Methane and nitrous oxide distributions across the North American Arctic Ocean during summer, 2015

by

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Abstract

We collected Arctic Ocean water column samples for methane (CH₄) and nitrous oxide (N₂O) analysis on three separate cruises in the summer and fall of 2015, covering a ~10,000 km transect from the Bering Sea to Baffin Bay. Our sampling program provides a large-scale, three-dimensional view of methane and nitrous oxide concentrations across contrasting hydrographic environments, from the deep oligotrophic waters of the deep Canada Basin and Baffin Bay, to the productive continental shelf regions of the Bering and Chukchi Shelves. Percent saturation relative to atmospheric equilibrium ranged from 30-800% and 75-145% for CH₄ and N₂O, respectively, with the highest concentrations of both gases occurring in waters overlying the continental shelf in the northern Chukchi Sea. Nitrification and denitrification in the sediments of the Bering and Chukchi Shelves constituted a major source of N₂O to the water column, and the resulting high N₂O concentrations were transported across the entire North American Arctic. Methane sources to the water column were more spatially heterogeneous, reflecting a greater variety of hydrographic influences, including likely inputs from sediments, rivers, and sea ice processes. Localized regions of high CH₄ concentrations were observed at various locations across our sampling transect, but unlike N₂O, CH₄ was rapidly consumed through microbial oxidation, as shown by the ¹³C enrichment of CH₄ at low concentrations. High CH₄ signatures were thus more localized across our sampling region. For both CH₄ and N₂O, surface super-saturation and sea-air fluxes were generally low across the region, with values of $1.3 \pm 1.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ and $-0.52 \pm 1.0 \mu\text{mol m}^{-2} \text{d}^{-1}$, for CH₄ and N₂O, respectively. Low surface water concentrations were at least partially attributable to dilution by low CH₄ and N₂O fresh water. Our results provide insight into the factors controlling the distribution of CH₄ and N₂O in the North American Arctic Ocean, and an important baseline data set against which future changes can be assessed.

Preface

This dissertation is based on a concept formed by my supervisor (Dr. Philippe Tortell) and myself. Fieldwork and sample collection was done by me, Dr. Tortell, and Department of Fisheries and Oceans scientists, Sarah Zimmermann and Bill Williams. Nutrient samples and CTD data for SWL 2015-09 and LSSL 2015-09 were collected and analyzed by the Institute of Ocean Sciences. Ammonium samples for SWL 2015-09 were collected by Lee Cooper and analyzed by the Nutrient Analytical Services Laboratory at the University of Maryland. Nutrient samples for ArcticNet 1502 were collected and analyzed by the research group of Jean Eric Tremblay (Université Laval). Ellen Damm (Alfred Wegner Institute, Bremerhaven, Germany) analyzed the $\delta^{13}\text{C}_{\text{CH}_4}$ samples and helped interpret the data. I was responsible for the analysis of CH_4 and N_2O samples using GC-MS, interpretation of data, and writing of the dissertation. Dr. Tortell thoroughly edited the thesis, provided advice and ideas, and helped interpret data. David Capelle, Ellen Damm, Kristina Brown, and Svein Vagle contributed valuable edits. A version of this thesis will be submitted as a manuscript with co-authors Philippe Tortell, David Capelle, Ellen Damm, Svein Vagle, Bill Williams, and Sarah Zimmermann.

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List of Abbreviations

ACW	Alaska Coastal Water
AOU	Apparent oxygen utilization
AW	Atlantic Water
BSW	Bering Sea Water
CAA	Canadian Arctic Archipelago
CH ₄	Methane
N ₂ O	Nitrous oxide
NH ₄ ⁺	Ammonium
NO ₃ ⁻	Nitrate
NO ₂ ⁻	Nitrite
O ₂	Oxygen
PML	Polar Mixed Layer
PSW	Pacific Summer Water
PW	Pacific Water
PWW	Pacific Winter Water
UHL	Upper Halocline Layer

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for Elaine and Don

1

Introduction

After carbon dioxide, methane (CH_4) and nitrous oxide (N_2O) are the two greenhouse gases that have most influenced climate warming over the past 250 years [IPCC, 2013]. While atmospheric concentrations of CH_4 and N_2O have been relatively stable for the past 12,000 years, transitions from glacial to interglacial climates have previously been accompanied by large atmospheric increases in both of these gases. More recently, the atmospheric concentrations of these gases have increased by 165% and 20%, respectively, since preindustrial times, as a result of various anthropogenic activities. The current values (1910 and 328 ppb for CH_4 and N_2O , respectively) have no precedent in the past 800,000 years (Data provided by NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA; <http://esrl.noaa.gov/gmd/>) [Schilt *et al.*, 2010]. Although the contribution of CH_4 and N_2O to radiative forcing in the atmosphere is clear, the cycling of these gases among various global reservoirs is still relatively poorly understood. Understanding the global budget and cycling of CH_4 and N_2O is a primary research objective in the Earth Sciences.

1.1 CH_4 AND N_2O IN THE OCEAN

The ocean plays a key role in the global cycles of greenhouse gases, including N_2O , and to a lesser extent, CH_4 . Surface ocean waters are estimated to account for ~2 and 20-60 % of the total emissions of CH_4 and N_2O to the atmosphere, respectively, resulting from a series of complex production and consumption processes [Reeburgh, 2007; IPCC, 2013]. A variety of biologically-mediated processes produce and consume CH_4 and N_2O within the ocean and the sediments that lie underneath. Depending on environmental conditions, the ocean can be a net source or sink of these gases.

N₂O cycling in the marine environment is controlled by two processes: nitrification and denitrification. The former, which is thought to be the dominant source of oceanic N₂O, is completed in two steps. The first, carried out by ammonia-oxidizing bacteria, oxidizes ammonium (NH₄⁺) to NO₂⁻. The decomposition of NH₂OH, an intermediate in the oxidation of NH₃ to NO₂⁻, produces N₂O as a by-product. The second step, performed by nitrite-oxidizing bacteria, oxidizes NO₂⁻ to NO₃⁻. Although nitrification is an aerobic process, N₂O yields are enhanced under low oxygen conditions. This is thought to be because of the “nitrifier-denitrification” process, or the tendency of nitrifiers to reduce NO₂⁻ to N₂O when they are O₂-limited [Codispoti *et al.*, 2005]. Denitrification is another key process in the N₂O cycle. This pathway is limited to suboxic to anoxic conditions, and reduces fixed nitrogen (NO₃⁻) to nitrogen gas (N₂), producing N₂O as an intermediate. At oxygen concentrations near the upper limit for denitrification, N₂O is mostly released, resulting in a net production of N₂O [Codispoti *et al.*, 2005]. Under low oxygen conditions, however, well-established denitrification systems proceed to completion, resulting in the biological consumption of N₂O. The highest production of N₂O occurs at the boundaries of oxygen minimum zones, where nitrification and incomplete denitrification occur simultaneously, yielding elevated N₂O concentrations [Codispoti *et al.*, 2005].

Sources of CH₄ to the ocean are varied, including inputs from gas hydrates (frozen CH₄ structures), abiotic serpentinization at mid-ocean ridges, and seepage from hydrocarbon deposits [Reeburgh, 2007]. The majority of CH₄ in the ocean likely is produced through sedimentary methanogenesis, during the anaerobic breakdown of organic matter [Reeburgh, 2007], and subsequent diffusion into the water column. Additional sources of CH₄ may come from freshwater runoff from regions with anaerobic sediments. Despite relatively large contributions from these sources, the CH₄ concentrations in much of the ocean remain below atmospheric saturation due to intense aerobic and anaerobic microbial oxidation in both the sediments and the water column. However, somewhat paradoxically, the well-oxygenated surface layer of the ocean sometimes contains a CH₄ maximum. Several hypotheses have been proposed to explain this enigma, including CH₄ production in the anoxic microenvironments such as the guts of zooplankton or within sinking particles [eg., Oremland, 1979; De Angelis and Lee, 1994; Karl and Tilbrook, 1994], the cleavage of methylated substrates by bacteria or phytoplankton [Karl *et al.*, 2008;

Damm et al., 2010], and advection from regions with hydrocarbon seeps or destabilized gas hydrates [*Naqvi et al.*, 2010 and references therein]. The cause(s) of this apparent 'methane paradox' remain poorly understood.

Kinetic isotope effects resulting from the production and oxidation of CH₄ impart a signature on the stable isotopic composition of CH₄ which can be used to discern between different CH₄ sources and differentiate between the operation of distinct processes [*Reeburgh*, 2007]. CH₄ from biogenic sources tends to have a $\delta^{13}\text{C}_{\text{CH}_4}$ value of <-50‰ VPDB, while CH₄ of thermogenic origin has a $\delta^{13}\text{C}_{\text{CH}_4}$ value of >-50‰ [*Whiticar*, 1999]. As light CH₄ is preferentially oxidized by microbes, the CH₄ pool becomes increasingly heavy as it is exposed to oxidative processes. This property can therefore be used to determine whether a decreasing CH₄ concentration is due to mixing or dilution, or due to biological oxidation [*Reeburgh*, 2007]. Previous studies have used this to determine the flow paths of CH₄, understand CH₄ cycling in ice-surrounded open areas, and identify recently biologically-produced CH₄ in the surface ocean [*Damm et al.*, 2005, 2007, 2008; *Sasakawa et al.*, 2008].

Among the various environmental conditions influencing CH₄ and N₂O cycling, oxygen concentrations are particularly important. As discussed above, low oxygen concentrations favour the production of both gases. Continental shelf seas, particularly those where low oxygen waters are exposed to the surface layers, or those that are underlain by low oxygen sediments, can release large quantities of CH₄ and N₂O to the atmosphere [*Nevison et al.*, 2004; *Naqvi et al.*, 2010]. Major marine oxygen-deficient zones in upwelling systems, such as those off Peru and Chile and in the Arabian Sea, have been linked to high sea-air fluxes of CH₄ and N₂O [*Bange et al.*, 1998; *Fariás et al.*, 2009]. The Peruvian upwelling system has been shown to contain some of the highest near-surface N₂O concentrations in the world, while measured sea-air fluxes of CH₄ on the Chilean margin range up to 59 $\mu\text{mol m}^{-2} \text{d}^{-1}$ [*Naqvi et al.*, 2010 and references therein]. In addition, regimes with abundant supplies of organic matter to the sediments, such as over the Namibian and Indian continental shelves, contain some of the highest near-surface CH₄ and N₂O concentrations in the open ocean, reaching up to 2900 nmol/L and 436 nmol/L, respectively [*Naqvi et al.*, 2006, 2010; *Brüchert et al.*, 2009]. However, many coastal and low oxygen areas have not been well-studied. High uncertainty in the estimates of global

oceanic emissions of CH₄ and N₂O exists due to the poor sampling resolution in key regions and large ambiguity in sea-air fluxes in many under-sampled areas.

