Dissolved methane in the Beaufort Sea and the Arctic Ocean, 1992–2009; sources and atmospheric flux

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Abstract

Methane concentration and isotopic composition was measured in ice-covered and ice-free waters of the Arctic Ocean during 11 surveys spanning the years of 1992–1995 and 2009. During ice-free periods, methane flux from the Beaufort shelf varies from 0.14 mg CH₄ m⁻² d⁻¹ to 0.43 mg CH₄ m⁻² d⁻¹. Maximum fluxes from localized areas of high methane concentration are up to 1.52 mg CH₄ m⁻² d⁻¹. Seasonal buildup of methane under ice can produce short-term fluxes of methane from the Beaufort shelf that varies from 0.28 mg CH₄ m⁻² d⁻¹ to 1.01 mg CH₄ m⁻² d⁻¹. Scaled-up estimates of minimum methane flux from the Beaufort Sea and pan-Arctic shelf for both ice-free and ice-covered periods range from 0.02 Tg CH₄ yr⁻¹ and 0.30 Tg CH₄ yr⁻¹, respectively to maximum fluxes of 0.18 Tg CH₄ yr⁻¹ and 2.2 Tg CH₄ yr⁻¹, respectively. A methane flux of 0.36 Tg CH₄ yr⁻¹ from the deep Arctic Ocean was estimated using data from 1993 to 1994. The flux can be as much as 2.35 Tg CH₄ yr⁻¹ estimated from maximum methane concentrations and wind speeds of 12 m/s, representing only 0.42% of the annual atmospheric methane budget of ~ 560 Tg CH₄ yr⁻¹. There were no significant changes in methane fluxes during the time period of this study. Microbial methane sources predominate with minor influxes from thermogenic methane oxidation is locally important on the shelf and is a methane sink in the deep Arctic Ocean.

Methane, a potent greenhouse gas, is a trace component of the atmosphere and is increasing at variable rates (Khalil and Rasmussen 1983; Steele et al. 1987; Dlugokencky et al. 1994, 1998, 2003, 2009, 2011; Bousquet et al. 2006; Fisher et al. 2011). The Arctic region with its large pool of carbon (McGuire et al. 2009; Semiletov et al. 2012) under rapid warming (Kvenvolden 1988, 1993; Lachenbruch et al. 1988; Walter et al. 2006) may add significantly to the atmospheric methane burden. Atmospheric methane concentration, its rate of increase, and the estimated lifetime in the atmosphere constrain the total global methane emissions to 500– 600 Tg methane per year (Dlugokencky et al. 2011). A recent assessment of the Arctic region identified 1000–2000 petagrams (Pg; 10¹⁵ g; 1,000,000–2,000,000 Tg) of stored carbon, mainly locked in buried plant matter but also including gas hydrate methane that is vulnerable to climate change over the next century (McGuire et al. 2009). In the terrestrial Arctic, wetlands, thaw lakes, fires, and leaking gas fields are important sources of methane (Walter et al. 2006; Mastepanov et al. 2008; Fisher et al. 2011; Ringeval et al. 2012; Kirschke et al. 2013) and are assumed to be partially responsible for an increase in global atmospheric methane.

The Arctic shelf is undergoing warming related to Late Pleistocene and Holocene sea level rise. During the last 10,000 yr, a transgression of warmer waters rapidly flooded the permafrost of the Beaufort Sea shelf (Hill et al. 1993), some of which may sequester gas hydrate. This thermal pulse is still propagating down into submerged permafrost resulting in thawing (Lachenbruch and Marshall 1986; Kvenvolden 1988; Lachenbruch et al. 1988; Serreze and Francis 2006; Paull et al. 2007). Over the last 30 yr, temperatures have dramatically increased throughout the Arctic region (NASA data, accessed 15 March 2016 http://data.giss.nasa. gov/gistemp/tabledata_v3/ZonAnn.Ts + dSST.txt). Past, present, and future methane fluxes from the Arctic regions need to be assessed for better climate change models.

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Additional Supporting Information may be found in the online version of this article.

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Recent studies present conflicting views of the current importance of sub-sea methane release. Reports on high methane flux from the Eastern Siberia Arctic shelf (ESAS; Shakhova et al. 2005, 2010) as well as reports on gas hydrate destabilization (but little transmission of methane to the atmosphere) offshore Svalbard (Westbrook et al. 2009) created concerns (Kerr 2010). Further studies concluded the marine Arctic is not yet at a point of runaway methane release from permafrost or gas hydrate (e.g., Dlugokencky et al. 2009; Kerr 2010) and marine methane release is currently not affecting atmospheric concentrations offshore Svalbard (Sowers 2006; Fisher et al. 2011).

There is a need for more thorough assessment of methane flux both into and through the water column to the atmosphere over different temporal and spatial scales. Here, we compare water column methane flux data from a 2009 field survey (Coffin et al. 2010) with similar studies from 1991 to 1995 (Kvenvolden et al. 1993; Lorenson and Kvenvolden 1995, 1997; Aagaard et al. 1996; Edwards and Coakley 2003). The majority of sampling efforts were conducted over the central Alaskan Beaufort Sea shelf and to a lesser degree deep waters of the Arctic Ocean including the North Pole. These studies were in part motivated by the hypothesis that the Holocene inundation of the Arctic shelf by relatively warmer Arctic Ocean waters may have induced gas hydrate dissociation resulting in a release of methane from shallow sediment.

Background

Arctic Ocean structure

Gas exchange between the ocean and the atmosphere as well as gas distribution within the water column strongly depends on the water column structure. There are four primary water masses in the stratified Western Arctic Ocean: the surface Polar mixed layer (PML) that includes mainly river run off, ice melt water, precipitation, and local input from the Pacific Ocean; The Pacific layer, a lower salinity surficial water inflowing from the Bering Straight; The warmer, more saline Atlantic layer entering via the Fram Straight and Barents Sea; and the lower Canadian Basin layer, mainly older modified, Atlantic-derived water (MacDonald and Bewers 1996; Carmack et al. 1997; Swift et al. 1997; McLaughlin et al. 2004). The Arctic Ocean is markedly stratified between 0 m and 150 m, the boundaries between the surface PML and the Pacific and Atlantic layers. This stratification results in low diffusion and heat transfer rates between water masses and is a fundamental reason why the Arctic Ocean is consistently ice covered. Ice cover restricts ventilation to the atmosphere; however, waters on the shallow shelf (< 100 m) do mix with the atmosphere, and are in some contact with the Arctic Ocean interior. The ice cover over the deep Arctic Ocean results in limited lateral ventilation of the Arctic Ocean focused along the shelf when the ice canopy is temporarily absent (Swift et al. 1997). Surface

circulation is dominated by the clockwise rotating Beaufort Gyre, and the Transpolar Drift moving water from Siberia to the Fram Strait. Localized nearshore currents can be variable and temporally influenced by river discharge. All this influences strongly influences the methane distribution and fluxes.

