ peak at BL4 at $\sigma_\Theta \approx 27.7$ (12.0 nmol kg$^{-1}$ at 280 m depth in 2017 and 11.7 nmol kg$^{-1}$ at 160 m depth in 2018) that was not observed in 2015 and 2016. For both BL4 and MK3, the highest CH$_4$ concentrations were found in 2016 (up to 26 nmol kg$^{-1}$, at $\sigma_\Theta \approx 25.8$ kg m$^{-3}$). These trends suggest significant interannual variability in CH$_4$ release from shelf and slope sediments, and potential variability in water column CH$_4$ production and consumption. Compared to stations BL4 and MK3, stations SLIP-1 in the Bering Sea, and AG5 and 312 in the Northwest Passage, displayed limited interannual variability and a narrower range in CH$_4$ concentrations. There were no apparent relationships between CH$_4$ concentrations and hydrographic water column properties across sampling years, providing further evidence for the importance of intermittent sedimentary sources of variability.
Figure 5. Depth profiles of N₂O and CH₄ concentrations at selected stations sampled in all four years. (a) Map showing station locations and distance along transect (black line, equivalent to the transect shown in Figure 1). Profiles of CH₄ (b–g) and N₂O (h–m) concentrations as a function of potential density anomaly (σθ); station names and bottom depths are indicated above each column. The grey bar highlights the density surface σθ = 25.5–26.9, which represents dense waters of the BCSW/BCWW that are transported into the Beaufort Sea. The black numbers represent distance along the transect in km.

Interannual variability in CH₄ distributions was evident along a transect through the Bering and Chukchi Seas south of Barrow Canyon (Figure 6). In the Bering Sea, CH₄ concentrations were consistently near equilibrium, apart from the bottom water at one station in the northern Bering Sea in 2018 (Figure 6j). The Chukchi Sea displayed higher CH₄ concentrations than the Bering Sea, but the locations and magnitude of peak CH₄ concentrations varied from year to year. In many cases, the highest CH₄ concentrations in the Chukchi Sea
occurred adjacent to the seafloor (Figure 2b), suggesting a sedimentary source, which is consistent with published measurements of CH$_4$ in surficial sediments in this region and reports of subseafloor permafrost in the eastern Chukchi Sea (Collett et al., 2011; Matveeva et al., 2015). In 2016 and 2018, the highest CH$_4$ concentrations occurred within the densest waters of the BCWW/BCSW (potential density $\geq$ 25.8 kg m$^{-3}$), whereas the highest CH$_4$ concentrations in 2015 and 2017 were found in less dense waters. These trends likely reflect the complex interplay of biogeochemical processes (sedimentary CH$_4$ production and water column CH$_4$ oxidation) with physical processes, such as water column stratification and sea ice formation and melt, which will affect the rate at which excess CH$_4$ is ventilated to the atmosphere.

![Figure 6](image1.png)

Figure 6. Distribution of CH$_4$, N$_2$O, and O$_2$ in the Bering and Chukchi Sea south of Barrow Canyon in 2015 (a–c), 2016 (d–f), 2017 (g–i), and 2018 (j–l). The section follows the first 900 km of the transect shown in Figures 1 and 5. The black contour line represents a potential density anomaly of 25.8 kg m$^{-3}$ (associated with the denser waters within the BCWW and BCSW), and the vertical dashed line represents the boundary between the Bering and Chukchi Seas (latitude 66.5°N). Black crosses (+) indicate sampling locations.

4.2 CH$_4$ spatial and temporal variability on a cross-slope transect in the Beaufort Sea

Repeat measurements along the BL hydrographic line in the Beaufort Sea, which spans an onshore-offshore transect, also exhibited strong interannual variability in CH$_4$ distributions (Figure 7). In 2016, a subsurface plume of CH$_4$ (up to 26 nmol kg$^{-1}$) appeared to diffuse from the sediments at ~200 m depth and be transported laterally offshore. Observations from 2017 and 2018 displayed lower peak CH$_4$ concentrations at each station, and in the both years there was a local minimum in CH$_4$ between 150–200 m depth at some of the off-shelf stations. This mid-depth CH$_4$ minimum may reflect spatial and temporal variability in CH$_4$ release along the
Beaufort slope, which has been reported in other regions (Philip et al., 2016; Veloso-Alarcón et al., 2019). The CH$_4$ distributions did not display a consistent correlation with depth, density, O$_2$, or chlorophyll (Figure 7). Similar temporal and spatial variability in CH$_4$ distributions was observed at other stations along the Beaufort Sea shelf and slope.

Figure 7. CH$_4$, N$_2$O, O$_2$, and chlorophyll $a$ distributions in the Beaufort Sea along the BL repeat hydrographic line in 2016 (a–d), 2017 (e–h) and 2018 (i–l). Black crosses (+) indicate the sampling locations and the white contour indicates water with a potential density anomaly 25.5 < $\sigma_\theta$ < 26.9 kg m$^{-3}$, equivalent to the denser waters of the BCWW and BCSW. The location of the BL line is shown in Figure 1.

Fenwick et al. (2017) identified the co-occurrence of subsurface chlorophyll and CH$_4$ maxima at many stations in the central Beaufort Sea (Canada Basin) in 2015. Most of these stations were not resampled in 2016–2018, and we did not observe this trend consistently at stations sampled repeatedly during 2015–2018 on the southern Beaufort Sea (shelf and slope regions). These observations support our hypothesis that the observed CH$_4$ supersaturation on the Beaufort slope is driven by intermittent sedimentary release, rather than water column production.