1.2 CH₄ AND N₂O IN THE ARCTIC OCEAN

The Arctic Ocean is thought to be a potentially significant source of CH₄ and N₂O to the atmosphere, and one that is particularly poorly sampled. The Arctic Ocean's large, shallow continental shelves are sites of significant CH₄ and N₂O production and emission. CH₄ and N₂O super-saturation of up to 125% and ~500%, respectively, has been documented in the surface waters of the Chukchi Sea [Savvichev *et al.*, 2007; Hirota *et al.*, 2009]. The high carbon export in this region is thought to generate CH₄ and N₂O through the decomposition of organic matter in the sediments [Savvichev *et al.*, 2007; Chang and Devol, 2009; Hirota *et al.*, 2009]. In addition, very high surface concentrations of CH₄ in the Eurasian Seas, (mean 18 nmol/L), has been attributed to the thawing of subsea permafrost on these marginal shelves [Shakhova *et al.*, 2010a; Kosmach *et al.*, 2015], while a lesser degree of CH₄ super-saturation has been previously found in the permafrost-free Chukchi Sea [Savvichev *et al.*, 2007; Kosmach *et al.*, 2015]. Sea ice also plays a role in regulating these gases by restricting sea-air flux and diluting surface water with low- CH₄ and N₂O melt water [Randall *et al.*, 2012; He *et al.*, 2013]. Recently, sea ice processes have been identified as potential CH₄ and N₂O sources associated with microbial activity in anoxic brine channels [Damm *et al.*, 2015a]. In the surface water of the Northwest Passage, the highest CH₄ and N₂O concentrations were under sea ice, while much lower concentrations were observed in open ocean [Kitidis *et al.*, 2010].

Examination of Arctic CH₄ and N₂O sources is particularly important in light of the rapid climate-dependent changes occurring in this region. Changes caused by warming alter the biology, chemistry, and circulation of the ocean. Arctic sea ice cover has been drastically thinned and reduced over the past 30 years [Maslanik *et al.*, 2011]. This reduction in sea ice could augment the sea-air flux of CH₄ and N₂O by lessening exposure to consumption processes [Kitidis *et al.*, 2010], but it may also influence the carbon and nitrogen cycles. The shorter ice cover period and longer growing season has resulted in a 30% increase in primary production in the Arctic Ocean and a northward shift of many species [Arrigo and van Dijken, 2011, 2015; Grebmeier, 2012]. The increased flux of organic

matter to the sediments may result in greater CH₄ and N₂O production due to decomposition processes. The thawing of subsea permafrost may introduce additional organic matter to the system, further increasing the production of these gases, as has been shown in the Eastern Siberian Arctic Seas [Shakhova *et al.*, 2015] and wetland sites in the high Arctic [Elberling *et al.*, 2010]. However, new evidence suggests that efficient anaerobic oxidation of CH₄ within the sediments may have the capacity to drastically limit the CH₄ flux to the ocean from this source [Overduin *et al.*, 2015]. Warming bottom waters have also caused the destabilization of gas hydrates, which require low temperatures and high pressures to remain stable on the continental slope, and have possibly accelerated the decomposition of the subsea permafrost “cap” which contains hydrates within continental shelf sediment [Ruppel, 2015; Shakhova *et al.*, 2015]. Gas hydrates, although very localized, have been shown to be regionally important sources of CH₄ [e.g., Heeschen *et al.*, 2005; Kessler *et al.*, 2006]. The Arctic contains ~100-9000 Gt CH₄ in the form of gas hydrates [James *et al.*, 2016]. The potential destabilization and sudden release of this huge carbon store has attracted much attention due to its association with previous climate change [Dickens *et al.*, 1995, 1997; Lamarque *et al.*, 2006; Archer, 2007; Archer *et al.*, 2009]. Without significant baseline data on the concentrations of CH₄ and N₂O across varying hydrographic regimes, it is difficult to predict how their concentrations will change into the future.

At present, our understanding of the controls on CH₄ and N₂O cycling in the Arctic Ocean is incomplete. Previous biogeochemical studies in the Arctic Ocean have been spatially segregated [Carmack and Wassmann, 2006], with particular programs focusing on localized regions of interest (e.g. the Bering and Chukchi Seas, Canada Basin, Beaufort Sea, or Davis Strait; Kvenvolden *et al.*, 1993; Hirota *et al.*, 2009; Punshon *et al.*, 2014; Zhan *et al.*, 2015). These studies have shown that CH₄ and N₂O are frequently supersaturated in the Arctic surface ocean with respect to atmospheric equilibrium values. Studies of Arctic CH₄ distributions have focused on the continental shelves, where surface waters are highly supersaturated [e.g., Kvenvolden *et al.*, 1993; Savvichev *et al.*, 2007; Shakhova *et al.*, 2010a], with the greatest attention paid to the high sea-air fluxes in the Siberian Arctic Seas [Shakhova and Semiletov, 2007; Shakhova *et al.*, 2010b, 2013; Kosmach *et al.*, 2015]. By comparison, few studies have sampled the deep basin waters [Damm *et al.*, 2010; Punshon

et al., 2014] or in the Canadian Arctic [Kvenvolden *et al.*, 1993; Kitidis *et al.*, 2010; Punshon *et al.*, 2014]. Previous work on N₂O has demonstrated high concentrations in the Chukchi Sea [Hirota *et al.*, 2009; Zhang *et al.*, 2015], under-saturation in the deep Canada Basin [Zhan *et al.*, 2015], and low concentrations in sea-ice melt water [Kitidis *et al.*, 2010; Randall *et al.*, 2012; Zhang *et al.*, 2015]. Kitidis *et al.* [2010] reported measurements of surface water CH₄ and N₂O concentrations across a broad range of Arctic waters. Their results revealed notable spatial patterns, including 'hot-spots' of high CH₄ and N₂O under sea ice and in marginal ice zones. These observations are consistent with the recently suggested role of sea-processes as potential CH₄ and N₂O sources [Damm *et al.*, 2015a], though more depth-resolved observations are needed to further examine this. The work of Kitidis *et al.* [2010] was largely focused on surface waters (only one depth profile was presented), and thus provided little insight into distribution of CH₄ and N₂O in sub-surface waters.

The goal of this study was to examine broad-scale, three-dimensional distribution of CH₄ and N₂O concentrations in the North American Arctic Ocean. During the summer of 2015, depth profiles at nearly 50 locations from the Bering Sea to Baffin Bay were taken in order to quantify the distributions of CH₄ and N₂O concentrations and sea-air fluxes, and examine potential source and sink terms (Figure 1). To my knowledge, the data set presented here represents the most comprehensive analysis of Arctic CH₄ and N₂O distributions across a single sampling season. The temporal coherence of the measurements is critical given the rapid changes currently underway in the Arctic. Our results show that N₂O is produced in the Bering and Chukchi Seas, and transported with Pacific water masses through to Baffin Bay, with dominant input terms associated with nitrification and denitrification in the Western Arctic. In contrast, CH₄ sources to the water column were far more ephemeral, with rapid microbial oxidation of CH₄ acting to decrease concentrations and limit eastward transport of CH₄. The carbon isotopic composition of CH₄ supported this conclusion, as low CH₄ concentrations were enriched in ¹³C due to oxidative processes. This synoptic coverage provides a snapshot of spatial CH₄ and N₂O variability, and an important baseline dataset for this rapidly changing ocean region.

Figure 1: Map of study area, showing the locations of depth profiles (yellow circles) and dominant Pacific Water boundary currents. The black line denotes the transect along which the contour plots (Figure 5 and Figure 10) were derived. Based on [Macdonald *et al.*, 2004].

2

Methods and Regional Setting

2.1 FIELD SAMPLING

Water samples were collected on three cruises over the period between July to October 2015, covering a transect from the Bering Sea to Baffin Bay (Table 1, Figure 1). At each of the 47 stations, a Sea-Bird CTD system (SBE 911+), equipped with ancillary sensors was used to measure salinity, temperature, and other hydrographic parameters. Discrete water samples for the various stations were collected at multiple depths using 10 L Niskin bottles mounted on a rosette. Salinity values measured by CTD were calibrated against discrete bottle samples analyzed on an Autosol salinometer calibrated to IAPSO standard seawater [Millero *et al.*, 2008].

Table 1: Cruise details

Ship	Cruise Number	Dates	Regions	Program(s)
CCGS Sir Wilfrid Laurier	SWL 2015-07	04/07/16 – 26/07/16	Bering Sea, Chukchi Sea	C3O, DBO
CCGS Amundsen	1502	10/07/16 – 20/07/16	Baffin Bay, Canadian Archipelago	ArcticNet, GEOTRACES
CCGS Louis St. Laurent	LSSL 2015-06	20/09/16 – 17/10/16	Canada Basin, Beaufort Sea	JOIS

2.2 DISSOLVED GAS CONCENTRATIONS AND $\delta^{13}\text{C}_{\text{CH}_4}$ VALUES

Water for CH_4 and N_2O analysis was sub-sampled from Niskin bottles into 60 mL glass vials using thick-walled silicon tubing. Sample vials were overfilled three times and poisoned with 100 μL of saturated HgCl_2 , taking care to avoid entrainment of bubbles while filling bottles. Bottles were crimp sealed with no headspace using butyl-rubber stoppers

and aluminum caps. Duplicate samples were taken at each depth, and stored at 4°C in the dark until analysis within ~1 month of sampling. CH₄ and N₂O concentrations were measured simultaneously using an automated purge and trap gas extraction system coupled with gas chromatograph-mass spectrometer (PT-GCMS) at the University of British Columbia according to the method of *Capelle et al.* [2015]. The pooled standard deviations of the duplicates were 0.88 and 0.58 nmol/L for CH₄ and N₂O measurements, respectively. As discussed by *Capelle et al.* [2015], the accuracy and precision of our automated system compares very well against methods by other leading laboratories around the world. Percent saturation relative to atmospheric equilibrium was calculated from the mean concentration of the duplicate samples and gas solubility was calculated following *Wiesenburg and Guinasso Jr.* [1979] and *Weiss and Price* [1980] for CH₄ and N₂O, respectively, using the CTD measured in situ temperature and salinity. Atmospheric concentrations of CH₄ and N₂O were taken as 1910 ppb and 328 ppb, respectively, based on the average mixing ratios in Barrow, Alaska in August 2015 (Data provided by NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA; <http://esrl.noaa.gov/gmd/>).