Trans-Arctic research cruises 1993–1994

Data is provided from two time periods in the Arctic Ocean. For SCience ICe EXercise (SCICEX, Morison 1996; Edwards and Coakley 2003) 1993-1994-water column methane concentrations and isotopic composition were analyzed with samples from two cruises during August-September 1993 and July-September 1994 (Fig. 1; Supporting Information Table S1). During July through September 1994, two ice breakers crossed the Arctic Ocean, the Canadian Coast Guard ship Louis S. St.-Laurent and the U.S. Coast Guard ship Polar Sea crossed the Arctic Ocean. The objective of the expedition was to investigate the biological, chemical, and physical systems that define the Arctic Ocean's role in global climate change. Water column measurements were collected from 35 hydrographic stations starting on the Chukchi shelf, moving across the Chukchi Abyssal Plain and Makarov Basin, down the Eurasian side of the Lomonosov Ridge to the North Pole (Fig. 1; Aagaard et al. 1996; Keating 1996; Tucker and Cate 1996; Wheeler 1997).

MITAS Cruise 2009

Methane in the Arctic Shelf/Slope (MITAS) expedition was conducted during September 2009 onboard the U.S. Coast Guard Cutter (USCGC) Polar Sea (WAGB-11), on the Alaskan Shelf/Slope of the Beaufort Sea. Expedition goals were to investigate spatial variations in methane (CH₄) source(s), vertical CH₄ flux in shallow sediments (< 10 mbsf), and CH₄ contributions to shallow sediment carbon (Fig. 2). Three transects across the Alaskan Beaufort Sea [Camden Bay (T1), Thetis Island (T2), and Cape Halkett (T3), (Fig. 2)] shelf ranged from 20 m to 2000 m and focused on methane in sediment, water column, and atmosphere.

Materials and methods

During the different cruises a various methodologies have been applied for studying the sediment, the water column and the atmosphere. Physical, chemical, and biogeochemical analyses were performed and over the years different methodologies have been used for the same analyses. They are explained in detail and are available in the Supporting Information material.

Results

Arctic Ocean 1993-1994

During SCICEX-93 72 water samples from depths of 5–400 m were collected at 12 stations through the ice pack for methane concentration measurements (Fig. 1). A south to north transect depicting methane concentration, temperature,



Fig. 1. Map of Arctic Ocean. Cruise tracks and sampling stations for the AOS094 (red), and the SCICEX-93 (green) expeditions. Large markers with numbers correspond to sample stations in Supporting Information Table S1 smaller markers without numbers indicate CTD stations where methane samples were not taken. Map modified from Aagaard et al. (1996). [Color figure can be viewed at wileyonlinelibrary.com]

and salinity data collected during SCICEX-93 together with data from nearshore Alaska (USGS, September 1993) is shown in Fig. 3. Methane concentrations range from 1.18 nM to 67.2 nM (Supporting Information Table S1; Fig. 3A) with higher values near the coast (5.5–44.4 nM, Lorenson and Kvenvolden 1995), the Chukchi shelf at 50 m (67.2 nM, Sta. 2) and up to 28.8 nM at the North Pole. Near-surface methane concentrations ranged from 2.46 nM to 13.7 nM representing values below and well above equilibrium with the atmosphere (3.69 nM; where water temp. = 0°C and atm. methane conc. is 1.81 ppmv). The temperature and salinity sections show some mixing between the upper PML and Pacific-derived waters and the Atlantic layer beneath it. Low-temperature water (< -2°C) near the surface concurrent with high salinity ~ 36 PSU indicates that ice is forming resulting

in residual brine. As this water sinks, it appears to drive convection cells in the Atlantic water beneath it (Fig. 3B,C).

Fifty-seven water samples collected between 67° N and 90° N during AOS-94 (Tucker and Cate 1996) were mainly obtained from water depths of 10–500 m, with some taken as deep as 2000 m. Surface to near-surface methane concentrations over the Chukchi Sea shelf ranged from 5.66 nM to 31.9 nM and increased with depth (Supporting Information Table S1). Offshore, methane concentrations in near-surface water below the ice cover ranged from 3.86 nM to 13.8 nM and are at or well above the equilibrium with the atmosphere (3.69 nM). Methane concentrations decreased with depth to as low as 0.91 nM and methane carbon isotopic compositions ranged from δ^{13} C -20.8% to -66.4% (Fig. 4A–C). Density stratification of the water masses below

Lorenson et al.



Fig. 2. Northern Alaska showing the area of USGS surveys from 1992 to 1995 and the MITAS transects conducted in 2009. Reference areas show where gas hydrates are inferred on the Beaufort Sea Slope and the region where gas hydrate stability zone associated with permafrost occurs on the North Slope and offshore on the Beaufort Sea Shelf. Also shown are known oil and gas fields in the Prudhoe Bay region and the location of the Canning seafloor mound (CSM). [Color figure can be viewed at wileyonlinelibrary.com]

100 m is apparent from the low salinity waters of the PML and Pacific layers perched above the Atlantic-derived ocean water. Methane concentrations and carbon isotopic composition observed during the SCICEX-93, AOS-94, and USGS Beaufort Sea shelf data measured in near-surface waters are contoured in Fig. 5A,B over a swath of the Arctic Ocean extending from the Beaufort and Chukchi Seas northward beyond the North Pole.

Beaufort Sea 1992–1995

Waters of the central Beaufort Sea shelf were surveyed seven times to a maximum depth of 100 m during ice-covered and ice-free seasons between 1992 and 1995. The region around Harrison Bay was chosen for its extensively mapped sub-sea permafrost (Neave and Sellmann 1982). Here, seismic analyses show that the seaward extent of the permafrost is limited to a water depth of about 20 m and is associated with sand-rich sediments on the Beaufort Shelf (Brothers et al. 2012).

Analyses of water samples from the ice-covered ocean yielded supersaturated methane concentrations (> 3.69 nM) in all four surveys. Maximum methane concentrations ranged from 12 nM to 275 nM with the highest concentrations found near the seafloor (Kvenvolden et al. 1993; Lorenson and Kvenvolden 1995, 1997; plotted in cross-section Fig. 6A–G, and plan view in Fig. 7A–M). Under ice, methane concentrations were higher by 20–200 nM than those measured

in the same place during ice-free times. Mean methane concentrations were lower overall during non-ice-covered times, but there were similar year-round local concentration maxima near the coastline corresponding to water less than \sim 15 m deep and proximity to river deltas.

