LETTERS

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Atmospheric observations of Arctic Ocean methane emissions up to 82° north

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Uncertainty in the future atmospheric burden of methane, a potent greenhouse gas[1], represents an important challenge to the development of realistic climate projections. The Arctic is home to large reservoirs of methane, in the form of permafrost soils and methane hydrates[2], which are vulnerable to destabilization in a warming climate. Furthermore, methane is produced in the surface ocean[3] and the surface waters of the Arctic Ocean are supersaturated with respect to methane[4,5]. However, the fate of this oceanic methane is uncertain. Here, we use airborne observations of methane to assess methane efflux from the remote Arctic Ocean, up to latitudes of 82° north. We report layers of increased methane concentrations near the surface ocean, with little or no enhancement in carbon monoxide levels, indicative of a non-combustion source. We further show that high methane concentrations are restricted to areas over open leads and regions with fractional sea-ice cover. Based on the observed gradients in methane concentration, we estimate that sea-air fluxes amount to around 2 mg d^{-1} m^{-2}, comparable to emissions seen on the Siberian shelf. We suggest that the surface waters of the Arctic Ocean represent a potentially important source of methane, which could prove sensitive to changes in sea-ice cover.

At present, methane (CH_4) is the second most important human-influenced greenhouse gas after carbon dioxide (CO_2; ref. 1). Recent changes in atmospheric CH_4 concentrations have been difficult to explain: a rapid rise in atmospheric levels post-industrialization[6], followed by a relatively level period in the 1990s with large year-to-year variability in the growth rate[7] and, most recently, a renewed uptick in the growth rate[8]. The Arctic is of particular concern when considering future climate, as large reservoirs of CH_4 reside both in permafrost and CH_4 hydrates[2]. Both of these reservoirs will be destabilized by a warming climate, presenting a positive feedback on global warming.

Potentially important sources of CH_4 from the Arctic have been reported recently, including thermokarst lakes[9], bursts of CH_4 during freezing of tundra[10] and degradation of subsea permafrost on the eastern Siberian shelf[11]. Isotopic analysis has highlighted the seasonal contribution of wetland emissions to Arctic CH_4 (ref. 12). Ocean surveys have found CH_4 to be supersaturated in surface waters of the Arctic far removed from continental shelves and attributed this observation to aerobic CH_4 production[4,5]. Other mechanisms for aerobic biological CH_4 generation have long been recognized[3,13]. The potential atmospheric impact of this Arctic marine source has not been previously assessed. Atmospheric trends in CH_4 arise from many sources[14,15]. To assess the influence of potentially vulnerable reservoirs of Arctic CH_4 (ref. 2), we need to understand present Arctic CH_4 emissions in terms of magnitude, distribution and response to global change.

Here we present atmospheric observations of CH_4 collected over the Arctic Ocean on five flights during the HIAPER Pole-to-Pole Observations programme (HIPPO; ref. 16): one conducted in January 2009, two in November 2009 and one each in March and April 2010. We find that notable enhancements of CH_4 are regular features of the remote Arctic boundary layer, providing clear evidence of strong emissions from surface water proximate to sea ice. The largest emission signals were observed in early November and April. Large areas of open water are not necessary, as fluxes of CH_4 from open leads were repeatedly observed and strong emissions were observed over fractured floating ice. From our atmospheric observations alone we cannot determine the process responsible, though biological production of CH_4 in the surface ocean, as discussed in ref. 4, seems a likely candidate.

Measurements were made *in situ* onboard the National Science Foundation (NSF)/National Center for Atmospheric Research (NCAR) Gulfstream V. CH_4 and carbon monoxide (CO) were measured by direct absorption spectroscopy with the Harvard University/Aerodyne Research Quantum Cascade Laser Spectrometer with 1σ precision of 0.5 ppb (nmol mol^{-1}) and 0.15 ppb, and accuracies of 1 ppb and 3.5 ppb, respectively[17,18]. Ozone (O_3) was measured by the National Oceanic and Atmospheric Administration (NOAA) O_3 photometer using direct absorption at 254 nm (ref. 19). The accuracy of the O_3 measurement is ±5% with a precision of 1.5×10^{10} molecules cm^{-3}. Water vapour was measured by two laser-based instruments with precisions of 1% and accuracies of 6% in the lower troposphere: a closed-path, dual-channel, tunable diode laser spectrometer, Maycomm Instruments system inside the Gulfstream V and the open-path vertical cavity surface-emitting laser hygrometer[20].