Samples for $\delta^{13}\text{C}_{\text{CH}_4}$ analysis were collected in either 160 mL or 250 mL glass vials in the same manner as above, and poisoned with either 300 μL or 500 μL HgCl₂, respectively. The values were determined using a Delta XP plus Finnigan mass spectrometer at the Alfred Wegner Institute in Bremerhaven, Germany. The samples were pre-concentrated through purging and subsequent trapping with PreCon equipment (Finnigan), and the isotopic ratios were given in delta notation relative to the Vienna Pee Dee Belemnite (VPDB) standard.

2.3 NUTRIENT ANALYSIS

For cruise LSL 2015-06, unfiltered nutrient samples from were analyzed for nitrate + nitrite, phosphate, and silicate on a three channel Seal Analytical Nutrient Auto-Analyser 3 (AA3) within 12 hours of collection. For cruise SWL 2015-07, nutrient samples were analysed by the same method, but were frozen prior to being analyzed at the Institute of Ocean Sciences 5 months after the cruise. Unfrozen ammonium (NH₄⁺) samples were analyzed by the Nutrient Analytical Services Laboratory at the University of Maryland, following the method described in *Parsons et al.* [1984].

2.4 BIOGEOCHEMICAL CALCULATIONS

N^* is a measure of the relative excess or deficit of fixed nitrogen relative to phosphate, calculated using the equation $N^* (\mu\text{mol/L}) = ([\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+] - 16^*[\text{PO}_4^{3-}] + 2.9$ of [Gruber and Sarmiento, 1997]. Assuming Redfield stoichiometry (C:N:P = 106:16:1), a negative N^* value indicates a deficit of dissolved inorganic nitrogen, while a positive value indicates N fixation [Redfield, 1942; Gruber and Sarmiento, 1997]. Apparent oxygen utilization (AOU) represents the amount of oxygen that has been consumed by remineralization since the water mass was last ventilated. AOU is calculated as difference between the dissolved oxygen concentration measured in a sample and the calculated concentration at equilibrium with the atmosphere [Redfield, 1942]. For the purposes of these calculations, we (and others) assume that temperature and salinity characteristics of waters masses have not been altered since they were last in contact with the atmosphere.

2.5 SEA-AIR FLUX CALCULATIONS

Sea-air fluxes of CH_4 and N_2O ($\mu\text{mol m}^{-2} \text{d}^{-1}$) at each station were calculated using a mixed layer depth computed based on a density difference criterion of 0.125 kg m^{-3} relative to 3m depth. If no measurement was taken within this calculated mixed layer, measurements within 3 m of the mixed layer depth were used instead for flux calculations. The disequilibrium of CH_4 and N_2O in the mixed layer was calculated by subtracting the atmospheric saturation value (by the same method described in section 2.2) from the observed concentration. Wind data were acquired from the NCEP Reanalysis data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their website at <http://www.esrl.noaa.gov/psd/>. The equation for the ocean-atmosphere flux was taken as the product of a gas exchange coefficient, k_w , and mixed layer disequilibrium, ΔC :

$$\text{Flux} = k_w \times \Delta C$$

The gas exchange coefficient (k_w) was calculated as a function of the Schmidt number (Sc) and wind speed according to the parameterization by *Nightingale et al.* [2000]. This equation was developed for ice-free conditions, which is appropriate for our calculations since we did not have any mixed layer gas samples for ice-covered stations. A weighting function [Reuer et al., 2007] was used to incorporate the effects of variability in wind speeds

in the 60 days prior to sample collection. The net result is a time-weighted piston velocity, where the weighting is based on the fraction of the mixed layer ventilated on any given day.

2.6 REGIONAL SETTING

In order to provide a context for our CH₄ and N₂O concentration data, we briefly review the dominant oceanographic properties of our broad survey region. We sampled across a number of distinct water masses, which are influenced by a range of physical and biological processes that impact salinity, temperature, and nutrient concentrations. These tracers allow us to better constrain the biogeochemical processes that influence trace gas cycling. We also briefly review the available information on CH₄ emissions from seafloor sediments across our survey region.

2.6.1 *Bering and Chukchi Seas*

The Bering and Chukchi Seas are dominated by northward flowing Pacific water that comprises several distinct water masses. As these water masses transit over the shallow Bering and Chukchi Shelves into the Arctic Basin, they are modified by biological and physical processes [e.g., *Yamamoto-Kawai et al.*, 2006]. In the northern region of the Bering shelf, three main water masses are present in the summer. The Anadyr Water occupies the western portion of the Bering Sea, and is composed of upwelled, saline, nutrient-rich deep water in the Gulf of Anadyr. The eastern Bering Sea is dominated by relatively fresh ($S < 31.8$), nutrient-poor ($< 1.5 \mu\text{mol/L NO}_3^-$) Alaskan Coastal Water (ACW). A central water mass with intermediate salinity is known as Bering Sea Water (BSW). Mixing of the BSW and Anadyr Water is enhanced in the Northern Bering Sea and Bering Strait, but some unaltered Anadyr Water and ACW persists into the Chukchi Sea [*Weingartner et al.*, 2005; *Grebmeier et al.*, 2006]. The BSW contains high dissolved nutrient concentrations due to the influence of the Anadyr Water, but seasonal differences in sea ice growth results in two distinct water masses, known as Pacific Winter Water (PWW) and the Pacific Summer Water (PSW). In the winter, convective overturning caused by brine rejection stirs up the sediments and adds regenerated sedimentary nutrients to the PWW [*Pickart et al.*, 2016], while imparting a low temperature and high

salinity signature [e.g., *Woodgate et al.*, 2005a; 2005b]. During summer, the fresher, northward flowing PSW gradually displaces the PWW on the Chukchi shelf, although remnant PWW is still present on the northern Chukchi Shelf [e.g., *Lowry et al.*, 2015; *Pickart et al.*, 2016]. At the northern-most point in our study area, in Barrow Canyon, all of these water masses converge and stratify [*Gong and Pickart*, 2015]. The dense PWW sinks to the deepest parts of the canyon (below 35m depth) and is overlain by PSW and ACW (5 - 35 m) as well as a surface melt-water layer (0 - 5 m) [*Gong and Pickart*, 2015].

The contrasting nutrient concentrations in the different water masses affect primary production, which has important implications for CH₄ and N₂O cycling. The high nutrient BSW sustains an annual productivity of up to ~ 500-700 g C m⁻² y⁻¹ in the northern Bering and southern Chukchi Seas, with values declining to ~ 50-100 g C m⁻² y⁻¹ in the northern Chukchi Sea [*Hameedi*, 1978; *Springer and McRoy*, 1993]. By contrast, the nutrient-poor southeastern Chukchi Sea supports primary production of less than 100 C m⁻² y⁻¹ [*Springer and McRoy*, 1993]. This east-west productivity gradient is also reflected in organic carbon fluxes and benthic oxygen consumption rates, which are both significantly higher in regions of elevated primary productivity [*Naidu et al.*, 2004]. The high oxygen consumption rates in the productive regions result in sediment anoxia, creating conditions conducive to anaerobic microbial processes associated with CH₄ and N₂O production. Indeed, denitrification has been well documented on the Bering and Chukchi shelves [*Devol et al.*, 1997; *Tanaka et al.*, 2004; *Yamamoto-Kawai et al.*, 2006], and methanogenesis has also been reported [*Savvichev et al.*, 2007]. These processes could add CH₄ and N₂O to the water column in the Bering and Chukchi, which could potentially be transported to other regions of the Arctic by eastward flowing waters.

Rivers are another potential source of CH₄ and N₂O to surface waters of the Western Arctic, delivering CH₄ released from terrestrial permafrost, and CH₄ and N₂O produced in riverine sediments to coastal regions. The Yukon River, whose drainage basin contains near-surface permafrost [*Pastick et al.*, 2014], is the second largest river in the North American Arctic [*Cooper et al.*, 2008]. Yukon river water feeds directly into the ACW, and high measured concentrations of CH₄ (up to 330 nmol/L) in this river and its tributaries have been attributed to the anoxic decomposition of the organic matter in its watershed [*Striegl et al.*, 2012]. We are unaware of any N₂O data for the Yukon River.

2.6.2 Canada Basin and Beaufort Sea

The Canada Basin comprises deep waters (~4000 m) bordered by shallow seas and continental shelf. Surface waters of the Canada Basin are characterized by a ~ 40 m thick Polar Mixed Layer (PML) that is relatively fresh (26.2-31.2 ‰) and nutrient-depleted [Macdonald *et al.*, 2004]. As Pacific waters enter the Canada Basin from the Chukchi Sea, they subduct below the PML into the Upper Halocline Layer (UHL) [Codispoti *et al.*, 2009]. Within the UHL, Pacific Summer Water (PSW) ($S = 31-32$, $T > -1^{\circ}\text{C}$, $D = 25-26 \sigma_t$) is found between ~40-100m, while Pacific Winter Water (PWW) ($S = 32-33.1$, $T < -1^{\circ}\text{C}$, $D = 26-26.5 \sigma_t$) sits between ~100-200m. Previous authors have used a salinity of 33.1 and temperature of -1.6°C as the signature characteristics of the PWW core [e.g., Aagaard *et al.*, 1981; Jones and Anderson, 1986; Carmack, 2000]. The ACW is only a very minor component of the UHL, and is generally considered part of the PSW once it enters the basin [Shimada *et al.*, 2001]. Below the UHL, the Lower Halocline Layer occupies a depth range of ~200-400 m and is largely of Atlantic origin, while Canada Basin Intermediate Water (CBIW) occupies a depth range of ~ 400-2000m. Canada Basin Deep Water (CBDW), which is found below ~2000m, has been isolated from the atmosphere for ≈ 450 years [Schlosser *et al.*, 1997; McLaughlin *et al.*, 2002; Timmermans *et al.*, 2003].