Maximum methane concentrations from ice-free water ranged from 5 nM to 56 nM excluding a recurring anomaly of higher methane concentration measured nearby a putative seep (concentrations here were up to 149 nM). Typically, methane concentrations were at a minimum very near the sea surface, remained nearly constant or increased with depth. Methane concentrations in the upper 3 m of water ranged from 7 nM to 36 nM and were commonly between 6 nM and 14 nM. Carbon isotopic values range from δ^{13} C -31.1_{∞}^{∞} to -80.5_{∞}^{∞} (Fig. 6H–K).

Water column methane oxidation rates were determined in selected samples during surveys conducted in May 1992, April 1993, September 1993, and May 1995, they ranged from below detection $(10^{-4} \text{ nM/d}; \text{September 1993})$ to 0.8 nM/d (Lorenson and Kvenvolden 1995, 1997). Methane oxidation rates are shown in transect cross sections in Fig. 8A–C, and in plan view in Fig. 7A–C. Highest rates occurred in both nearshore and in local anomalies highlighting the variability in methane oxidation rates. The ocean was ice-covered during these times and the water temperatures were less than -1.5° C with the exception of September 1993.



Fig. 3. A south to north transect collected during SCICEX-93 nearshore Alaska showing; (A) Methane concentration, (B) seawater temperature, and (C) salinity. [Color figure can be viewed at wileyonlinelibrary.com]

Lorenson et al.



Fig. 4. The south to north transect collected during AOS-94 showing (A) methane concentration; (B) methane carbon isotopic composition, and (C) salinity. [Color figure can be viewed at wileyonlinelibrary.com]

MITAS Beaufort Sea 2009

The three transects, sampled in 2009 (MITAS) consisting of water, sediment, and atmospheric measurements across the Alaskan Beaufort Sea (20–2000 m water depth) offshore of Camden Bay (T1), Thetis Island (T2), and Cape Halkett (T3) (Fig. 2). CTDderived physical (temperature, salinity, and density) and chemical data (oxygen) show that the PML was generally less than 40 m thick with surface water temperatures less than 0.7° C, salinity



Fig. 5. (**A**) Surface methane concentrations and (**B**) carbon isotopic composition observed during the AOS-94 cruise nearshore Alaska in August 1994. Note that the ice pack covered most of the surveyed area north of 72° and the sea was largely out of direct contact with the atmosphere.[Color figure can be viewed at wileyonlinelibrary.com]



Fig. 6. Methane concentration (**A**–**G**) and methane carbon isotopic composition (**H**–**K**) along transect 2 from 1992 to 1995. Note various methane concentrations ranges in panel A–G and slightly different distance scales. The inset shows the location of transect 2. Two methane hotspots occur; near the coastline (**A**, **D**, and **F** coinciding with ice-covered periods) and near the 20 m isobath (**A**, **B**, **E**, **F**, and **G**). [Color figure can be viewed at wileyonlinelibrary.com]



Fig. 7. Montage of contoured mean surface measurements of methane concentration and oxidation rates for 1992–1995 and 2009 used to calculate methane fluxes. Integrated mean methane values were calculated from these surfaces on a 1 km² grid using a GIS algorithm (see Table 1 for results). The figure is organized in rows according to year and into columns corresponding to mean methane oxidation rates, ice-covered mean methane concentration of surface water, and non-ice mean methane concentration of surface water. Note variations in scale in each figure. [Color figure can be viewed at wileyonlinelibrary.com]



Fig. 8. Methane oxidation rates (nM CH₄/d) measured by ¹⁴C incubations along transect 1 in (**A**) May 1992, (**B**) April 1993, and (**C**) May 1995. The inset map shows the location of the transects. Note various depth and intensity ranges in each panel. [Color figure can be viewed at wileyonlinelibrary.com]

ranging from 26 to 29 PSU (cross sections of all three transects and further explanations can be found in Hamdan et al. 2013).

Methane concentration in the water were similar to those found in the 1990s, ranging from 0.40 nM to 83.9 nM

between 20 m and 2290 m water depth (Supporting Information Table S2). High concentrations occurred nearshore along the shelf break at transect 2 and 3, and in deep water in transect 3 (Fig. 9A–C). Low methane concentrations are common



Fig. 9. Methane concentration (nM) measured in seawater during the MITAS expedition from the shelf across the upper slope. The map shows the location of transects. (**A**) The Hammerhead transect (T1), (**B**) The Thetis Island transect (T2), and (**C**) The Cape Halkett transect (T3). [Color figure can be viewed at wileyonlinelibrary.com]

to deeper and offshore waters. These areas correspond to differences in salinity and temperature suggesting that the methane distribution may be related to mixing of the Polar mixed and the upper Pacific layers.

Bottom water methane concentrations were elevated (up to 76 nM) in shallow water (~ 20 m) of the Thetis Island transect (T2) where previous measurements in the 1990s had found high methane concentrations too (Table 2). Methane concentrations well above background were also measured from the slope regions of T3 where elevated bottom water methane concentrations (71 nM) corresponded to sediment rich in methane (~ 2 mM, Hamdan et al. 2013). Sediment cores PC 12, 13, and 14 had anomalously high concentrations methane (Table 3) and bottom water concentration reached a high of 82.8 nM where core PC 14 was taken in 1461 m water depth.

Hydrocarbon gases (methane through butane) were extracted and methane concentration ranged from 6.5 mM to 5.38 nM (Table 3) Ethane, propane, and iso-butane was present in very low concentrations in some samples. Isotopic composition of δ^{13} C-CH₄ ranged from -80.0% to -96.9%, δ D-CH₄ from -201% to -229% and δ^{13} C-CO₂ from -4.0% to -24.4%; the deepest section of core PC 14 showed a very high methane concentration (6.5 mM) and very low δ^{13} C-CH₄ values -96.6% (see also Coffin et al. 2013). Sediment void gas had similar isotopic compositions.

Discussion

Quantifying methane sources is critical in future climate modeling and any mitigation efforts that may be planned. Currently, microbial sedimentary and/or deep-seated thermogenic sources are thought to contribute far more methane to the Arctic environment (McGuire et al. 2009; Lorenson et al. 2011a; Walter Anthony et al. 2012) than any in situ microbial water source (e.g., Damm et al. 2010); however, in situ methanogenesis is not well studied. While the fermentation of sedimentary organic matter is documented in abundance here by high methane concentrations and isotopic compositions expected from microbial sources, especially near coastlines and river deltas, methane from thermogenic sources should be considered as well since occasionally thermogenic gas was found in the water column.