4.3 CH$_4$ distributions in the Northwest Passage, Baffin Bay, and Davis Strait

As previously discussed (section 3.2, Figure 2d–e), CH$_4$ concentrations in the Northwest Passage, Baffin Bay, and Davis Strait were generally low. Some seafloor seeps are present along the coast of Baffin Island (Cramm et al., 2021; Punshon et al., 2019). For example, as reported in Cramm et al. (2021), we measured bottom water CH$_4$ concentrations at the Scott Inlet methane seep ranging from 9 to 592 nmol kg$^{-1}$ during five repeat measurements over 24 h in 2017, and video surveys with a remotely operated vehicle confirmed the presence of active ebullition from the seafloor at this site. Punshon et al. (2019) reported bottom-water CH$_4$ concentrations of ~60
nmol kg$^{-1}$ near Scott Inlet in 2012.

The sampling stations in the Northwest Passage, Baffin Bay, and Davis Strait varied significantly from year to year, making detection of interannual variability more challenging in these regions. Nonetheless, nearly all measured CH$_4$ concentrations in these regions were less than 10 nmol kg$^{-1}$ (median 3.8, and 0.05- to 0.95-quantile 1.0 to 8.6 nmol kg$^{-1}$), suggesting limited variability, and in good agreement with previous observations (Kitidis et al., 2010; Punshon et al., 2014, 2019).

4.4 CH$_4$ isotopic measurements support occurrence of water column oxidation

Paired measurements of CH$_4$ concentration and isotope ratios can provide information on CH$_4$ sources and sinks (Whiticar, 1999). Dissolved CH$_4$ in equilibrium with the atmosphere has a $\delta^{13}$C-CH$_4$ of $\approx -46.7\permil$, and a concentration of 4 nmol kg$^{-1}$ CH$_4$ at $S = 31$ PSS, $T = 0$ °C. This $\delta^{13}$C-CH$_4$ value is based on atmospheric measurements of $-47.5\permil$ at Barrow, Alaska from 2015–2018 (White et al., 2018) and an 0.8‰ enrichment in $^{13}$C in water relative to air due to kinetic isotope fractionation during air-water gas transfer (Happell et al., 1995; Knox et al., 1992).

Microbial oxidation of CH$_4$ to CO$_2$ (which occurs through the intermediate CH$_3$OH) acts to enrich the residual CH$_4$ in $^{13}$C, resulting in an increase in $\delta^{13}$C-CH$_4$ (Coleman et al., 1981). The effect of CH$_4$ oxidation on the composition of CH$_4$ can be approximated with the following modified Rayleigh fractionation equation (Coleman et al., 1981; Mariotti et al., 1981)

$$\delta^{13}C_R = \delta^{13}C_{R,0} + \left(\frac{1}{13\alpha_{R/P}} - 1\right) \ln f.$$  \hspace{1cm} (5)

Here $f$ represents the fraction of reactant that is remaining, the subscripts $R$ and $P$ represent reactant and product, respectively, and the subscript $\theta$ represents the initial value (at $f = 1$). The fractionation factor ($\alpha$) is defined as:

$$^{13}\alpha_{R/P} = \frac{^{13}R_R}{^{13}R_P}.$$  \hspace{1cm} (6)

Other studies have fit CH$_4$ concentration and isotope data to Rayleigh fractionation equations and interpreted the resulting patterns to determine the extent of water column CH$_4$ oxidation (Damm et al., 2005, 2007, 2015; Li et al., 2021). Fenwick et al. (2017) showed that measurements of $\delta^{13}$C-CH$_4$ and [CH$_4$] from the Bering and Chukchi Seas in 2015 (water column depth $\leq 112$ m) were consistent with a Rayleigh fractionation curve with initial [CH$_4$] of 30 nmol kg$^{-1}$, initial $\delta^{13}$C-CH$_4$ of $-40\permil$ vs. VPDB and a fractionation factor $^{13}\alpha_{CH4/CH3OH} = 1.002$. This fractionation factor was similar to results reported in other studies, which are typically in the range of 1.002 to 1.025 (Coleman et al., 1981; Damm et al., 2005, 2007, 2015; Li et al., 2021; Whiticar, 1999; Whiticar & Faber, 1986). This result suggested that CH$_4$ in the Bering and Chukchi Seas reflected a relatively homogeneous source (uniform initial concentration and isotopic composition) and that this CH$_4$ underwent partial oxidation in the water column.

With our expanded multi-year dataset, we show that the Beaufort Sea data cannot be represented with a single Rayleigh relationship, and that some CH$_4$ in the Beaufort Sea is more $^{13}$C-depleted than CH$_4$ in the Bering/Chukchi Seas. The broader range of $\delta^{13}$C-CH$_4$ values in the Beaufort Sea reflects the wider range of water masses present in this region, including CH$_4$-rich waters transported eastward from the Chukchi Sea, and CH$_4$-depleted waters from the Atlantic,
all of which are likely impacted by in situ oxidation. The range of $\delta^{13}$C-CH$_4$ values also suggests that some of the endmember CH$_4$ sources within the Beaufort Sea may have a different isotopic composition compared to the Bering/Chukchi Seas. Specifically, the highest CH$_4$ sample in the Bering and Chukchi Seas had a CH$_4$ concentration of 30 nmol kg$^{-1}$ and $\delta^{13}$C-CH$_4$ of $-41\%$o. In contrast, the Beaufort Sea dataset from 2016 had four samples with CH$_4$ ranging from 24 to 27 nmol kg$^{-1}$ and $\delta^{13}$C from $-51$ to $-47\%$o (collected at stations MK1, MK4, and BL1). The Beaufort Sea isotope data also reflect the spatiotemporal variability of CH$_4$ in the Beaufort Sea: in 2015, CH$_4$ concentrations at station MK1 ranged from 2 to 9 nmol kg$^{-1}$ and $\delta^{13}$C-CH$_4$ ranged from $-39$ to $-36\%$o, whereas in 2016, the maximum CH$_4$ concentration at MK1 was 27 nmol kg$^{-1}$, with a $\delta^{13}$C-CH$_4$ of $-47\%$o (Figure 8 c-d).