Strong salinity stratification in the surface waters of the Canada Basin results in low surface water nutrient concentrations and, thus, restricted primary productivity [Sakshaug, 2004]. This, in turn, results in low carbon export to sub-surface waters, which have been isolated from the atmosphere for decades or longer [Macdonald *et al.*, 2004]. As a result, the chemistry of deep basin waters is relatively homogenous [Timmermans *et al.*, 2003]. The Beaufort Sea, in the southern Canada Basin, is primarily influenced by the Upper Halocline water masses of the Canada Basin, including both PSW and PWW [Carmack *et al.*, 2006]. Additionally, the ACW wraps around Barrow Point and is transported into the Beaufort Sea. This inflowing ACW is retained close to the coast, and was not likely sampled during our surveys. The carbon export in the ACW inflow is considerably lower than that of the Bering and Chukchi Seas (due to lower nutrient concentrations), resulting in lower benthic productivity and oxygen consumption [Naidu *et al.*, 2004].

2.6.3 Canadian Arctic Archipelago

The Canadian Arctic Archipelago (CAA) is a vast stretch of islands and channels that lies to the north-east of the Beaufort Sea (Figure 1). This region receives Pacific-derived water from the west, with PML and UHL waters flowing eastward over the sill demarcating the entrance to the Amundsen Gulf. Westward flow is limited by a shallow sill near Resolute, such that almost all of the water in the CAA (even as far east as Lancaster Sound) is derived from Pacific-origin water masses with only a limited influence of Atlantic-derived waters [Jones, 2003; Michel *et al.*, 2006]. The complex network of shallow, narrow straits in the CAA is subject to significant regional and small-scale variability. River input modifies the inflowing water, and imparts a low salinity signature on the southern CAA [McLaughlin *et al.*, 2004]. Local mixing and tidal processes through the narrow straits and channels also reduce stratification and increase nutrient concentrations [McLaughlin *et al.*, 2004, 2011]. High sea ice cover also influences biogeochemical cycling in the CAA. Sea ice acts as a semi-permeable barrier to sea-air exchange of dissolved gasses [e.g., Loose *et al.*, 2011], and has been suggested as an explanation for the accumulation of high CH₄ and N₂O concentrations in the surface waters of the CAA [Kitidis *et al.*, 2010; Damm *et al.*, 2015a].

Primary productivity estimates in the CAA vary from 10 to 55 g C m⁻² y⁻¹ [Welch *et al.*, 1992; Sakshaug, 2004]. Sea ice algae are an important part of this production, contributing 5 to 10 g C m⁻² y⁻¹ [Smith *et al.*, 1988; Michel *et al.*, 2006]. The linkages between primary productivity and benthic remineralization have not been well-studied within the CAA, but recent data have shown relatively high benthic remineralization rates in Lancaster Sound, and much lower rates in the Amundsen Gulf and Baffin Bay [Darnis *et al.*, 2012]. Regions with high remineralization rates may be sources of CH₄ and N₂O to the CAA.

2.6.4 Seafloor methane sources

The shallow shelves of the Arctic Ocean were once vast coastal plains which developed layers of thick permafrost during the Late Pleistocene (Brigham and Miller, 1983). Gas from petroleum deposits or biological production deep in the crust migrated upwards and was frozen in place as gas hydrates [Ruppel, 2015]. A post-glacial sea level rise of 120m since ~12ka inundated these plains, thawing the permafrost deposits and likely causing the

dissociation of permafrost-associated gas hydrates [Ruppel, 2015]. This release of gas in unstable hydrates, either entrained in or capped by a permafrost layer, are thought to be the sources of the large methane emissions on the wide Eastern Siberian Arctic Shelf and other Eurasian shelves [Shakhova *et al.*, 2010b, 2015]. In contrast, the North American Arctic only holds permafrost deposits (extending to ~100m depth) and shallow gas hydrates on the narrow Beaufort Shelf [Paull *et al.*, 2007, 2011; Ruppel, 2015]. Widespread gas plumes have been documented on the continental margin of the Beaufort Sea, and these have been attributed to decomposing permafrost and gas hydrates [Paull *et al.*, 2011]. Deepwater gas hydrates (~300-1200m) are also present on the Beaufort Slope [Weaver, J.S., Stewart, 1982; Dallimore, 1999; Ruppel, 2015]. These hydrates on the continental slope are generally considered the most sensitive to disruption due to climate change [Kvenvolden, 1993; Ruppel, 2011]. Warming over the past 60 years has been implicated in the potential destabilization of gas hydrate deposits between 300 and 550 m depth [Phrampus *et al.*, 2014]. Additionally, a survey of the slope sediments has shown elevated sediment-ocean fluxes of CH₄ from 280-1500 m depth on the western Beaufort slope, potentially attributable to gas hydrate dissociation [Coffin *et al.*, 2013].

Hydrocarbon deposits may also play a role as a CH₄ source. Much of the Chukchi Sea and Canada Basin, including the Beaufort Sea, is underlain by hydrocarbon-bearing source rocks [Burlin and Shipel'kevich, 2006; Grantz and Hart, 2012]. These can contribute CH₄ to the water column through upward migrations along faults and fractures in the rock [Reeburgh, 2007]. Thermogenic gas seepages are widespread in areas where oil and gas deposits occur, and are often used as targets of commercial exploration [Hovland *et al.*, 1993]. However, there is only limited published information on the exact location of such seepage sites [Hovland *et al.*, 1993]. As the Chukchi and Beaufort Seas have been extensively explored for offshore oil and gas, it is likely that thermogenic seepages exist in these areas and contribute to the CH₄ cycling.

3

Results and Discussion

For the purpose of describing gas distributions, we divide our study area into three sub-regions: a) Bering Sea and Chukchi Sea, b) Canada Basin and Beaufort Sea, and c) Canadian Arctic Archipelago and Baffin Bay. This grouping was based on the similarity of hydrography and CH₄ and N₂O distributions within these regions. We first provide an overview of CH₄ and N₂O concentrations across our full transect, and then focus on the processes occurring in each of these sub-regions. Since the cycling of CH₄ and N₂O is influenced by distinct biogeochemical processes, we discuss each of these gases separately.

3.1 NITROUS OXIDE

Nitrous oxide concentrations across the entire transect ranged from 10.9 to 24.6 nmol/L, with corresponding saturation levels of 77% to 145%. As shown in Fig. 2, concentrations of N₂O exhibited a ubiquitous maximum in the Pacific Winter Water (PWW), with persistent low values in the surface fresh-water layer and ACW (Figure 2). This feature can be seen in Fig. 3, where the average profiles of N₂O from the Bering, Chukchi and Beaufort Seas, and the CAA region are plotted on density surfaces. As discussed below, this high N₂O signal in the PWW originates in the Bering and Chukchi Seas and is transported across the Arctic Ocean on the 26.5 σ_t density surface until it is attenuated in the Canadian Arctic Archipelago. In deeper waters, N₂O concentrations tend to decrease with increasing density, while N₂O concentrations in the lower-density surface waters are more variable because they are influenced by sea-ice cover, water mass mixing, and sea-air exchange.

Figure 2: Salinity vs. temperature plot showing the different water masses observed in the North American Arctic. The top panel shows percent saturation of N₂O, while the bottom panel shows percent saturation of CH₄. Circles, squares, and triangles denote measurements from the Bering and Chukchi Seas, Canada Basin, and Canadian Arctic Archipelago, respectively.

Figure 3: Density vs. concentration plots averaged by sub-region. The grey shaded area is the standard deviation of the mean.

3.1.1 N_2O in the Bering and Chukchi Seas

Across all sampling depths, N_2O concentrations ranged from values just under atmospheric equilibrium in the Northern Bering Sea (11.8 nmol/L) to a maximum of 24.6 nmol/L (145% saturation) at the northernmost station in the Chukchi Sea (Figure 4). Surface water N_2O concentrations were low, and typically less than the atmospheric equilibrium concentration of ~13 nmol/L. These concentrations are consistent with observations reported previously for this region (~11–25 nmol/L) [Hirota *et al.*, 2009; Zhang *et al.*, 2015]. The nearly ubiquitous under-saturation of N_2O in surface waters may reflect dilution by sea ice meltwater which contains little N_2O [Randall *et al.*, 2012]. In contrast to previous observations in our study area [Hirota *et al.*, 2009; Zhang *et al.*, 2015] we did not detect high (>120%) surface super-saturations of N_2O in the Bering and

Chukchi Seas. The lower concentrations we observed may reflect a difference in the geographic region and/or seasonal timing of our sampling compared to previous studies. *Hirota et al.* [2009] sampled stations further to west, with significant influence of high-nutrient Anadyr Water, which likely fuels high productivity and oxygen depletion in the sediments leading to increased N_2O concentrations.

Below the surface layer, N_2O distributions appeared to be influenced by local water masses and biological processes in the sediments. In particular, differences in nutrient availability and biological productivity across distinct water masses appeared to influence N_2O accumulation as water transited through the Bering and into the Chukchi Sea. The northern Bering Sea contained low and near atmospheric equilibrium N_2O concentrations throughout the water column, averaging 14.4 nmol/L (Figure 4). In the southern Chukchi Sea, two separate patterns emerge, with differences in N_2O concentrations in the ACW and PSW likely related to contrasting productivity and carbon export in these waters [e.g., *Naidu et al.*, 2004]. Some of the lowest N_2O concentrations along the transect were measured in ACW waters that were characterized by low nutrient concentrations and biological productivity (stations UTN-1, SEC-5, SEC-7, Figure 4). This low productivity results in lower carbon fluxes [*Naidu et al.*, 2004], limiting denitrification and nitrification sources of N_2O . In contrast, the PSW-influenced central channel waters were characterized by higher nutrient concentrations and phytoplankton biomass, and high benthic oxygen consumption has been previously measured in this region [*Grebmeier*, 1993]. As expected, we observed higher N_2O concentrations in the central channel (stations UTN-3, UTN-7, SEC-1, SEC-3).

Figure 4: Map and corresponding N_2O depth profiles in the Bering and Chukchi Seas. Black filled circles denote a measurement, while the error bars represent the standard deviation of the duplicate samples. The grey dotted line is the atmospheric equilibrium concentration.

The highest N_2O concentrations along the entire transect ($24.6 \text{ nmol/L N}_2\text{O}$) were measured at the northernmost stations (BarC-8) in the remnant PWW at a depth of 65 m. On average, the N_2O concentration below the shallow (5-15m) fresher water surface layer was 18.0 nmol/L , representing an increase of 3.6 nmol/L relative to the PSW. Similarly, the accumulation of N_2O in the bottom waters of the northward-flowing Bering and Chukchi Seas was also observed by Hirota et al. (2009). To further illustrate this latitudinal gradient in N_2O concentration, Fig. 5 shows a latitude-depth contour plot highlighting the strong north-south N_2O gradient along the 26.5 isopycnal ($\sigma_t \approx 33$) (Figure 5). This pattern may reflect the accumulation of N_2O in the bottom waters as they flow over the Chukchi Shelf.