Dissolved methane in river water

Dissolved methane is locally important for high volume rivers, for example in the freshwater lens of the Lena River delta (Bussmann 2013), but is confined to the nearshore and therefore has to be considered a minor source of methane to the Arctic Ocean. In contrast to the Lena River, water from the Sagavanirktok River near Prudhoe Bay, Alaska had low a methane concentration of 13 nM in April 1993, and thus is not a likely source of methane to the Beaufort Sea or Arctic Ocean. Higher methane concentrations were measured in the water just offshore the Colville River delta west of Prudhoe Bay, however methane concentrations were greater during ice covered periods and increased with water depth implying decomposing sedimentary organic matter as the source rather than dissolved methane from river water.

Sedimentary methane sources

The entire Beaufort shelf and North Slope of Alaska is a world-class petroleum province (Houseknecht and Bird 2006; Gautier et al. 2009; Bird and Houseknecht 2011). Thermogenic gas seeps are abundant onshore (Burruss et al. 2003). To the east, the Mackenzie River Delta is a well-explored oil and gas province with confirmed thermogenic gas seeps both onshore and offshore (Bowen et al. 2008; Paull et al. 2011). A multitude of seeps along the shelf edge and on the slope offshore the Mackenzie delta is reported by Paull et al. (2011) and from pingo-like features (PLF's) and pockmarks by Paull et al. (2007). Microbial methane ($\delta^{13}C - 72_{00}^{\circ}$ to -99%) from the Kugmallit pockmark field, near the mouth of the Mackenzie Delta is isotopically similar to methane emanating from sampled PLF's. Methane in deeper gas hydrates of the Mackenzie delta is of thermogenic origin (mean value δ^{13} C -42.7% Lorenson et al. 1999).

The Prudhoe Bay oil field in the Beaufort Sea terminates at the structural high of the Barrow Arch located under the shelf corresponding with water depths of about 20 m. Gas hydrate from the nearby onshore Mount Elbert gas hydrate well has methane with an isotopic composition ranging from $\delta^{13}C$ –48.4‰ to –46.6‰ (Lorenson et al. 2011a) while methane from the nearby Prudhoe Bay oil fields ranges from $\delta^{13}C$ –56.3‰ to –36.2‰ (Masterson et al. 2001). Other regional thermogenic gas sources that may be available to nearshore regions include oil-associated methane and coal bed methane.

Thermogenic methane seepage that maybe associated with gas hydrate dissociation is apparent in Fig. 6I and possibly Fig. 6H near the 10-20 m isobaths and coincides with (nearby) high bottom-water methane concentrations (Fig. 6D,E). In addition further offshore anomalously high methane concentrations were seen on three occasions within the same area; 94 nM at 20 m in May 1992 (δ^{13} C not measured), as well as 56.4 nM at 14 m (δ^{13} C -31.1%), and 149 nM at 20 m (δ^{13} C -46.4%) in August 1994 (Lorenson and Kvenvolden 1995). It is uncertain if this seepage can be solely related to gas hydrate decomposition because methane with this carbon isotopic composition is found in the adjacent Kuparuk River and West Sak oil fields that extend offshore onto the shelf (Lorenson et al. 2011a). However, these observations remain the most compelling geochemical observation suggesting the destabilization of gas hydrate on the Alaskan Beaufort Sea shelf. Subsequent sampling in 1995 and 2009 could not confirm these observations.

In the deep Beaufort Sea multichannel seismic (MCS) reflection, data show a widespread bottom simulating reflection (BSR) indicating that the Beaufort Sea slope hosts gas hydrate (area is outlined in Fig. 2; example shown in Fig. 10). Using similar sections for guidance, the Canning

Table 1 centration blue are o	 L. Estimates c n; and mean calculated usi 	of methane carbon iso ing the met	fluxe topic thod o	s to th comp of prev	ne atm osition vious r	iosphere fro n and oxida researchers	om the Be ation rates for direct	eaufort Sea durir i in surface in se comparison wit	ng 1992- awater. '	-1995 and 2 Values in gra Iculations.	009 deteri y are usec	mined f I in the	rom mean dissol present assessm	ved methane con- ent, while those in	
										mg CH₄ m	-2 d ⁻¹				
Period		Integrated	-					Mean					Beaufort Sea Integrated	Pan-Arctic Shelf Integrated	
lce	Mean CH ₄	mean				No.	Mean	CH ₄ ox.rate		Integrated			mean	mean	
covered	[Mn]	CH ₄ [nM]	SD	Min.	Max.	Samples δ	; ¹³ CH4 %	, nmol L ⁻¹ D ⁻¹	Mean	mean	Min.	Мах.	Tg CH₄ yr ^{−1}	Tg CH₄ yr ^{−1}	
										Flux to atmos	phere from	surface	using $k = 0.24 U^2$ (3)	sc/660) ^{-0.5}	
Surface wa	nter														
May-92	42.3	39.0	34.4	23.1	112	9		0.019	0.80	1.01	0.40	3.10	0.18	2.22	
Apr-93	27.2	17.8	31.0	3.10) 175	27		0.033	0.68	0.41	-0.02	4.92	0.07	0.08	
Apr-94	54.0	34.3	75.0	10.1	275	15			1.45	0.88	0.18	7.82	0.16	1.93	

0.62 0.99

0.05 0.08

5.57 7.82

0.42 -0.02

0.28 0.45

1.33 1.08

0.048

-63.52

20 68

18.4 197 3.10 275

41.3

13.5 19.4

49.8 41.1

Non-ice covered Composite May-95

44.6 18.4

Sep-93	10.3	8.60	4.35	5.40 18.8	17			0.20	0.15	0.05	0.46	0.03	0.33
Aug-94	9.08	8.10	13.9	5.40 13.9	15			0.17	0.14	0.05	0.31	0.02	0.30
Aug-95	15.9	8.10	8.63	6.00 36.3	25			0.38	0.14	0.07	1.00	0.02	0.30
Sep-09	16.7	18.0	12.5	1.18 53.5	35			0.40	0.43	-0.08	1.52	0.08	0.95
Composite	14.0	12.1	9.60	1.18 53.5	92	-57.11		0.32	0.26	-0.08	1.52	0.05	0.57
								Legacy m	ethod flux to	atmosphe	tre from s	urface using $k = 0$.31 <i>U</i> ² (Sc/660) ^{-0.5}
Surface water													
May-92	42.3	39.0	34.4 2	3.1 112	9		0.019	1.43	1.31	0.52	4.01	0.23	2.87
Apr-93	27.2	17.8	31.0	3.10 175	27		0.033	0.87	0.52	-0.02	6.33	0.09	1.14
Apr-94	54.0	34.3	75.0 1	0.1 275	15			1.87	1.14	0.24	10.1	0.20	2.49
May-95	49.8	13.5	44.6 1	8.4 197	20		0.048	1.71	0.36	0.55	7.17	0.07	1.80
Composite	41.1	19.4	41.3	3.10 275	68	-63.52		1.39	0.58	-0.02	10.1	0.10	1.28
Non-ice covere	pa												
Sep-93	10.3	8.60	4.35	5.40 18.8	17			0.26	0.20	0.07	0.60	0.03	0.43
Aug-94	9.08	8.10	13.9	5.40 13.9	15			0.22	0.18	0.07	0.41	0.03	0.39
Aug-95	15.9	8.10	8.63	6.00 36.3	25			0.48	0.18	0.09	1.29	0.03	0.39
Sep-09	16.7	18.0	12.5	1.18 53.5	35			0.51	0.56	-0.10	1.96	0.10	1.23
Composite	14.0	12.1	9.60	1.18 53.5	92	-57.11		0.41	0.33	-0.10	1.96	0.06	0.73
Values used ir	n flux calculat	tions.		U oo									