Figure 8. CH$_4$ isotope data from 2015–2017. Relationship between CH$_4$ and $\delta^{13}$C-CH$_4$ for (a) all data and (b) Beaufort Sea data only. The white star represents CH$_4$ at equilibrium with the
Our $\delta^{13}$C-CH$_4$ and [CH$_4$] data in the Beaufort Sea are comparable with previous measurements of $\delta^{13}$C-CH$_4$ from the water column and seafloor in this region. On the Beaufort Sea shelf near Prudhoe Bay, Alaska (water depth from 2–38 m), Sparrow et al. (2018) reported $\delta^{13}$C-CH$_4$ of $-72$ to $-49\%$ at CH$_4$ concentrations of 10 to 51 nmol kg$^{-1}$, and used radiocarbon analyses to demonstrate the CH$_4$ was a mixture of modern and ancient sources. Hart et al. (2011) reported $\delta^{13}$C-CH$_4$ of $-55$ to $-59\%$ in a methane hydrate core collected from the Beaufort Sea slope (2538 m depth). Our samples from the Beaufort Sea had $\delta^{13}$C-CH$_4$ ranging from $-52$ to $-33\%$ at sample depths ranging from 5 to 1529 m (bottom depths from 60 to 2096 m). The observations from other research groups support our conclusion that most of our Beaufort Sea samples experienced some degree of water column CH$_4$ oxidation, based on their enriched $^{13}$C signatures relative to the methane hydrate samples, and samples from shallower shelf waters with shorter gas residence times. However, more data are needed to better characterize the spatial variability in $\delta^{13}$C-CH$_4$ across the range of potential sedimentary CH$_4$ sources affecting isotope signatures in the Arctic water column.

By limiting our analysis of the Beaufort Sea dataset to only CH$_4$ concentrations $\leq 11$ nmol kg$^{-1}$ and density surfaces $\leq 26.9$ kg m$^{-3}$ (including the BCWW/BCSW and fresh surface waters, but not denser, Atlantic-derived waters), we were able to fit a Rayleigh curve with initial [CH$_4$] of 11 nmol kg$^{-1}$, initial $\delta^{13}$C-CH$_4$ of $-42\%$ vs. VPDB and a fractionation factor $^{13}u_{\text{CH}_4/\text{CH}_3\text{OH}} = 1.006$ (Figure 8b). This Rayleigh relationship may reflect a baseline CH$_4$ source that was present throughout the lower density waters within the Beaufort Sea. A small number of samples from the Beaufort Sea had higher CH$_4$ concentrations ($\geq 15$ nmol kg$^{-1}$) and lower $\delta^{13}$C-CH$_4$ values ($\leq -45\%$), which may reflect sporadic sedimentary sources (e.g., 50 m depth at station MK1 in 2016, Figure 8c–d). High CH$_4$ concentrations within the Beaufort Sea appear to be rapidly oxidized and/or mixed with lower CH$_4$ waters, resulting in strong interannual variability in CH$_4$, as shown in Figures 5 and 7. These processes resulted in localized effects on the CH$_4$ concentration-isotope relationship.

In the Northwest Passage, Baffin Bay, and Davis Strait, $\delta^{13}$C-CH$_4$ ranged from $-43$ to $-32\%$ at CH$_4$ concentrations of 1–8 nmol kg$^{-1}$, with no clear relationship between concentration and isotopic composition (Figure 8a). All samples showed $^{13}$C enrichment relative to present-day atmospheric equilibrium ($-46.7\%$), and many of the subsurface samples were undersaturated in CH$_4$, supporting the occurrence of CH$_4$ oxidation in the water column (Punshon et al., 2014). The lower CH$_4$ concentrations observed in the Northwest Passage and Baffin Bay likely reflect the reduced importance of sedimentary CH$_4$ inputs at the stations sampled in these regions, compared to the Beaufort and Chukchi Seas.
Isotopic measurements were also performed on CH$_4$ samples from seven rivers draining into the Northwest Passage collected in 2017. The river with the highest CH$_4$ concentration (15 nmol kg$^{-1}$) had $\delta^{13}$C-CH$_4$ of $-48\%$ and the two samples with the lowest CH$_4$ concentration (4 nmol kg$^{-1}$) both had $\delta^{13}$C-CH$_4$ of $-42\%$ (Figure 8a). Given the large range of geological conditions across the rivers sampled, and likelihood of variability in $\delta^{13}$C-CH$_4$ source signatures, more data from individual rivers (e.g., at multiple locations along a single river) would be needed to verify the importance of CH$_4$ oxidation and characterize the source isotope signatures in these rivers.