An additional explanation for the high N_2O concentrations is the slower circulation rates of PWW over the shelf [Woodgate *et al.*, 2005a], which would result in an increased time for N_2O accumulation in the winter water, as denitrification rates remain constant throughout the year [Devol *et al.*, 1997; Chang and Devol, 2009]. Furthermore, brine rejection during ice growth in the winter generates convective overturning, stirring the sediments and likely adding N_2O to the PWW [Pickart *et al.*, 2016].

Figure 5: Nitrous oxide and density contour plots. The top two panels show the distribution of N_2O and density along a ~1500km transect from the Bering to the Beaufort Sea (black line on Fig. 1), respectively. The bottom panel shows the mean concentration of N_2O on the 26.5 density surface, illustrating the accumulation of N_2O along this isopycnal.

To determine the sources of N_2O in the Bering and Chukchi Sea regions, we examined the relationship between N_2O concentrations and other hydrographic variables. Water column N_2O production in these shallow regions may be limited, as nitrifying bacteria are potentially light-inhibited [Ward, 2008], and water column oxygen concentrations are too high for denitrification. Rather, sedimentary processes likely represent the predominant N_2O source to the water column, and this is consistent with the observation of maximum

concentrations in the bottom waters (Figure 4). Previous studies have attributed the high N_2O concentrations on the Bering and Chukchi Sea shelves to denitrification in the sediments [Hirota *et al.*, 2009]. Indeed, we observed a negative correlation between $\Delta\text{N}_2\text{O}$ and N^* (Figure 6) in this region, providing evidence that denitrification is a source of N_2O to the water column. Although the relationship between N^* and N_2O is statistically significant ($p < 0.0001$), it exhibits significant scatter ($r^2 = 0.18$). Some of this variability is likely attributable to the influence of other nitrogen cycling processes in N_2O production. Recently, nitrification-denitrification coupling has been identified as an important process on the Bering and Chukchi Sea shelves [Granger *et al.*, 2011; Horak *et al.*, 2013; Brown *et al.*, 2015]. This pairing has been shown to be an important mechanism in N_2O production [Naqvi *et al.*, 1998]. Typically, the correlation of $\Delta\text{N}_2\text{O}$ with AOU is used to determine if nitrification is a source of N_2O . In our data set, we found no significant relationship between the two variables. This result may be attributable to large differences between the oxygen concentration in the water column ($>230 \mu\text{mol/L O}_2$) compared to the sediments (due to high benthic O_2 consumption; Grebmeier *et al.*, [2006b]), such that the water column AOU does not reflect the conditions of N_2O production. Although we cannot determine the exact mechanism of N_2O formation, it is apparent that the active nitrogen cycling on these shelves is the predominant source.

Figure 6: ΔN_2O vs. AOU and N^* plots, broken down by sub-region. Only the Canada Basin UHL is shown in order to better compare the properties of the Pacific water masses between regions. Trend lines are shown where there is a statistically significant regression model ($p < 0.05$).

3.1.2 N_2O in the Canada Basin and Beaufort Sea

Nearly all the N_2O profiles in the Canada Basin and Beaufort Sea follow the same pattern, with under-saturated surface water concentrations (91-98% saturation), increasing to a maximum in PWW, then decreasing to a minimum in the CBDW (~75% saturation) (Figure 7). The high N_2O signature of the Bering and Chukchi seas is transported with the Pacific Winter Water into the Canada Basin and Beaufort Sea. The pronounced N_2O maximum is tightly constrained to values ranging from 18.5-19.6 nmol/L, and it occurs at $S \sim 33\text{‰}$ ($26.5 \sigma_t$), in the core of the PWW (Figure 3).

Figure 7: Map and N₂O depth profiles in the Canada Basin and Beaufort Sea.

We observed a positive correlation of $\Delta\text{N}_2\text{O}$ and AOU in the Canada Basin samples (Figure 6). In previous studies, this relationship has been taken as evidence of a primary nitrification source for N₂O in seawater [Nevison *et al.*, 1995]. However, several lines of evidence suggest that the nitrification is only a minor source of N₂O in the Canada Basin. Based on the slope of the AOU vs. $\Delta\text{N}_2\text{O}$ in the UHL of the Canada Basin (40-200m), we calculate 0.016 nmol of N₂O produced for every μmol of O₂ consumed. Assuming Redfield stoichiometry, with 17% of oxygen consumption attributed to NH₄⁺ oxidation [Ward, 2008], we derive an N₂O yield from nitrification of 0.01%. This value falls within the range previously observed for waters of the Subarctic Pacific Ocean (0.004-0.028%; [Yoshida *et al.*, 1989; Grundle *et al.*, 2012]). Previous studies have reported a $\sim 1.4 \mu\text{mol/L}$ difference between the NH₄⁺ concentration on the Chukchi shelf and that in the Canada Basin [Zhang *et al.*, 2015]. The nitrification of $1.4 \mu\text{mol/L}$ NH₄⁺ would therefore produce 0.14 nmol/L N₂O, which represents approximately 7% of the observed N₂O surplus in the Canada Basin PWW ($\sim 2.0 \text{ nmol/L}$). Even assuming nitrification of up to $6 \mu\text{mol/L}$ NH₄⁺ (the highest concentration of NH₄⁺ documented on the Chukchi shelf [Brown *et al.*, 2015]), only $\sim 0.6 \text{ nmol/L}$ N₂O would be produced. This suggests that the high N₂O signature in the Canada Basin is set by processes occurring in the Bering and Chukchi shelves, with

only a negligible amount added by in situ water column nitrification within the Canada Basin. This notion is supported by the negative correlation of $\Delta\text{N}_2\text{O}$ with N^* in the UHL of the Canada Basin, which implies that denitrification is a major source of N_2O (Figure 6), similar to the relationship we observed on the Bering and Chukchi Sea shelves. Previous authors have raised concerns about the use of N_2O -AOU relationships as an indicator of nitrification as a primary N_2O source [Nevison *et al.*, 2003; Bange, 2008]. In particular, Yamagishi *et al.* [2005] showed that denitrification-sourced N_2O assumed a linear relationship with AOU when diffusing into deep waters,. This implies that a linear relationship between N_2O and AOU can result from water mass mixing rather than remineralization processes.

The Beaufort Sea is strongly influenced by the upper layers of the Canada Basin. Our observations point to physical processes, rather than microbial ones, as key determinants of N_2O distributions. As an example of this, our results demonstrate the regional importance of upwelling on N_2O distributions. This was especially evident at CB28aa, where PWW from MK1 upwelled onto the shelf, replacing the water at this shallow shelf station with PWW and yielding high N_2O concentrations in shallow (<60m) waters (Figure 7).

Deep Canada Basin waters contain low and relatively constant concentrations of N_2O , with an average value of 13 nmol/L (80% saturation). Our observations are in good agreement with those of Zhan *et al.* [2015], who observed an average concentration of 12.5 nmol/L in these waters. These authors attributed the large apparent under-saturation to the historical characteristics of the deep water. Deep Canada Basin waters were last exposed to the atmosphere ~450 years ago [Schlosser *et al.*, 1997], when atmospheric N_2O concentrations were 16% lower than modern values [Flückiger *et al.*, 1999]. Using the equation by Weiss and Price [1980], and assuming an atmospheric mixing ratio of 270 ppb for the year 1700 [Flückiger *et al.*, 1999], the equilibrium concentration at that time was ~13 nmol/L, which is equal to our average concentration in the deep Canada Basin waters. This provides an explanation for the strong apparent under-saturation of these waters when expressed relative to modern equilibrium values.

3.1.3 N_2O in the Canadian Arctic Archipelago

Surface concentrations of N_2O in the CAA varied from 13.1 nmol/L (95% saturation) to 17.8 nmol/L (110% saturation). Concentrations greater than atmospheric equilibrium were generally observed in association with ice cover (CAA-4, CAA-7, VS), and a maximum of 16.0 – 18.5 nmol/L was observed in the Pacific Winter Water ($26.5 \sigma_t$) (Figure 8). These maximum concentrations were lower than those measured in the Canada Basin. Below the N_2O maximum, concentrations generally decreased with depth to near atmospheric equilibrium values (~ 14.5 nmol/L). We observed a notable decrease in the maximum N_2O concentration east of the Amundsen Gulf, with the exception of stations AN-312 and AN-314, which were too shallow to contain PWW. Similar to the other regions, we observed a negative correlation between ΔN_2O and N^* (Figure 6), implying that the N_2O maximum in the CAA originates from the Pacific shelves. This result suggests that the N_2O signal is being transported thousands of kilometers across the Arctic Ocean along the $26.5 \sigma_t$ isopycnal, until it is attenuated in the CAA (Figure 3). The reduction in N_2O concentrations in the CAA can be attributed to sea-air flux (see below), and the mixing of the PW with low N_2O sea ice melt-water and/or river water.

In Baffin Bay, N_2O concentrations were close to atmospheric equilibrium values through much of the water column, increasing with depth to a sub-surface maximum at 1500 m of 18.0 nmol/L (115% saturation) (Figure 8). A similar deep N_2O maximum in Baffin Bay was reported by *Kitidis et al.* [2010], who attributed this feature to sedimentary denitrification in the sediments just off of Greenland [*Rysgaard et al.*, 2004].

Figure 8: Map and depth profiles of N_2O in the CAA.

3.2 METHANE

Across our entire sampling transect, CH_4 concentrations varied greatly, ranging from 0.7 to 30.5 nmol/L, corresponding to percent saturation of 30% to 800%. We observed the highest concentrations of CH_4 in the remnant PWW of the northern Chukchi Sea (Figure 9). Unlike N_2O , CH_4 was oxidized relatively rapidly in the water column, limiting the transport of high CH_4 concentrations in eastward flowing waters (Figure 3). As a result, the high CH_4 concentrations present in the Chukchi Sea, at a density surface of $26.5 \sigma_t$, were not observed in either the Beaufort Sea or CAA region. In the Canada Basin, a ubiquitous and stable maximum in the UHL associated with the Pacific Summer Water (PSW) was measured at $25.5 \sigma_t$ (Figure 3). By contrast, CH_4 concentrations below the UHL varied

greatly, ranging from 1 to 24 nmol/L. CH₄ concentrations in the Canadian Arctic Archipelago (CAA) showed large surface maxima, up to 15.0 nmol/L, and decreasing concentrations with depth to near atmospheric equilibrium values. This spatial and temporal variation underscores the ephemeral nature of CH₄ sources and sinks.