Ice covered; U = 7.4 m/s; salinity = 31 psu; temp. = 0°C. Non-ice covered; U = 7.4 m/s; salinity = 26 psu; temp. = 2°C. Atmospheric methane [1.81 ppm]; Sep. 09 [1.88 ppm].

Methane flux = k(Cw-Ce).

 $k = \text{gas transfer velocity} = 0.24 U^2 \times (\text{Sc/660})^{-0.5}$ or $0.31 U^2 \times (\text{Sc/660})^{-0.5}$; U = windspeed m/s. Sc, Schmidt number; Cw, methane concentration in water; Ce, methane equilibrium concentration in water. Beaufort Sea area $\sim 476,000 \text{ km}^2$. Arctic Shelf area $\sim 6,000,000 \text{ km}^2$.

Period Ice covered	Mean CH₄ [nM]	No. samples	SD	Min.	Max.	Mean δ^{13} CH ₄ %	Mean CH ₄ ox.rate nmol L ⁻¹ d ⁻¹
Bottom water		-					
May-92	52.3	6	40.5	17.1	112		0.032
Apr-93	26.9	27	31.4	31.0	175		0.440
Apr-94	57.2	15	73.4	11.2	275		
May-95	49.4	20	49.4	19.7	197		0.141
Composite	42.4	68	48.1	3.10	275	-60.27	
Non-ice covered							
Sep-93	16.4	17	9.89	5.50	44.4		
Aug-94	26.6	15	36.9	6.20	149		
Aug-95	33.9	25	17.4	6.00	56.0		
Sep-09	21.7	35	15.9	1.42	82.8		
Composite	24.8	92	20.9	1.42	149	-57.64	

Table 2. Mean dissolved methane concentration and carbon isotopic composition in bottom water.

Table 3. Gas concentration and carbon isotopic composition extracted from sediment. Fractionation factors between methane and carbon dioxide (α) are also expressed in ε ; the carbon isotope separation as defined by Whiticar (1999).

Transect	Core	Latitude N	Longitude W	Water Depth m	Sample Depth cm	CO₂ ppm	C ₁ nM	C ₂ nM	C₃ nM	iC₄ nM	C ₁ / C ₂	δ ¹³ C ₁ ‰	δDC 1 ‰	δ ¹³ CO ₂ ‰	ε C 1-CO2	αC _{1-CO2}
1	PC2	-71.00380	145.45061	566	626		8.15									
1	PC3	-70.97464	145.48690	490	713		10.2									
1	PC4	-71.19974	145.24919	2077	387	1100	44.7							-20.3		
2	PC6	-71.39228	148.35877	2255	324		2.08									
2	PC7	-71.25543	148.61553	985	164		2.66									
2	PC8	-71.20739	149.22443	137	239	2500	2420	0.48	2.29	5.50	873	-88.1	-229	-19.8	68.3	1.0749
2	PC9	-71.21907	149.22056	306	417	2400	3830	3.79						-24.4		
3	PC10	-71.86734	151.78186	1999	595		5.38	1.93								
3	PC11	-71.77805	151.87845	1430	574		7.68	0.04								
3	PC12	-71.54952	152.06135	342	598	2700	2210	0.08	1.18		1751	-80.0	-206	-4.7	75.3	1.0818
3	PC13	-71.53105	152.07924	277	602	8600	2250	2.89	0.46	0.46	673	-81.9	-206	-4.0	77.9	1.0848
3	PC14	-71.62770	151.98952	963	645	850	6490					-96.6	-214	-15.0	81.6	1.0903
		l	atitude	Longitu	de		C02	C ₁			δ^1	³ C ₁ δ	DC ₁	δ ¹³ CO ₂		

		Latitude	Longitude			CO ₂	C 1	$\delta^{13}C_1$	δDC_1	$\delta^{13}CO_2$		
Transect	Sample	Ν	W			ppm	ppm	%	‰	%	εC _{1-CO2}	αC _{1-CO2}
3	PC 13 void gas	-71.53105	152.07924	342	467	460	32.0			-11.6		
3	PC 12 void gas	-71.62770	151.98952	277	466	570	2670	-82.9	-201	-13.0	69.9	1.0762

Chemical analysis based on standards accurate to within 2%.

For the chemical analysis, blank fields not detected/below detection limit or not measured.

Carbon isotope separation $\varepsilon = \delta^{13}C_1 - \delta^{13}CO_2$.

Carbon isotope fractionation factor $\alpha = (\delta^{13}C CO_2 + 1000)/(\delta^{13}C CH_4 + 1000)$.

Seafloor Mound (CSM) north of Camden Bay in 2530 m deep water was cored (Hart et al. 2011) resulting in the recovery of methane-saturated sediment and gas hydrate 2 m below the seafloor. The isotopic composition of the methane from the CSM ranged from $\delta^{13}C$ –59.2‰ to –50.4‰ indicating a mixed source of microbial and thermogenic origin but becoming more thermogenic in character with increasing depth. Trace quantities of thermogenic gases,

n-butane, n-pentane, and hexane to octane gases in the sediment are evidence for at least a partial thermogenic genesis (Lorenson et al. 2011b).

Gas hydrate exposed on the seafloor at places like the CSM can contribute some unknown amount of methane to the overlying ocean through its dissolution. Gas hydrate outcrops on the seafloor experience dissolution at highly variable rates (e.g., 150 cm yr^{-1} ; Rehder et al. 2004), also influenced by



Fig. 10. The 1977 USGS high resolution 2D seismic line used to guide for locations of coring site along the Cape Halkett (T3) transect. The section is highlighted with coring sites PC 10-14. Horizons of interest are indicated BSR; bottom simulating reflector commonly perceived as the base of gas hydrate stability; yellow and red bands denoting possible gas accumulations; and SMT; the sulfate-methane transition depth (cmbsf: centimeters below sea floor measured in cores). [Color figure can be viewed at wileyonlinelibrary.com]

biofilms or oil (Lapham et al. 2010). Buried gas hydrate will dissolve at a much slower rate of about 0.02 cm yr^{-1} and is highly dependent on methane flux rates from below (Lapham et al. 2010). In general gas hydrate bearing mounds like the CSM are often associated with active methane seepage and thus, features like the CSM may contribute methane into the deep Arctic Ocean through the processes of methane seepage and from gas hydrate dissolution.