### 4.5 N$_2$O variability at repeat stations between the Bering Sea and Northwest Passage

N$_2$O concentrations in the shallow Bering and Chukchi Seas showed significant interannual and spatial variability (Figure 5 and 6). This variability may reflect heterogeneity in sedimentary or water column N$_2$O production as suggested previously (Fenwick et al., 2017; Hirota et al., 2009; Toyoda et al., 2021; Zhang et al., 2015), and could also be influenced by interannual differences in physical processes, such as water column stratification, or sea ice cover. The highest N$_2$O concentrations along our surveys were most frequently associated with the BCWW and BCSW (potential density anomaly $\sigma_0 > 25.5$ kg m$^{-3}$, Figure 5). Elevated N$_2$O concentrations can accumulate in these dense waters when they are isolated from the atmosphere due to water column stratification, with subsequent ventilation to the atmosphere when the water column is mixed.

Fenwick et al. (2017) reported an increase in N$_2$O concentrations along the northeast flow path of BCWW toward the Beaufort Sea. In contrast, we did not detect such a pattern in our four-year data set (Figure 6). Rather, our results were more indicative of localized, transient N$_2$O accumulation and in the shallow Bering and Chukchi Seas, with regional and temporal differences in water column stratification and sea ice cover influencing ventilation of N$_2$O at some stations and subsurface accumulation at others. A positive correlation between N$_2$O and AOU is frequently used as evidence that water column nitrification is the dominant source of N$_2$O to the water column (Nevison et al., 2003; Yoshinari, 1976). In our measurements from the Bering, Chukchi, and Beaufort Seas, we did not observe such a correlation (Figure 3). As discussed in section 3.3, one possibility is that rapid ventilation of water in the shallow Bering and Chukchi Seas may have attenuated any N$_2$O excess generated from nitrification, such that variability in observed N$_2$O concentrations may reflect removal processes rather than source terms.

### 4.6 N$_2$O variability on a cross-slope transect in the Beaufort Sea

We observed a persistent subsurface maximum in N$_2$O associated with the BCSW/BCWW on the Beaufort Sea slope and in adjacent deeper waters. Figure 7 shows this feature along a cross-slope transect along the BL repeat hydrographic line in the western Beaufort Sea, and similar trends were present at other stations in the Beaufort Sea. The N$_2$O peak concentration at each station was typically 18–19.5 nmol kg$^{-1}$ (compared to equilibrium of ~16 nmol kg$^{-1}$), and centered at a potential density anomaly $\sigma_0$ of ~26.5 kg m$^{-3}$ and a depth of ~150
m. The peak N$_2$O concentration for each profile in the Beaufort Sea was similar to peak concentrations observed in the bottom waters of the Bering and Chukchi Seas (Figure 2g-h). In the deeper (Atlantic-derived) waters, N$_2$O concentrations decreased and became undersaturated, reflecting lower atmospheric concentrations at the time of ventilation of the Atlantic Water (minimum N$_2$O concentrations of ~12 nmol kg$^{-1}$; equilibrium relative to present-day atmospheric concentration is ~15 nmol kg$^{-1}$).

4.7 N$_2$O variability in the Northwest Passage, Baffin Bay, and Davis Strait

Our sampling stations varied significantly from year to year within the Northwest Passage, Baffin Bay, and Davis Strait. However, N$_2$O concentrations throughout these regions were usually close to equilibrium values (Figure 3), with the exception of the deepest waters of Baffin Bay where N$_2$O supersaturation was associated with sedimentary denitrification and upward diffusion into the deep waters (Lehmann et al., 2019). The surface waters of the Northwest Passage, Baffin Bay/Davis Strait, and the Beaufort Sea were frequently undersaturated in N$_2$O and this trend was likely driven by physical processes. Melting sea ice is a potential source of N$_2$O-undersaturated water, as reported by Randall et al. (2012) from sea ice samples collected in the Beaufort Sea and Northwest Passage. Solubility effects, resulting from the strong temperature-dependence of N$_2$O solubility (increasing by 4% for every 1 °C temperature decrease) could also lead to undersaturation of N$_2$O. We conclude that these regions do not exhibit strong interannual variability in summer N$_2$O distributions.

4.8 Sea-air fluxes of CH$_4$ and N$_2$O

We observed significant regional and interannual variability in CH$_4$ and N$_2$O fluxes (Table 1 and Figure 9). Across the four-year dataset, all regions acted as net sources of CH$_4$. Median CH$_4$ saturation anomalies ranged from 5 to 50%, while median short-term sea-air fluxes, integrated over the mixed layer residence time, ranged from 0.3 μmol m$^{-2}$ d$^{-1}$ in Baffin Bay to 2.1 μmol m$^{-2}$ d$^{-1}$ in the Chukchi Sea. N$_2$O was close to equilibrium values in all regions (median saturation anomalies ranged from −3 to 3%), and short-term sea-air fluxes were lowest in the Beaufort Sea (median −1.0 μmol m$^{-2}$ d$^{-1}$) and highest in the Chukchi Sea (median 0.4 μmol m$^{-2}$ d$^{-1}$).

Of the five regions sampled, the Chukchi Sea displayed the highest median sea-air fluxes of both CH$_4$ and N$_2$O, and the strongest interannual variability (Table 1 and Figure 9). Our four-year dataset suggests that the Bering and Chukchi Seas acted as a net N$_2$O sink during 2015 but a net N$_2$O source during 2016–2018, albeit with significant variability between stations (Figure 9). In this region, both CH$_4$ and N$_2$O sea-air fluxes were highest in 2016, when dense BCWW/BCSW was present near the surface at several stations (Figure 6). In contrast, during conditions of strong water column stratification (due to the presence of sea ice and/or meltwater), the BCWW and BCSW can be isolated from the surface, limiting sea-air exchange and allowing elevated levels of CH$_4$ and N$_2$O to accumulate in subsurface layers. Subsequent water column mixing leads to the ventilation of these CH$_4$ and N$_2$O-rich waters to the atmosphere.