3.2.1 CH₄ in the Bering and Chukchi Seas

Methane concentrations in the Bering and Chukchi Seas were almost ubiquitously supersaturated throughout the water column. Concentrations ranged from slightly greater than atmospheric equilibrium in the surface of the Bering Sea (~3 nmol/L) to values close to 800% saturation (30.5 nmol/L) in the northern Chukchi Sea (Figure 9). CH₄ distributions appeared to be more influenced by local sources than N₂O, including potential sources from rivers feeding into the ACW, and sediment-derived CH₄ in the northern Chukchi Sea water column. Surface water CH₄ concentrations were frequently supersaturated, averaging 4.8 nmol/L (150% saturation). No spatial concentration gradient was discernable within our study area. The surface water CH₄ concentrations we measured were lower than the average surface CH₄ concentrations previously reported for the Chukchi Sea by *Kosmach et al.* [2015] and *Savvichev et al.* [2007] (8.1 nmol/L and 11.2 nmol/L, respectively). These previous studies sampling further west in the Chukchi Sea, where higher CH₄ concentrations have previously been reported relative to the eastern sections [*Savvichev et al.*, 2007].

Figure 9: Map and depth profiles of CH_4 in the Bering and Chukchi Seas

Below the surface mixed layer CH_4 concentrations increased considerably from the northern Bering Sea (mean ~ 5 nmol/L) to the northern Chukchi Sea (mean ~ 17 nmol/L) (Figure 10). Our measurements from just south of the Bering Strait contained increasing concentrations of CH_4 with depth (up to ~ 7.0 nmol/L, 210% saturation). In the southern Chukchi Sea, elevated CH_4 concentrations (mean 8.7 nM, range: 5.3-12.3 nmol/L) were observed in the ACW (stations UTN-1, SEC-5, SEC-7) while lower CH_4 concentrations (mean 6.3 nmol/L, range: 3.7-10.1 nmol/L) were measured in the more PSW-influenced western stations (UTN-3, UTN-7, SEC-1, SEC-3). This is somewhat surprising given that rates of methanogenesis in the sediments of the southern central Chukchi Sea have been found to be five times greater than those near the Alaskan Coast [Savvichev *et al.*, 2007]. Instead, the greater concentrations of CH_4 in the ACW may reflect the high CH_4

concentrations associated with river inputs into the ACW, which results from the methanogenesis of organic material in degrading permafrost [Striegl *et al.*, 2012]. This implies that methanogenesis in oceanic sediments is perhaps only minor compared to the contribution of CH₄ by rivers.

Figure 10: Methane and density contour plots. The top panel shows the distribution of CH₄ along a ~1500 km transect from the Bering to the Beaufort Sea (black line on Fig. 1). The bottom panel shows the density distribution along the same transect.

The highest dissolved CH₄ concentrations in the study area were observed in the sea ice-influenced remnant PWW in the Northern Chukchi Sea (30.6 nmol/L) near the sediments. Previous work has demonstrated high concentrations of CH₄, averaging ~2200 nmol/L, in the upper 2 cm of sediments of the northern Chukchi Sea (Lapham *et al.*, submitted). Brine rejection, as a result of sea ice growth, causes convective overturning of the water column and mixes the sediments, releasing regenerated nutrients and gases into the PWW [Pickart *et al.*, 2016]. As this process only occurs in the winter, it may account for the higher CH₄ concentrations in the PWW compared to the PSW.

The origin of seafloor CH₄ sources is unclear. As this area does not contain subsea permafrost or gas hydrates [Ruppel, 2015], it is uncertain whether the elevated CH₄ signature results from methanogenesis in the sediments or perhaps upward migration of

thermogenic gas. Rates of methanogenesis of up to $67 \mu\text{mol m}^{-2} \text{d}^{-1}$ have been measured in the sediments of the Chukchi Sea [Savvichev *et al.*, 2007], implying that this may be a major source of the water column CH_4 . This area is also in the Chukchi Sea Oil and Gas Lease Sale No. 193, suggesting likely geologic gas deposits.

In addition to the elevated CH_4 concentrations in bottom waters of the Chukchi Sea, we also observed CH_4 maxima within the upper water column at a few stations (Figure 9) (DBO4.3, DBO4.2, BarC-10, BarC-6, BarC-4). These signatures may be due to in situ methane production within the water column. The most likely processes are methanogenesis in anoxic microenvironments [de Angelis and Lee, 1994; Holmes *et al.*, 2000] or the cleavage of methane from DMSP [Damm *et al.*, 2010]. The cleavage of methyl groups from methanophosphates is unlikely in this case because this region is not phosphate limited [Karl *et al.*, 2008]. Methane has been found to be produced in the ocean where suspended sediments accumulate, presumably in the anaerobic niches provided by these particles [Holmes *et al.*, 2000]. However, we did not find any relationship between the transmissivity of the water column (a proxy for suspended particle loads) and CH_4 concentrations. The second possible pathway is the bacterial metabolism of DMSP, a compound produced by phytoplankton, producing precursors for methane formation. A methyl group may be cleaved when bacterioplankton use DMSP as a source of carbon, which occurs predominantly when they are nitrate-limited [Kiene *et al.*, 2000; Damm *et al.*, 2010]. Indeed, we did observe some co-occurrence of high CH_4 with high chlorophyll in this region (Figure 13), implying a potential phytoplankton-derived source of DMSP, could stimulate CH_4 release during bacterial DMSP metabolism. In the absence of subsurface DMSP data for this region, we cannot conclusively link DMSP metabolism to CH_4 production.

3.2.1.1 Stable isotopic composition of CH_4 in the Bering and Chukchi Seas

The large range of our CH_4 concentrations in our data suggests that sources of CH_4 are variable, and processes that both consume and produce CH_4 are pervasive. We used the stable isotope composition of CH_4 to provide insight into CH_4 cycling in the water column. Some of the lightest $\delta^{13}\text{C}_{\text{CH}_4}$ values ($\sim -41.5\text{‰}$) were found in the bottom waters of the northern Chukchi Sea, associated with high concentrations of CH_4 (up to 31 nmol/L). This

-41.5‰ minimum is indicative of a more recent source. Although it is relatively heavy for methane produced by microbial methanogenesis (normally considered <-50‰ [Whiticar, 1999]), this may reflect the oxidation of biogenic methane within the sediments and the water column. Biological oxidation preferentially uses $^{12}\text{C}_{\text{CH}_4}$, causing the $\delta^{13}\text{C}_{\text{CH}_4}$ value to increase.

Carbon isotope ratios of CH_4 can also allow us to differentiate oxidation and dilution processes in the water column. We calculated a Rayleigh distillation model using the equation by [Coleman *et al.*, 1981]: $\delta^{13}\text{C}_t = 1000 \times \left(\frac{1}{\alpha} - 1\right) \times \ln(f) + \delta^{13}\text{C}_0$. The starting stable isotope composition ($\delta^{13}\text{C}_0$) is -40‰, and f is the fraction of the residual methane remaining (initial = 31 nmol/L) (Figure 11). The calculated oxidation curve has a kinetic isotope fractionation factor (α) of 1.002, which is in the range of expected values for oxidation processes [Whiticar and Faber, 1986]. Samples with high CH_4 concentrations have low $\delta^{13}\text{C}_{\text{CH}_4}$ values, while samples with low CH_4 concentrations have high $\delta^{13}\text{C}_{\text{CH}_4}$ values due to the enrichment of ^{13}C during oxidation. Slight deviations from the oxidative curve are expected, as the initial concentration and stable isotope composition of the CH_4 will not be identical everywhere. As the measurements follow the oxidation curve, they are not considerably altered by dilution which would cause lower CH_4 concentrations to also have low $\delta^{13}\text{C}_{\text{CH}_4}$ values. This affirms that oxidation is the main sink for CH_4 in the water column.

Figure 11: Oxidation curve calculated using a Rayleigh distillation model with an initial concentration of 31 nmol/L, a $\delta^{13}\text{C}_{\text{CH}_4}$ value of -40‰ VPDB, and an isotopic fractionation factor of 1.002.

3.2.2 CH_4 in the Canada Basin and Beaufort Sea

Like N_2O , the CH_4 distribution pattern in the Canada Basin and Beaufort Sea was similar at all of the stations. CH_4 concentrations were slightly supersaturated in the PML (<5.3 nmol/L, $<130\%$ saturation), increasing to a subsurface maximum in the PSW (up to 11.5 nmol/L, $\sim 300\%$ saturation), and then declining through the CBIW and CBDW (Figure 13). Surface concentrations were lower than those in the PSW likely due to melt-water dilution in the polar mixed layer and air-sea flux (Section 3.3). The slight surface super-saturation could be attributed to a combination of upward diffusion from the PSW maximum and a sea ice source. Brine channels within sea ice are frequently anaerobic, providing the necessary conditions for anoxic processes such as methanogenesis [Rysgaard *et al.*, 2008]. In the winter, the CH_4 is mixed throughout the winter mixed layer with the rejected brine, and as the ice melts in the spring, any remaining brine is released into the surface melt water layer [Damm *et al.*, 2015a]. This process has been recently shown to cause similar surface super-saturation in the central Arctic Ocean [Damm *et al.*, 2015a].

The PSW contained a surprisingly widespread and consistent CH_4 maximum (averaging 9.1 nmol/L, 250% saturation) at a density of $25.5 \sigma_t$ ($S = 31.8$) and associated with the chlorophyll maximum (Figure 13). This peak is surprising because CH_4 is normally consumed relatively quickly in oxygenated waters, and should not be produced under aerobic conditions [Reeburgh, 2007]. As discussed above, DMSP metabolism may be a source of water column CH_4 production, particularly under NO_3^- limiting conditions [Damm *et al.*, 2010, 2015b]. This relationship implies that DMSP may be an in-situ source of these high CH_4 concentrations, providing an explanation for this ubiquitous signal.

Figure 12: Map and depth profiles of CH_4 concentrations in the Canada Basin and Beaufort Sea

Figure 13: This is a representative depth profile of CH_4 and fluorescence, showing the co-occurrence of the CH_4 and chlorophyll maxima. Filled black circles denote CH_4 concentration and error bars represent the standard deviation of the duplicates. The dotted line is fluorescence.