Sediment from the deepest section of each MITAS core revealed that the upper slope sediments have high methane concentrations. The upper slope corresponds to the upper part of the gas hydrate stability field (Fig. 10; see Fig. 2 for location) and was targeted because of the intersection of the BSR with the seafloor in conjunction with enhanced near-surface reflectors interpreted as methane gas. Pore water in sediment cores exposed to atmospheric pressure retained methane concentrations of up to 6500 nM pointing to even higher in situ concentrations. The origin of methane is mainly microbial via carbonate reduction as illustrated in Fig. 11A,B. Several of these methane rich cores have trace quantities of thermogenic propane and isobutane indicating some connection to deeper thermogenic gas sources. The sulfate-methane transition zones

(SMT), indicated for transect 3 on Fig. 10 are very shallow and almost at the seafloor, similar to other known seep sites, demonstrating that these areas are regions of high methane flux with deeper geological connections. In contrast, sediment sampled on the shelf and in deeper waters of the slope contains much less methane (Table 3).

These results and occurrence of high methane concentrations in the bottom water over these areas (e.g., Sta. 33, 330 m, 36.13 nM) indicate that the upper slope is capable of actively discharging methane into the water column, but we did not see any direct evidence from geochemical or acoustic water column measurements that methane from these areas transits to the atmosphere. However, the sediment geochemistry and geophysical findings clearly show that along the entire ~ 650 km length of the Beaufort upper slope where the BSR intersects or underlies the seafloor there is potential for sizable methane emissions where the seafloor is breached by faulting, or affected by submarine landslides.

Methane concentration and sources in the Arctic Ocean

Concentrations and carbon isotopic signatures of methane varied widely between oceanographic provinces and



Fig. 11. (A) Generic gas source plot modified from Whiticar (1994, 1999) showing MITAS core gas and local onshore gases. (B) Carbon isotopic separation between coexisting methane and carbon dioxide of the same set of gas samples. [Color figure can be viewed at wileyonlinelibrary.com]

water masses. Three areas with high concentrations occur within the PML (0–100 m) and one high-methane area was found at a mixing zone between the Pacific and Atlantic

layers at ~ 200 m (Fig. 3A). Methane with the highest concentrations (55.6 nM) and most ^{13}C depleted isotopic signature ($\delta^{13}C$ –59.1‰ to –66.4‰) occurs within the PML over



Fig. 12. Plot of cruise AOS-94 methane concentration and concurrent methane carbon isotopic values as a function of cumulative distance from the Chukchi Sea shelf. [Color figure can be viewed at wileyonlinelibrary.com]

the Chukchi Sea shelf and are likely from shelf sedimentary sources or aerobic oligotrophic production of methane in the water column. There are occasional methane concentration spikes at depths below the Pacific layer with enigmatic sources (Supporting Information Table S1). Damm et al. (2010) noted that in situ methane production is observed in the Pacific Layer, but not in the Atlantic Layer provided that nitrate is depleted and phosphorous is available. They suggest that a low N : P ratio enhances the ability of bacteria to compete for phosphate that breaks down the phytoplankton metabolite dimethylsulfoniopropionate (DMSP) with methane being generated as a by-product.

Over the entire Arctic Ocean, the concentration of methane in the upper 50 m of water corresponding in part with the PML (0-100 m) decreases with increasing distance from the shelf. An analysis of near-surface methane incorporating the 1993 and 1994 summer season data shows that methane concentrations in non-shelf surface water ranged from 2.46 nM to 13.8 nM and up to 31.9 nM on the Chukchi Sea shelf. A plot of surface methane concentrations and isotopic data vs. the cumulative distance from Sta. 1 (closest to shore) shows that as distance increases the methane concentration decreases while the carbon isotopic composition becomes ¹³C-enriched (Fig. 12; Supporting Information Table S1). The sea surface methane concentration approached atmospheric equilibrium values (3.47 nM; at 2°C and atm. methane conc. of 1.81 ppmv) at Sta. 1 whereas at Sta. 2, next to the ice cover, it was supersaturated in methane with isotopic values

indicated a microbial-source. Beyond Sta. 2, methane concentrations slowly approached equilibrium values, while the isotopic compositions became more ¹³C-enriched than atmospheric values ($\delta^{13}C - 47.4_{\infty}^{\circ}$ Quay et al. 1999); this is consistent with methane oxidation and similar to observations by Damm et al. (2007).

Over deep water, yet still within the PML the δ^{13} C values range from δ^{13} C -35.8% to -52.3% with the highest 13 Cenriched samples corresponding with the lowest methane concentrations; this is similar to observations by Damm et al. (2008) offshore Svalbard. During AOS-94, the methane concentrations were low, 0.75–4.33 nM and highly ¹³C enriched ($\delta^{13}\text{C}$ –20.8‰ to –41.5‰) within the Atlantic layer (below ~ 100 m) indicating that methane oxidation clearly affects the concentration and isotopic composition in the Atlantic layer. A simple mixing model between two sources (e.g., water equilibrated with the atmosphere and an assumed seepage related source) or models showing Rayleigh fractionation dependent changes in δ^{13} C do not give a simple explanation for our data suggesting that there are other processes involved and that methane sources and concentrations change over time (Supporting Information Fig. S1A,B).

Methane oxidation

Microbial oxidation is a significant sink for methane in the water column (Reeburgh 2007), especially for deep water sedimentary sources where methane is predominantly dissolved. It is less a factor in extremely shallow water where



Fig. 13. Process plots of methane oxidation, δ^{13} C and concentration. (**A**) Methane concentration contoured as a function of depth and isotopic composition, (**B**) methane oxidation rate contoured as a function of depth and methane concentration, and (**C**) methane oxidation rate contoured as a function of depth and methane isotopic composition. [Color figure can be viewed at wileyonlinelibrary.com]

ebullition or water advection can transport methane through the water column (Leifer et al. 2006). In April 1993, high oxidation rates were localized adjacent to the shoreline (Fig. 8B) while in May 1992 and 1995 (Fig. 8A,C) the greatest rates occur near the seafloor (18–20 m depth). The highest oxidation rates of over 0.8 nM/d occurred within an area of high methane concentrations and isotopic composition that strongly suggested a thermogenic gas source (Fig. 6A,E,F,I). Secondary methane oxidation areas have been detected near the coastline and the 30 m isobath in 1992 (cross section Fig. 8A).