As observed in the Chukchi Sea, Bering Sea N$_2$O fluxes were highest in 2016 (median 1.2 μmol m$^{-2}$ d$^{-1}$) and lowest in 2015 (median −0.7 μmol m$^{-2}$ d$^{-1}$) (Figure 9). The Bering Sea was a net source of CH$_4$ in all four years, but median fluxes in this region were lower than in the Chukchi Sea, likely reflecting lower sedimentary CH$_4$ sources. The Bering and Chukchi Sea sampling took place between mid to late July in each year, and annual variability in the timing
and extent of ventilation of bottom waters could contribute to the observed interannual variability in sea-air fluxes. Other groups have also reported significant spatiotemporal variability in CH$_4$ and N$_2$O fluxes and distributions in the Chukchi and Bering Seas (Cline et al., 1986; Hirota et al., 2009; Zhang et al., 2015).

Across our four-year dataset, the Beaufort Sea, Northwest Passage, and Baffin Bay/Davis Strait all acted as net N$_2$O sinks (median fluxes $-0.2$ to $-0.9 \text{ mmol m}^{-2} \text{ d}^{-1}$), with the strongest ocean uptake occurring in the Beaufort Sea. These same regions acted as net CH$_4$ sources (median fluxes 0.3 to 1.7 mmol m$^{-2}$ d$^{-1}$), with the largest sea-air flux occurring in the Northwest Passage. Most stations were supersaturated in CH$_4$ at the surface, but the highest CH$_4$ concentrations were typically observed in the subsurface. These trends may reflect competing production and loss terms, including release of CH$_4$ from sediments, production in the upper water column and/or sea ice (Damm et al., 2005, 2015), sea-air gas exchange, and consumption via gas exchange. For example, upward transport of sediment-derived CH$_4$ could potentially lead to elevated surface concentrations and sea-air fluxes at the shallowest stations where excess CH$_4$ is not fully consumed below the mixed layer (Sparrow et al., 2018).

Table 1. Short-term and annual CH$_4$ and N$_2$O sea-air fluxes (positive values represent a flux from the sea to the air), and surface saturation anomalies, based on pooled observations from 2015–2018. Median values include the 0.25- to 0.75-quantile range in square brackets, and mean values are reported with the standard deviation in parentheses. Short-term fluxes are calculated using a weighting scheme integrated over the residence time of the gas in the mixed layer, accounting for variability in wind speed and sea ice over this residence time (section 2.4). Annual fluxes are calculated using the wind speed, sea ice and sea level pressure over the calendar year in which each sample was collected (section 2.4). See Table S2 and Figure S1 for the boundaries for each region.