At depths below 200 m in the Canada Basin, CH_4 concentrations were extremely variable, ranging from 1.0 nmol/L (27% saturation) to 24.3 nmol/L (~700% saturation), with a median value of 3.1 nmol/L (~90% saturation) below 1000 m. This under-saturation could reflect lower atmospheric CH_4 concentrations at the time of ventilation (as discussed above for N_2O), and/or oxidation of CH_4 by methanotrophs in the deep water column. Unlike N_2O , the CH_4 under-saturation was not consistently observed throughout the

Canada Basin, making it more difficult to attribute to a particular process. Rather, the large range of CH₄ concentrations suggest the importance of ephemeral point sources. Notwithstanding the highly variable nature of CH₄ concentrations, we are still able to examine the potential contribution of biological and physical processes to the observed under-saturation at certain stations. The CBDW has been isolated for ~450 years [Schlosser *et al.*, 1997; Timmermans *et al.*, 2003]. At the time that this water mass was last exposed to the atmosphere, the CH₄ mixing ratio was ~675 ppb [Raynaud and Chappellaz, 1993]. Assuming that the temperature and salinity characteristics of this water mass have not been appreciably altered since it left the surface, the predicted equilibrium CH₄ would be 1.4 nmol/L, which is 1.7 nmol/L lower than our observations. Even if some changes in temperature and salinity did occur, this would only have a small effect on our calculations. For instance, a difference in temperature of 1°C would change the solubility of CH₄ by less than 0.1 nmol/L, while a salinity change of 1‰, would alter CH₄ solubility by ~0.03 nmol/L. Our results thus suggest that CH₄ has been added to the deep water by other, presumably biological processes. In contrast, the minimum CH₄ concentration we measured was only 1.0 nmol/L, which is 0.4 nmol/L less than the atmospheric equilibrium concentration 450 years ago. This lower value, therefore, can only have been obtained through biological consumption. The lack of persistently high CH₄ concentrations in the deep basin thus provides additional evidence for the microbial oxidation in these waters.

In addition to very low CH₄ concentrations, we observed more episodic, deeper maxima in the Canada Basin. Two of these CH₄ maxima are particularly large and warrant further explanation. There was a maximum on the Beaufort shelf at 170 m (18 nmol/L), and just off the slope at 1000 m (24 nmol/L). Considering that both of these stations are deeper than the maximum depth of subsea permafrost on the Beaufort shelf (~120m), there are three possible sources that may explain these high concentrations: destabilized hydrates on the Beaufort Slope, methanogenesis in sediments, and thermogenic seeps. Gas hydrates are stable only under specific temperatures and pressures and underlie much of the Arctic Ocean below a depth of ~300m [Ruppel, 2015]. The temperature of the water on the Beaufort Shelf has changed considerably over the last 60 years, potentially leading to a destabilization of gas hydrates between 300 and 550 m [Ruppel, 2015]. Indeed, “old” (low ¹⁴C) CH₄ has been found in gas vents on the Beaufort shelf, implying that it is sourced from gas

hydrates [Paull *et al.*, 2011]. Secondly, sedimentary methanogenesis may produce high CH₄ concentrations. The maximum in the western Beaufort shelf, which is contrasted by low concentrations on the eastern shelf (mean = 4.1 nmol/L), is in agreement with the observations of Coffin *et al.* [2013], who measured elevated CH₄ flux from the sediments to the water column of the western Beaufort Sea (near the BL stations) and low sediment-water column fluxes in the eastern Beaufort (near the MK stations). This sedimentary CH₄ was primarily biogenic, implicating methanogenesis as the dominant CH₄ source. Lastly, the entire Canada Basin is underlain by oil and gas deposits [Ruppel, 2015]. Gas may migrate through fractured rock and enter the sediments, and may be released through vents in the sea floor.

3.2.3 CH₄ in the Canadian Arctic Archipelago

Throughout the Canadian Arctic Archipelago, CH₄ concentrations decreased from south (mean 7.3 nmol/L) to north (mean 3.8 nmol/L). In contrast to the other regions in our study area, we observed extremely high concentrations in surface waters of the CAA, with maximum values in excess of 420% saturation (15.3 nmol/L), and decreasing concentrations with depth (Figure 14). This surface maximum was most prominent at the southern stations (AN-314, AN-312, and VS), but was also observed at some of the northern stations (CAA-4 and CAA-7) (Figure 14). Super-saturation of CH₄ in surface waters of the CAA was previously observed by Kitidis *et al.* [2010], who ascribed it to greater ice cover in the CAA limiting sea-air flux. Indeed, we observed high ice cover at many of the stations with elevated surface CH₄ concentrations in the CAA.

Figure 14: Map and depth profiles of CH_4 concentrations in the CAA and Baffin Bay

While increased sea ice cover may contribute to the accumulation of high CH_4 in CAA surface waters, ice cover, *per se*, may also represent a CH_4 source. We found a strong negative correlation between CH_4 and salinity across all regions we sampled in the CAA (Figure 15), suggesting a freshwater source of CH_4 from ice and/or rivers. Rivers could supply CH_4 from degrading permafrost or methanogenesis in riverine sediments to the CAA. Sea ice, on the other hand, contains brine channels which can contain high concentrations of CH_4 [Damm *et al.*, 2015a]. As the sea ice begins to melt, this brine drains into the surface layer of the ocean. The super-saturation we observe in the surface water at many of the stations in the CAA may be due to this partial melting of sea ice acting both as a CH_4 source and a semi-permeable barrier to sea-air flux.

Figure 15: CH₄ vs. salinity scatter plot of all samples collected in the CAA and Baffin Bay

East of Lancaster Sound, in Baffin Bay, we observed a modest CH₄ maximum (4.7 nmol/L, ~130% saturation) in the upper 50 m of the water column, with under-saturated concentrations below 100 m, reaching a minimum of <1 nmol/L. Our results are consistent with those obtained by *Punshon et al.* [2014] who observed near-equilibrium concentrations in the top ~200m of Baffin Bay, with increasing under-saturation in deeper waters. These authors attributed the depth-dependent decrease in CH₄ to microbial methane consumption. In contrast with our results, *Kitidis et al.* [2010] observed high concentrations in the upper 150 m water column in Baffin Bay, in a depth profile taken in close proximity to our sampling station BB3. The reason for this discrepancy is unclear, but highlights the temporal variability in CH₄ concentrations.

3.3 SEA-AIR CH₄ AND N₂O FLUXES

Sea-air fluxes of both CH₄ and N₂O across our full survey region were low compared to previous estimates from other Arctic regions, but similar to those from the global ocean (Table 2, Table 3) [*Rhee et al.*, 2009]. Overall, our study area was a source of CH₄ with sea-air flux averaging 1.3 $\mu\text{mol m}^{-2} \text{d}^{-1}$ (range = -0.4 to 4.9 $\mu\text{mol m}^{-2} \text{d}^{-1}$), and a minor sink for N₂O, with an average sea-air flux of -0.52 $\mu\text{mol m}^{-2} \text{d}^{-1}$ (range = -4.1 to 2.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$).

These findings are comparable to typical sea-air fluxes from the world ocean, which range from 0.2-1.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$ and 0.3-0.6 $\mu\text{mol m}^{-2} \text{d}^{-1}$, for CH_4 and N_2O , respectively [Rhee *et al.*, 2009]. At station CB28aa in the eastern Beaufort Sea, we observed high sea-air fluxes of both CH_4 and N_2O . At this station, we observed upwelling of deep water onto the shelf (based on its high density) implying that upwelling is a source of these gases to the atmosphere. This observation is in good agreement with previous studies showing the importance of coastal upwelling as a source of elevated CH_4 and N_2O sea-air fluxes in various marine systems [eg., Nevison *et al.*, 2004; Frame *et al.*, 2014; Capelle and Tortell, 2016].

Table 2: Sea-air flux of N_2O

Region	Sea-air flux ($\mu\text{mol N}_2\text{O m}^{-2} \text{d}^{-1}$)	Reference
Bering Sea	2 ± 1	[Hirota <i>et al.</i> , 2009]
	-0.5 ± 0.5	This study
Western Chukchi Sea	12 ± 9	[Hirota <i>et al.</i> , 2009]
Eastern Chukchi Sea	-0.4 ± 0.7	This study
Canada Basin	-0.9 ± 1.4	This study
CAA	5 ± 8	[Gagné, 2015]
	-0.2 ± 1.1	This study

Although our N_2O sea-air fluxes are relatively close to previous studies (Table 2), our CH_4 fluxes are much lower than those measured on Eurasian shelves, in CH_4 “hotspots”, and in polynya waters (Table 3). There are several reasons for this. Instead of taking the instantaneous ship wind speed, as is often done for air-sea flux calculations, we used a weighted mean over the 60 days prior to sampling. This approach incorporated variability in wind-speed, and thus produces piston velocity estimates that are more reflective of the average conditions experienced over the time of mixed layer ventilation. The more recent wind speeds are more heavily weighted, causing the wind speeds within the 7 days prior to sampling to have the most influence on the piston velocity (k_w). These derived weighted piston velocities are often lower than those based on instantaneous or daily mean wind speed data. Indeed, we obtained significantly higher (by up to 190%) sea-air fluxes when using mean daily wind speeds. An additional explanation for our lower derived CH_4 sea-air fluxes relates to the strong spatial variability in CH_4 concentrations. Unlike many

previous studies, we did not specifically sample any areas considered “hotspots” for CH₄, so our estimates should be considered a conservative background level. Understanding the significance of CH₄ hotspots to Arctic Ocean CH₄ fluxes requires careful sampling that avoids statistical bias in the over-representation of either high or low CH₄ waters. Carefully designed sampling programs, coupled with an objective analysis will provide a better perspective on the spatial distribution of these “hotspots”, as well as a more complete picture of the overall distribution of CH₄ concentrations.

Although sampling biases and different calculation approaches may explain the somewhat lower sea-air fluxes we observed relative to previous studies, there are also several hydrographic properties that would act to limit sea-air gas exchange. In general, low sea-air fluxes of CH₄ and N₂O can be attributed to the dilution of surface gas concentrations by melt-water, as previously suggested by *Kitidis et al.* [2010]. Indeed, fresh water contained low surface concentrations of both gases (Figure 2, Figure 3), resulting in low CH₄ and N₂O fluxes in the upper layer that exchanges with the atmosphere (Table 2, Table 3). As we did not have measurements within the mixed layer for stations that were partially covered with sea-ice, we did not calculate fluxes for these locations.