Specific oxidation rate constants for methane found in the Beaufort Sea are comparable to estuarine and oxic/anoxic boundary layer values (10^{-4} to 10^{-3} /d). Rates of ~ 9 × 10^{-2} /d were observed by Kitidis et al. (2010) in the Canadian Beaufort Sea in 2005. While these rates are generally higher

Table 4. Estimates of methane fluxes to the atmosphere from the Arctic Ocean in 1993 and 1994. Values at the top of the table are used in the present assessment, while those listed below are calculated using the method of previous researchers for direct comparison with our calculations.

				Calculat	ed methane flux to atr	nosphere
Time	<i>k</i> Coeff.	Wind speed Ave. m/s	Methane [nM]	mg $CH_4 m^{-2} d^{-1}$	Tg CH₄ deep Arc- tic Ocean yr ^{−1}	Tg C deep Arctic Ocean yr ⁻¹
Surface water						
Aug 1993 and Sep 1994	0.24	7.4	7.70	0.12	0.36	0.24
Aug 1993 and Sep 1994	0.24	12.0	7.70	0.32	0.95	0.71
Maximum observed methane concentration	0.24	12.0	13.8	0.80	2.35	1.76
Legacy calculation method	1					
Aug 1993 and Sep 1994	0.31	7.4	7.70	0.16	0.47	0.35
Aug 1993 and Sep 1994	0.31	12.0	7.70	0.41	1.22	0.92
Maximum observed methane concentration	0.31	12.0	13.8	1.02	3.02	2.27

Values used in flux calculations.

U = 7.4 or 12 m/s; salinity = 31 psu; temp. = 1°C; atmospheric methane [1.81 ppm].

Methane flux = k(Cw-Ce); Cw = methane concentration in seawater, Ce = equilibrium methane concentration in air at seawater conditions at Cw.

 $k = \text{gas transfer velocity} = 0.24U^2 \times (\text{Sc/660})^{-0.5}$; Legacy calculation method, $0.31U^2 \times (\text{Sc/660})^{-0.5}$; U = windspeed m/s.

Sc, Schmidt number; Cw, methane concentration in water; Ce, methane equilibrium concentration in water.

than typical open ocean rates ($< 10^{-4}$ /d), methane loss due to oxidation is small compared to, e.g., flux to the atmosphere (Reeburgh 2007). Water column oxidation rates would account for only 1-2% of the methane pool available in the water column (Lorenson and Kvenvolden 1997). This supports our previous conclusions that methane accumulated during the winter months is ventilated to the atmosphere during the summer and contributes to the observed seasonal atmospheric methane cycle (McLaughlin et al. 1996). Results show that during ice covered periods (May 1995) methane oxidation rates are much higher than in ice-free periods when rates were undetectable (e.g., September, 1993). Thus, there is a seasonal increase in the methane oxidation rate by bacteria living in the water column. In contrast to our results, a simple model of a 10 m thick sea water surface layer proposed by Kitidis et al. (2010) suggests that methane oxidation accounts for $\sim 37\%$ of the methane loss during ice-free conditions and up to 46% during ice-covered periods.

The relationships between methane concentration, methane isotopic composition, and methane oxidation rates as a function of water depth are apparent in Fig. 13A–C. Methane hotspots located in the near surface are associated with microbial methane (δ^{13} C -80% to -60%), whereas a subsea source located at about 20 m water depth is isotopically similar to gas hydrate methane (δ^{13} C -46%) found just onshore ~ (Fig. 13A). Methane oxidation rates are enhanced where methane concentration exceeds 35 nM and in water depths less than ~ 20 m very near the coast (Fig. 13B, upper right and upper center). Here, methane oxidation likely focuses in areas of microbial methane production (-80% to -70% in these locations) enhancing the¹³C methane in the residual methane pool resulting in methane isotopic compositions of δ^{13} C -70% to -55% (Fig. 13C).

Role of methane frozen into sea ice

Typically coastal sea ice inshore from 15 m water depth initially forms as a mobile mass of frazil, anchor, and brash ice a few decimeters thick. This mass gradually solidifies into granular "fast" or stationary ice by late fall. Subsequently the fast ice grows to a thickness of about 2 m over a fixed point on the seafloor. Ice seaward of about 15 m water depth, the seasonal ice pack, is formed in a similar manner but is subject to intense deformation and is mobile throughout the winter. Thus, fast ice is more likely to trap methane in transit from seawater to the atmosphere at a fixed location, whereas offshore ice more likely traps methane from nonfixed locations as it thickens. The widespread correspondence of high methane concentrations in fast ice over shallow water (< 10 m) with potential sedimentary methane sources, and the enrichment of methane in the upper 50 cm of ice implies that methane is mainly trapped during initial freeze up. This is in agreement with the observation of bursts of methane from permafrost occurring during initial freezing of sediment (Mastepanov et al. 2008).

Our previous results show that methane in sea ice can reach concentrations as high as 1280 nM in the upper 50 cm of fast ice, but are a modest 14 nM in non-fast sea ice (Lorenson and Kvenvolden 1995; and Table 3 in Lorenson and Kvenvolden 1997). High methane concentration in sea ice and lake ice has also been reported by others (Walter et al. 2007; Shakhova et al. 2010). We conclude that the spatial extent of fast ice is relatively small although the total amount of methane is difficult to constrain, thus fast icetrapped methane is likely a small seasonal source of methane to the atmosphere during melting.

Methane flux from the Beaufort Sea into the atmosphere

During the sampling hiatus between 1995 and 2009 and to the present, major climatic changes have occurred in the Arctic Ocean and elsewhere. The minimum annual sea ice extent has diminished to a record low of less than 3.8×10^6 km² in 2012 (26% of the Arctic Ocean surface) from an average in the 1990s of $\sim 7 \times 10^6 \text{ km}^2$ (48%) preceded in 2007 when the ice diminished to $\sim 4.1\,\times\,10^{6}~{\rm km}^{2}$ (28%) (Japan Aerospace Exploration Agency, Earth Observation Research Center data, downloaded from: http://www.ijis.iarc.uaf.edu/en/home/ seaice_extent.htm). In conjunction with diminished ice coverage, the greenhouse gases CH₄, CO₂, and NO₂ were at record levels in 2011, and their radiative forcing has risen by 30% since 1990 (United Nations World Meteorological Organization report, 20 November 2012). As part of the MITAS study we collected atmospheric measurements of methane and carbon dioxide correlated with wind speed that showed no apparent anomalies (Supporting Information Fig. S2A-D).