<table>
<thead>
<tr>
<th>Region</th>
<th>Area (km$^2$)</th>
<th>Median surface CH$_4$ saturation anomaly (%)</th>
<th>Median short-term CH$_4$ flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Mean short-term CH$_4$ flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Median annual flux (Gg CH$_4$ y$^{-1}$)</th>
<th>Mean annual flux (Gg CH$_4$ y$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>Northern Bering Sea (N = 32)</td>
<td>265 000</td>
<td>11 [−1, 50]</td>
<td>0.5 [0, 2.0]</td>
<td>1.2 (1.9)</td>
<td>1.6 [−0.1, 6.7]</td>
<td>3.7 (5.7)</td>
</tr>
<tr>
<td>Eastern Chukchi Sea (N = 53)</td>
<td>196 000</td>
<td>50 [33, 92]</td>
<td>2.2 [1.5, 4.6]</td>
<td>3.7 (4.1)</td>
<td>3.3 [1.7, 6.3]</td>
<td>4.5 (4.1)</td>
</tr>
<tr>
<td>Southern Beaufort Sea (N = 58)</td>
<td>309 000</td>
<td>18 [6, 44]</td>
<td>1.1 [0.3, 2.6]</td>
<td>2.3 (3.1)</td>
<td>0.9 [0.3, 2.2]</td>
<td>1.6 (2.0)</td>
</tr>
<tr>
<td>Northwest Passage (N= 39)</td>
<td>452 000</td>
<td>31 [9, 62]</td>
<td>1.7 [0.8, 4.0]</td>
<td>2.7 (3.2)</td>
<td>1.8 [0.7, 4.3]</td>
<td>4.0 (5.4)</td>
</tr>
<tr>
<td>Baffin Bay/ Davis Strait (N = 21)</td>
<td>1 123 000</td>
<td>5 [−4, 22]</td>
<td>0.3 [−0.2, 0.8]</td>
<td>0.4 (0.7)</td>
<td>1.8 [−0.8, 3.5]</td>
<td>1.7 (2.8)</td>
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<tr>
<td>Total (N = 203)</td>
<td>2 345 000</td>
<td></td>
<td></td>
<td></td>
<td>9 [2, 23]</td>
<td>15 (20)</td>
</tr>
<tr>
<td>Region</td>
<td>Area (km²)</td>
<td>Median surface N₂O saturation anomaly (%)</td>
<td>Median short-term N₂O flux (µmol m⁻² d⁻¹)</td>
<td>Mean short-term N₂O flux (µmol m⁻² d⁻¹)</td>
<td>Median annual flux (Gg N y⁻¹)</td>
<td>Mean annual flux (Gg N y⁻¹)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>-----------------------------------------</td>
<td>------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Northern Bering Sea (N = 32)</td>
<td>265 000</td>
<td>−1 [−4, 6]</td>
<td>−0.1 [−0.7, 1.1]</td>
<td>0.2 (1.2)</td>
<td>0 [−2.1, 7.6]</td>
<td>2.2 (6.1)</td>
</tr>
<tr>
<td>Eastern Chukchi Sea (N = 53)</td>
<td>196 000</td>
<td>3 [−3, 5]</td>
<td>0.4 [−0.4, 1.0]</td>
<td>0.5 (1.4)</td>
<td>1.0 [−1.1, 2.4]</td>
<td>1.1 (2.9)</td>
</tr>
<tr>
<td>Southern Beaufort Sea (N = 58)</td>
<td>309 000</td>
<td>−3 [−6, −2]</td>
<td>−0.9 [−1.6, −0.3]</td>
<td>−1.0 (1.5)</td>
<td>−1.0 [−2.6, −0.5]</td>
<td>−1.3 (1.7)</td>
</tr>
<tr>
<td>Northwest Passage (N = 39)</td>
<td>452 000</td>
<td>−3 [−4, −1]</td>
<td>−0.4 [−0.9, −0.1]</td>
<td>−0.4 (0.9)</td>
<td>−1.1 [−2.0, −0.4]</td>
<td>−0.6 (2.4)</td>
</tr>
<tr>
<td>Baffin Bay/Davis Strait (N = 21)</td>
<td>1 123 000</td>
<td>−2 [−7, 0]</td>
<td>−1.2 [−0.8, 0.1]</td>
<td>−0.3 (0.7)</td>
<td>−1.9 [−5.7, 0.9]</td>
<td>−1.1 (9.2)</td>
</tr>
<tr>
<td>Total (N = 203)</td>
<td>2 345 000</td>
<td></td>
<td></td>
<td></td>
<td>−3 [−13, 10]</td>
<td>0 (22)</td>
</tr>
</tbody>
</table>
Figure 9. Map of short-term sea-air fluxes (μmol m$^{-2}$ d$^{-1}$) of CH$_4$ (left column) and N$_2$O (right column) at stations in the Bering, Chukchi and eastern Beaufort Seas from 2015–2018 integrated over the residence time of each gas in the mixed layer prior to the sampling date. Dashed lines indicate boundaries between the Bering, Chukchi and Beaufort Seas. The median [interquartile range] fluxes for each year for the Bering and Chukchi Seas are reported in the lower right corner of each panel. Positive values represent a flux from the sea to the air.
To situate our results in a broader context, we compared our CH$_4$ and N$_2$O flux estimates with other recently published values from our study region. In the Chukchi Sea, Heo et al. (2021) reported mean sea-air N$_2$O fluxes of 2.3 ± 2.7 μmol m$^{-2}$ d$^{-1}$ in the southern Chukchi Sea and −1.3 ± 1.5 μmol m$^{-2}$ d$^{-1}$ in the Northern Chukchi Sea in summer 2017, based on instantaneous wind speeds at the time of sampling. Another study in the Chukchi Sea by Toyoda et al. (2021) reported sea-air N$_2$O fluxes ranging from −4.2 to 2.6 μmol m$^{-2}$ d$^{-1}$ in September to October 2014 and 2015, based on instantaneous shipboard wind speeds. These results are comparable to our mean estimates of 0.5 ± 1.4 μmol m$^{-2}$ d$^{-1}$ in the Chukchi Sea in July of 2015–2018. In the Beaufort Sea, primarily in shallow shelf waters <100 m depth, Lorenson et al. (2016) estimated summertime CH$_4$ sea-air fluxes in 1993–1995 and 2009 of ~16 μmol m$^{-2}$ d$^{-1}$, assuming a mean surface CH$_4$ of 12 nmol kg$^{-1}$. This flux rate is significantly higher than our estimates in this study, based on mean surface CH$_4$ concentrations of 4.8 nmol kg$^{-1}$. We note that we sampled stations across a broader range of water depths in the Beaufort Sea, which likely resulted in the lower mean surface CH$_4$ concentrations and sea-air fluxes compared to the study of Lorenson et al. (2016). In Davis Strait, Punshon et al. (2014) calculated mean sea-air fluxes of 1.6 μmol CH$_4$ m$^{-2}$ d$^{-1}$, while Gagné (2015) estimated N$_2$O fluxes with mean of 5 (standard deviation 8) μmol N$_2$O m$^{-2}$ d$^{-1}$ in the eastern Northwest Passage and Baffin Bay, and noted that different regions acted as sources and sinks.

Overall, the estimated annual CH$_4$ fluxes from our study region (representing 2.3 million km$^2$ or ~0.6% of the global ocean surface area) have a median value of 0.009 and mean of 0.015 Tg CH$_4$ y$^{-1}$ (Table 1). From this estimate, we conclude that the North American Arctic Ocean CH$_4$ emissions represent a small fraction (~0.1%) of global oceanic emissions (mean 9 Tg CH$_4$ y$^{-1}$, range 5–17 Tg CH$_4$), as derived from the Global Methane Budget program (Saunois et al., 2020). Methane emissions from the North American Arctic Ocean are also significantly lower than the East Siberian Arctic Shelf, where sea-air fluxes of ~3 Tg CH$_4$ y$^{-1}$ have been estimated by Thornton et al. (2016, 2020). Our results thus suggest that the North American Arctic Ocean currently plays a small role in the global ocean CH$_4$ budget.