Table 3: Sea-air flux of CH₄

Region	Sea-air flux ($\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$)	Reference
Bering Sea	0.2 ± 0.4	This study
Eastern Chukchi Sea	1.9 ± 1.4	This study
Western Chukchi Sea	5 - 57	[Savvichev <i>et al.</i> , 2007]
Eastern Siberian Arctic (area-weighted mean flux, summer)	~7 - 17	[Shakhova and Semiletov, 2007]
East-Siberian Arctic Sea (CH ₄ hotspots, summer)	45 - 95	[Shakhova and Semiletov, 2007]
Barents Sea	~5	[Lammers <i>et al.</i> , 1995]
Canada Basin	1.3 ± 1.1	This study
CAA	1.2 ± 1.1	This study
Davis Strait	~1.6	[Punshon <i>et al.</i> , 2014]
Storfjorden polynya	26 - 104	[Damm <i>et al.</i> , 2007]

Based on the average sea-air flux for each sub-region and its area (Table 4), we calculated the annual emission of CH₄ and N₂O for the entire study region. We estimated

an annual flux of CH₄ on the order of 0.014 ± 0.013 Tg CH₄ yr⁻¹, equating to approximately 0.14 % of the yearly global oceanic CH₄ emissions, which are thought to be ~ 10 Tg yr⁻¹ [Reeburgh, 2007]. This is a conservative estimate, as it does not take into account CH₄ accumulation under sea ice and subsequent release after sea ice break up, storm events (that increase the depth of the mixed layer), or “hotspots” that may be significant local sources of CH₄. It is important to note that the Eastern Siberian Seas have been estimated to emit 1 – 8 Tg CH₄ yr⁻¹ alone [Shakhova *et al.*, 2005, 2010a], so our sea-air fluxes represent a minimum for the Arctic Ocean. We found that the North American Arctic Ocean was a minor sink of N₂O, with an integrated sea air flux on the order of $\sim -0.01 \pm 0.023$ Tg N yr⁻¹. This low balance can be attributed to freshwater input in the summer which creates a low dissolved gas layer at the surface of the Arctic Ocean [Macdonald *et al.*, 2004]. Our Chukchi Sea flux is much lower than previous estimates by Hirota *et al.* [2009], who determined the flux in the entire Chukchi Sea to be ~ 0.07 Tg N yr⁻¹ (Table 2). However, this previous calculation was based on much fewer measurements, of which the majority were in the western region. Thus, we consider our estimate to be more representative for the eastern Chukchi Sea.

Table 4: Regional annual fluxes of CH₄ and N₂O

Region	Mean sea-air flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	Area (km ²)	Annual flux
Northern Bering Sea	-0.5 $\pm$ 0.5 N ₂ O 0.2 $\pm$ 0.4 CH ₄	320,000	-1.7 $\pm$ 1.5 Gg N 0.3 $\pm$ 0.7 Gg CH ₄
Eastern Chukchi Sea	-0.4 $\pm$ 0.7 N ₂ O 1.9 $\pm$ 1.4 CH ₄	210,000	-0.9 $\pm$ 1.4 Gg N 2.3 $\pm$ 1.7 Gg CH ₄
Canada Basin	-0.9 $\pm$ 1.4 N ₂ O 1.3 $\pm$ 1.1 CH ₄	700,000	-6.1 $\pm$ 10.2 Gg N 5.5 $\pm$ 4.6 Gg CH ₄
CAA	-0.2 $\pm$ 1.1 N ₂ O 1.2 $\pm$ 1.1 CH ₄	840,000	-0.9 $\pm$ 9.6 Gg N 5.7 $\pm$ 5.5 Gg CH ₄
Total flux:			-0.0097 $\pm$ 0.023 Tg N 0.014 $\pm$ 0.013 Tg CH ₄

4

Conclusions

4.1 MAIN FINDINGS

This study covers a larger sampling region than any previous depth-resolved study of either CH₄ or N₂O in the Arctic Ocean. This synoptic perspective enables a pan-arctic view of the distributions of these gases, and reveals several important patterns. The highest concentrations of both gases were measured in the bottom waters of the shallow Chukchi Sea, where active microbial metabolism under low O₂ conditions leads to high rates of net CH₄ and N₂O production. The high N₂O concentrations that result from the denitrification and nitrification in the sediments on the shelf, are transported through the Canada Basin until they are attenuated in the CAA. In contrast, the CH₄ is rapidly oxidized in the water column so that the high CH₄ signature has a much more limited spatial extent. Both large super-saturation and under-saturation of CH₄ were measured, likely owing to the diversity and ephemerality of its sources, and the high capacity for CH₄ consumption in oxygenated waters. Indeed, the heavy $\delta^{13}\text{C}_{\text{CH}_4}$ signatures of low CH₄ concentrations were likely a result of consumption within the water column, indicating that this is a key sink of CH₄. Conversely, sources of CH₄ in the Arctic Ocean may result from sedimentary methanogenesis, decomposing permafrost, dissociating gas hydrates, migration from geologic gas deposits, river input, methanogenesis in sea ice, and in situ water column production. Additionally, sea ice formation and melting were important processes in the cycling of these climate-active gases. Convective overturning due to brine rejection stirred up the sediments, likely adding CH₄ and N₂O to the water column where seafloor production of these gases is high. Production within sea ice was also likely a source, and may have caused the super-saturation of CH₄ areas where sea ice was only partially melted. Although we measured elevated concentrations of both of CH₄ and N₂O in the water

column, sea-air fluxes of these gases were relatively low compared to previous studies in the Arctic Ocean [e.g., *Hirota et al.*, 2009; *Shakhova et al.*, 2010]. The freshwater layer at the surface acted to dilute the concentrations of the gases within the mixed layer, limiting the associated sea-air fluxes.

This study adds a major new set of observations to the currently limited data set of Arctic Ocean CH₄ and N₂O, with the first depth profiles of CH₄ in the Canada Basin and Canadian Arctic Archipelago (CAA), and N₂O depth profiles in the Beaufort Sea and much of the CAA. Our large-scale data set, combined with other hydrographic and oceanographic measurements, allowed us to examine likely processes driving the cycling of CH₄ and N₂O in the North American Arctic Ocean. We show that the Pacific Winter Water mass (PWW) is characterized by the highest N₂O concentrations in the North American Arctic, and this signature persists as far east as the CAA. We also examined the importance of permafrost in relation to the water column concentrations of CH₄ by comparing the sea-air fluxes in the Eastern Siberian Arctic Sea with those from the permafrost-free Chukchi Sea. We studied the role of sea ice in the biogeochemical cycling of CH₄ and N₂O. We documented the subsurface CH₄ maximum in the Canada Basin as well as the surface super-saturation, but under-saturation at depth at stations partially covered with sea-ice in the CAA.

A major contribution of this thesis is the provision of baseline CH₄ and N₂O concentration data for the Arctic. These baseline data will provide a benchmark for comparison against future studies as the Arctic environment undergoes rapid changes. Based on the results we obtained, we are able to speculate on how CH₄ and N₂O accumulation in Arctic waters may be influenced by climate-driven environmental change. The outcome will mainly depend on changes in carbon export and organic matter availability in shallow sediments, the reduction of the sea ice barrier to air-sea exchange, and the stability of shallow gas hydrate deposits on continental shelves.

4.2 CAVEATS AND LIMITATIONS

As this study was conducted on three separate cruises in different regions of the North American Arctic, we did not obtain the same resolution in all areas. The Beaufort Sea and CAA did not have the same density of stations as the northern Bering Sea and Chukchi Sea,

limiting the conclusions we could draw from these regions. We also did not have as many $\delta^{13}\text{C}_{\text{CH}_4}$ isotope samples in the Canada Basin and Beaufort Sea or the CAA as we did in the Bering and Chukchi Seas, so we were unable to determine the CH_4 sources east of the Chukchi Sea. As we only conducted sampling during the summer, our temporal resolution is also limited and we are unable to resolve seasonal changes in CH_4 and N_2O concentrations.

4.3 FUTURE OUTLOOK

This study reveals interesting new questions to guide future research. Additional CH_4 studies should focus characterizing CH_4 distributions in areas with subsea permafrost. The Beaufort Sea and Banks Island are the only regions in the North American Arctic Ocean with significant subsea permafrost deposits [Ruppel, 2015]. However, the Beaufort Sea has not been analyzed for CH_4 in any comprehensive study since the early 1990's [Macdonald, 1976; Kvenvolden *et al.*, 1993], and no measurements have been made in the vicinity of Banks Island. Additional samples for isotopic analysis, particularly ^{14}C , would also be especially useful to differentiate between CH_4 sourced from the methanogenesis of recent carbon, or CH_4 derived from old carbon sources such as degrading permafrost and gas hydrates. Future studies should also investigate the source of the ubiquitous subsurface maximum in the Canada Basin. This feature is unusual because of the low primary productivity, yet higher CH_4 concentrations than typically observed in open ocean subsurface maxima ($\sim 3\text{-}5$ nmol/L) [Reeburgh, 2007]. Potential processes leading to this sub-surface maximum could be investigated using stable isotopes ($\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$), CH_4 production rate measurements, and DMSP-addition experiments.

Future N_2O research should focus on following the PWW as it transits through the northern CAA. It remains unclear whether the N_2O from the maximum is ventilated to the atmosphere or is diluted by river input and meltwater. Sampling with high spatial resolution in the northern archipelago may elucidate the specific processes that cause the decrease in N_2O concentrations as the water moves eastward. Additionally, N_2O studies should focus on the Eurasian shelves. N_2O distributions have not been studied outside of the North American Arctic Ocean, although the low oxygen concentrations and decomposing permafrost on these marginal shelves may produce significant quantities of

N₂O. Finally, the relationship between sea-ice cycling and CH₄ / N₂O dynamics is still poorly understood. In our study, fresh water acted to limit sea-air flux (due to dilution of gas concentrations), while we observed high gas concentrations in the surface water under marginal sea-ice conditions. It remains unclear what happens to the gas distribution as sea-ice breaks up in the spring and re-forms in the fall. High temporal resolution sampling (depth profiles, sea ice, and brine) during these critical times could provide an explanation for the high super-saturation observed under sea ice, relative to the underlying water column. It may also help us understand the sources of CH₄ and N₂O to the water column, and the seasonal variability in their sea-air flux. Such time-series work could be conducted at a number of field stations, including the soon to be completed Canadian High Arctic Research Stations (CHARS), located in Cambridge Bay, Nunavut.

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