The flux of methane from the ocean to the atmosphere for our results show a seasonal variability where ice free conditions have diminished methane concentrations available at the sea surface, relative to those that build up under ice for most of the year. The ice-free fluxes are not significantly different between the early 1990s and 2009 (Table 1). We have never measured the water column methane or the resulting flux during ice break up, but there is good reason to assume that there is an amplified signal when this occurs sometime between July and August near the coastline. The coastline is clear of ice for ~ 100 d a year, although ice-free days are increasing as the Arctic ice pack shrinks with an observed significant difference between the early 1990s and present (Serreze et al. 2007; Day et al. 2012). Flux estimates using the gridded mean surface methane concentration averaging all of our observations are shown in Fig. 7H,M. These plots are subject to data gaps where nearby values are interpolated, adding an unknown degree of uncertainty.

Ice covered seawater flux calculations represents a onetime inventory of methane that is available to the atmosphere once ice is removed, and as such, is considered a short-term maximum methane flux from the ocean. The potential mean flux of methane calculated for an ice covered grid-integrated scenario for the Beaufort shelf varies from 0.28 mg CH₄ m⁻² d⁻¹ to 1.01 mg CH₄ m⁻² d⁻¹ while simply taking the mean of all surface values results in flux estimates of 0.68–1.45 mg CH₄ m⁻² d⁻¹. Maximum fluxes over hotspots are up to 7.82 mg CH₄ m⁻² d⁻¹.

During ice-free periods the grid-integrated mean flux ranges from 0.14 mg CH₄ m⁻² d⁻¹ to 0.43 mg CH₄ m⁻² d⁻¹ while the mean of surface measurements yields similar fluxes of 0.17-0.43 mg CH_4 m⁻² d⁻¹. Maximum fluxes over hotspots are up to 1.52 mg CH₄ m⁻² d⁻¹. Scaled-up estimates of methane flux can serve as a gross indicator of fluxes from much broader areas but results must be viewed with caution and related interpretations need to be discussed critically. Our scaled-up methane flux estimates for the Beaufort Sea (476,000 km²) and pan-Arctic Shelf (6,000,000 km²) using data from our limited survey area and grid-integrated means vary from 0.05 Tg CH₄ yr^{-1} to 0.57 Tg CH₄ yr^{-1} , respectively. These values are significantly lower than those calculated by Shakhova et al. (2010) who report a mean value for the 3,000,000 km² East Siberian shelf of 2.19 Tg CH_4 yr⁻¹ for summertime diffusive methane flux with additional inventories from wintertime build-up and venting totaling 7.98 Tg CH_4 yr⁻¹.

Potential methane flux from the entire Arctic Ocean

The flux of methane from the entire Arctic Ocean (area $\sim 8.1 \times 10^6 \text{ km}^2$) is made on limited legacy data collected in 1993 and 1994. Table 4 summarizes these results and shows a potential surface flux of methane are only 0.12 mg CH_4 m⁻² d^{-1} resulting in a discharge of 0.36 Tg CH₄ yr⁻¹. The flux may increase to as much as 2.35 Tg CH_4 yr⁻¹ (1.76 Tg C) using the maximum observed methane concentration (13.8 nM) and a high wind velocity of 12 m/s as reported by Kort et al. (2012). Regardless, the amounts we measured are less than 0.42% (more likely $\sim 0.064\%$) of the average annual methane input into the atmosphere of \sim 560 Tg (Cicerone and Oremland 1988). These results differ by an order of magnitude when compared to those postulated by Kort et al. (2012; 0.5-8.0 mg CH₄ $m^{-2} d^{-1}$ with a mean of 2.0 mg CH₄ $m^{-2} d^{-1}$). Their emission rates were lower than background rates calculated for the eastern Siberian Arctic shelf of 3.7 mg CH_4 m⁻² d⁻¹ attributed to subsea permafrost degradation by Shakhova et al. (2010).

Summary

In the Beaufort Sea, the sources of methane available for release into the water column are primarily from microbial degradation of sedimentary organic matter and secondarily from thermogenic gas seepage or decomposing gas hydrate that can have both microbial or thermogenic derived methane. There is no unequivocal geochemical evidence that this gas seepage can be associated with the thermal dissociation of gas hydrates. We observed isolated occurrences of enhanced methane seepage with an isotopic composition expected from thermogenically sourced gas hydrate on the Beaufort Sea shelf and high concentrations of microbial methane in sediment with enhanced bottom water methane concentrations overlying the upper limit of gas hydrate stability on the upper slope of the Beaufort Sea. Deep-water mounds hosting gas hydrate may contribute modest amounts of methane to the deep sea provided that gas hydrate is directly exposed to the ocean or that concurrent methane gas seepage occurs. Methane oxidation rates measured on the shelf are modest; the process is a factor in reducing methane in the water column only in shallow shelf waters and only where methane concentrations are enhanced.

There was no significant difference in the methane flux from ice-free waters between the 1990s and 2009. The potential short-term ice-covered mean flux of methane from the Beaufort shelf varies from 0.28 mg $CH_4 m^{-2} d^{-1}$ to 1.01 to mg $CH_4 m^{-2} d^{-1}$. Maximum fluxes over localized areas of high methane concentrations are up to 7.82 mg $CH_4 m^{-2} d^{-1}$. During ice-free periods the integrated mean flux of methane from the Beaufort shelf varies (0.14–0.43 mg $CH_4 m^{-2} d^{-1}$) and maximum localized fluxes are up to 1.52 mg $CH_4 m^{-2} d^{-1}$. Scaled-up estimates of minimum methane flux from the Beaufort Sea and pan-Arctic Shelf for both ice-free and ice covered periods range from 0.02 Tg $CH_4 yr^{-1}$ and 0.30 Tg $CH_4 yr^{-1}$, respectively and for maximum concentrations the flux ranges from 0.18 Tg $CH_4 yr^{-1}$ and 2.20 Tg $CH_4 yr^{-1}$, respectively.

Methane flux calculations for the open Arctic Ocean were made from data collected in 1993 and 1994 resulting in a potential flux of up to 0.36 Tg CH₄ yr⁻¹ or as much as 2.35 Tg CH₄ yr⁻¹ using the maximum observed methane concentration and a high wind velocity of 12 m/s. Regardless, these estimates are less than 0.42% of the average (more likely ~ 0.064%) annual methane input of ~ 560 Tg CH₄ into the atmosphere (Cicerone and Oremland 1988), suggesting that the Arctic Ocean has been a negligible atmospheric methane source for the time of our observations.

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Lorenson et al.

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Conflict of Interest

None declared.

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