The estimated annual N$_2$O fluxes from our study region have a median of −0.003 and mean of 0 Tg N y$^{-1}$, with median surface concentrations across all regions within 3% of atmospheric equilibrium. A recent study estimated global oceanic N$_2$O emissions are 4.2 ±1.0 Tg N y$^{-1}$ (Yang et al., 2020), which is similar to previous estimates from the IPCC AR5 report of 3.8 (1.8–9.4) Tg N y$^{-1}$ (Ciais et al., 2013). These results suggest that the North American Arctic Ocean also likely plays a small role in the global budget of N$_2$O.

We note the potential for strong seasonality in near-surface gas saturation state and concentrations in the Arctic Ocean, for example due to accumulation of gases under ice during winter and rapid ventilation during ice melt (Kvenvolden et al., 1993; Manning et al., 2020). This seasonality and its impact on sea-air fluxes could not be assessed in this study, due to the timing of the field campaigns; however, this remains an important area for future work.
5 Conclusions

Based on extensive measurements between 2015–2019, we have characterized spatial and interannual variability in CH$_4$ and N$_2$O water column distributions and sea-air fluxes across a ~7000 km transect of North American Arctic Ocean. Our results show that N$_2$O is generated within the highly productive Bering and Chukchi Seas and transported into the Beaufort Sea, where it forms a persistent subsurface maximum across years. CH$_4$ distributions are more dynamic, with the highest concentrations and greatest variability occurring at repeat stations on the Beaufort Sea shelf and slope, likely under the influence of sedimentary sources. Calculated sea-air fluxes, accounting for variability in wind speed and sea ice coverage, demonstrate that the North American Arctic Ocean currently plays a small role in the global budgets of CH$_4$ and N$_2$O. Continued monitoring programs will enable scientists to determine how anthropogenic climate change is altering the cycling of CH$_4$ and N$_2$O in these regions.

Data Availability Statement

All CH$_4$, N$_2$O, temperature, salinity, pressure, O$_2$, and δ$^{13}$C-CH$_4$ data, as well as derived sea-air flux estimates, have been submitted to PANGAEA, and a DOI will be included in the final published manuscript. For early access to the data, please contact the corresponding author (cmanning@alum.mit.edu).

Atmospheric CH$_4$ and N$_2$O concentrations and δ$^{13}$C-CH$_4$ values from Barrow, Alaska are available from the NOAA Earth System Research Laboratories Global Monitoring Division website (https://doi.org/10.15138/53g1-x417, https://doi.org/10.15138/VNCZ-M766). The CCMP V2.0 ocean vector wind speed analysis product is available from https://www.remss.com. Sea ice concentration products are available from EUMETSAT OSI-SAF (https://osi-saf.eumetsat.int/). The NCEP/NCAR sea level reanalysis product is available from https://psl.noaa.gov/data/gridded/. Bathymetric data is from the NASA ETOP01 1 Arc-Minute Global Relief Model (Amante & Eakins, 2009; NOAA National Geophysical Data Center, 2009).

Ancillary biogeochemical and CTD rosette data collected through the Beaufort Gyre Exploration Project is available at https://www2.whoi.edu/site/beaufortgyre/data/ctd-and-geochemistry/ and ancillary biogeochemical and CTD rosette data from the DBO program is available at the NSF Arctic Data Center (https://doi.org/10.5065/D6QN6544, https://doi.org/10.18739/A23B5W875 https://doi.org/10.18739/A2P843X00 for 2015, 2016, and 2017, respectively). Ancillary CTD data from the ArcticNet/Amundsen Science is available through the Polar Data Catalogue (Amundsen Science Data Collection, 2020) at http://doi.org/10.5884/12713.

Acknowledgments

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Fisheries and Oceans Canada at the Institute of Ocean Sciences. The samples collected on the CCGS Louis S. St-Laurent were collected as part of the Joint Ocean Ice Studies (JOIS) program lead by Fisheries and Oceans Canada at the Institute of Ocean Sciences in collaboration with the NSF Arctic Observing Network’s Beaufort Gyre Observing System, led by researchers from Woods Hole Oceanographic Institution. Data are made available by the Beaufort Gyre Exploration Project based at Woods Hole Oceanographic Institution. Additional funding sources for the research include an NSERC postdoctoral fellowship to CCMM, NSERC Alexander Graham Bell fellowship to RWI, NSERC Discovery Grant to PDT and a POLAR Northern Scientific Training Program Grant to RWI.

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Supporting Information for


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Introduction

The Supporting Information includes the following materials: Text S1, which describes the impact of calculation methodology on the sea-air flux estimates; Figure S1, which shows the regions used to calculate annual sea-air fluxes; Table S1, which lists the timing and number of samples for each research cruise; and Table S2, which lists the latitude and longitude limits for the regions used to calculate annual sea-air fluxes.

Text S1. Impact of methodology on calculated sea-air fluxes

Gas transfer velocities and sea-air fluxes integrated over the mixed layer gas residence time differed significantly from those calculated using instantaneous wind speeds. The median ratio of the instantaneous flux to the 60-day weighted flux was 0.50 (interquartile range 0.16 to 1.22) and 0.44 (interquartile range 0.16 to 1.23) for CH4 and N2O, respectively. The lower instantaneous fluxes result, in part, from the quadratic dependence of gas transfer velocities on wind speed, such that high wind speeds play a disproportionate role in driving sea-air flux over the residence time of mixed layer gases (Wanninkhof et al., 2009). We thus recommend that future studies use a time-weighted approach when calculating short-term sea-air fluxes from instantaneous water column dissolved gas measurements.
We note that for 94% of the stations, the mixed layer residence time of CH$_4$ and N$_2$O was significantly less than 30 days, and similar sea-air fluxes were derived with either a 30-day or 60-day weighting period (difference of 5% or less). At the remaining 6% of stations, the 30-day weighting was most commonly biased low compared to the 60-day weighting (the ratio of the 30-day to 60-day weighted fluxes ranged from 0.74 to 1.13). In general, stations with a longer mixed layer gas residence time (deep mixed layer depths and/or low instantaneous gas transfer velocity) were most likely to have 30-day weighted fluxes that were significantly lower than the 60-day weighted fluxes.

The difference between the residence time-integrated fluxes (short-term fluxes) and the annual fluxes varied significantly by region. For example, the median daily CH$_4$ flux from the Northwest Passage was 0.7 and 1.7 μmol m$^{-2}$ d$^{-1}$ when calculated using the annual approach and with the residence time-integrated approach, respectively. In contrast, the median daily CH$_4$ flux from all stations in the Bering Sea was higher when calculated over a 12-month period than when derived from the residence time-integrated approach (1.0 and 0.5 μmol m$^{-2}$ d$^{-1}$, respectively). In the Northwest Passage, high ice cover for most of the year reduced the gas transfer velocity, causing the median fluxes to be lower when 12 months of environmental data were considered. In the Bering Sea, the annual fluxes were higher than the short-term fluxes because the gas transfer velocity was highest in months when samples were not collected, and because the ice-covered season in the Bering Sea is shorter compared to the Northwest Passage. Since samples were only collected one time per year, our annual estimates do not account for seasonal variability in gas concentrations.

Figure S1. Regional boundaries and station locations used in annual flux calculations (see Table S2 for more details).
### Table S1. Summary of research cruise dates, regions, and number of stations included in this study

<table>
<thead>
<tr>
<th>Ship (CCGS)</th>
<th>Year</th>
<th>Cruise ID</th>
<th>Sampling dates</th>
<th>Number of stations</th>
<th>Region</th>
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<tbody>
<tr>
<td>Laurier</td>
<td>2015</td>
<td>2015-07</td>
<td>Jul 14–21</td>
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<td>Bering and Chukchi Seas</td>
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<td>2017-93</td>
<td>Jul 14–22</td>
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<td>Bering and Chukchi Seas</td>
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<tr>
<td>St-Laurent</td>
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<td>2015-06</td>
<td>Sep 21–Oct 14</td>
<td>13 ocean</td>
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<td>2016-16</td>
<td>Sep 23–Oct 15</td>
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<td>Beaufort Sea and southwestern Northwest Passage</td>
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<td>2017-11</td>
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<td>2018-81</td>
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<td>Amundsen</td>
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<td>AN1902</td>
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<td>10 rivers*</td>
<td>Near Ellesmere Island and eastern Northwest Passage</td>
</tr>
</tbody>
</table>

*Oceanographic data from the Amundsen 2019 expedition will be published in a separate manuscript.*
Table S2. Latitude and longitude boundaries for calculating regional fluxes. For the Northwest Passage, all observations from regions 4a and 4b were pooled to calculate the annual fluxes over the total area of 452 000 km$^2$. For Baffin Bay/Davis Strait, all observations from regions 5a and 5b were pooled to calculate the annual fluxes over the total area of 1 123 000 km$^2$.

<table>
<thead>
<tr>
<th>Region #</th>
<th>Region</th>
<th>Min lon (°)</th>
<th>Max lon (°)</th>
<th>Min lat (°)</th>
<th>Max lat (°)</th>
<th>Area (km$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Northern Bering Sea</td>
<td>-176</td>
<td>-160</td>
<td>61.5</td>
<td>66.5</td>
<td>265 000</td>
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<td>2</td>
<td>Eastern Chukchi Sea</td>
<td>-170</td>
<td>-155</td>
<td>66.5</td>
<td>72</td>
<td>196 000</td>
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<tr>
<td>3</td>
<td>Southern Beaufort Sea</td>
<td>-155</td>
<td>-125</td>
<td>68</td>
<td>72.5</td>
<td>309 000</td>
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<tr>
<td>4a</td>
<td>Northwest Passage – southern portion</td>
<td>-125</td>
<td>-85</td>
<td>67</td>
<td>71.5</td>
<td>287 000</td>
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<tr>
<td>4b</td>
<td>Northwest Passage – northeast portion</td>
<td>-105</td>
<td>-80</td>
<td>71.5</td>
<td>75</td>
<td>165 000</td>
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<td>4</td>
<td>Northwest Passage – total</td>
<td></td>
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<tr>
<td>5a</td>
<td>Baffin Bay – northern portion</td>
<td>-80</td>
<td>-50</td>
<td>70</td>
<td>78</td>
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<tr>
<td>5b</td>
<td>Baffin Bay/Davis Strait – southern portion</td>
<td>-66.5</td>
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<td>60</td>
<td>70</td>
<td>697 000</td>
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<tr>
<td>5</td>
<td>Baffin Bay/Davis Strait – total</td>
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<td></td>
<td></td>
<td></td>
<td>1 123 000</td>
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</tbody>
</table>

References