Arctic flights departed from and returned to Anchorage, Alaska, with low approaches at Fairbanks, Alaska, and either Barrow or Deadhorse, Alaska, followed by a series of low- and high-altitude legs over both coastal and far reaches of the Arctic Ocean. Vertical profiles over the ocean and sea ice typically extended between ~0.15 and 8.5 km, sometimes up to 12 km (in January profiles descended to ~0.3 km). Supplementary Fig. S1 shows the five

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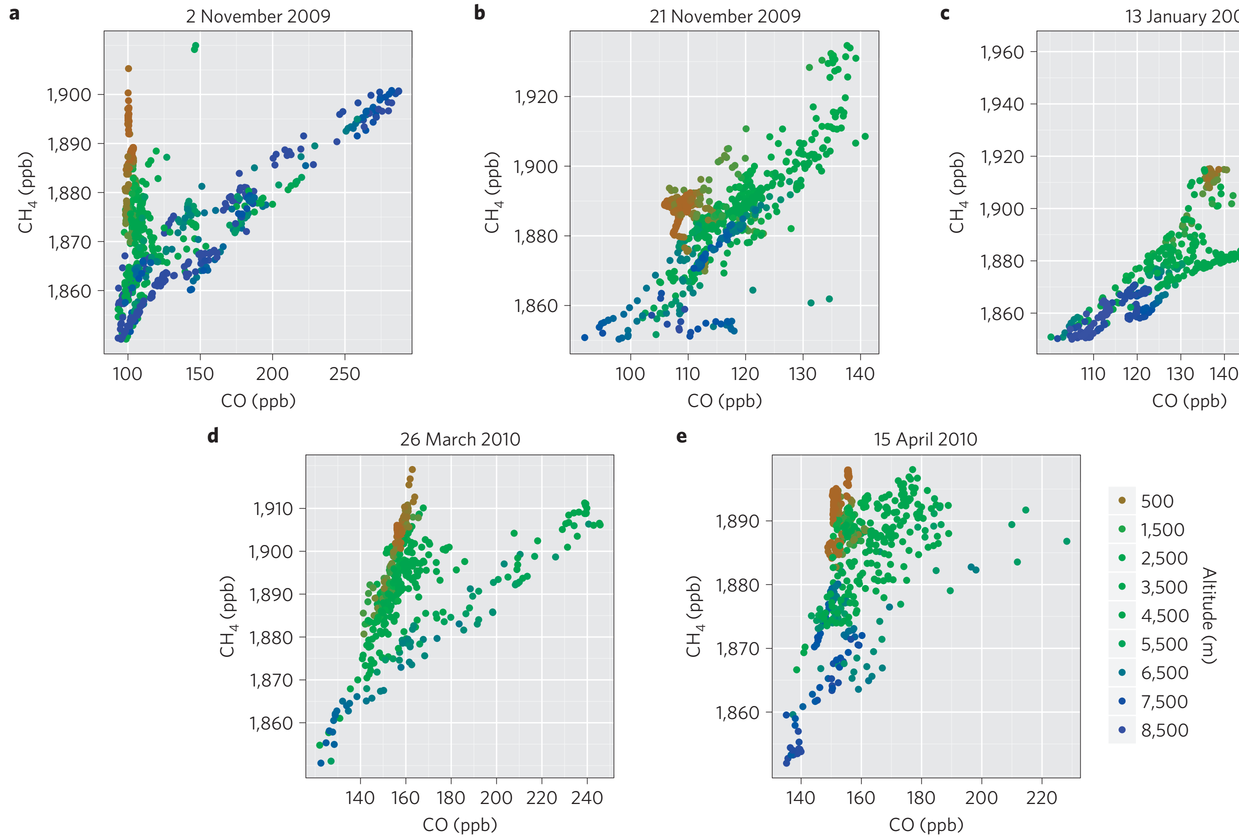

Figure 1 | Correlations between 10 s average CH$_4$, CO and altitude for Arctic flights. Subset of data at >72° N and CH$_4$ > 1,850 ppb for **a**, 2 November 2009; **b**, 21 November 2009; **c**, 13 January 2009; **d**, 26 March 2010 ; and **e**, 15 April 2010.

flight routes, with dip locations overlaid on fractional sea-ice coverage from special sensor microwave imager F-13 (until May 2009) and advanced microwave scanning radiometer-E thereafter (Marine Modeling and Analysis Branch, National Centers for Environmental Prediction; ref. 21).

Layers of increased CH$_4$ concentrations are encountered at different altitudes on Arctic flights (Fig. 1). Some of these layers, primarily in the free troposphere, show tight positive correlations with CO, indicating sources from either anthropogenic activities or biomass burning. The apparent CH$_4$:CO ratio in these layers varies somewhat depending on the origin and age of the air mass. Near the ocean surface however, most CH$_4$ enhancements had little or no corresponding CO enhancement, indicating a non-combustion source (for example 2 November 2009 and 15 April 2010, Fig. 1a,e, respectively). In April, CH$_4$ enhancements near the surface were observed to correlate with strongly depleted O$_3$ associated with O$_3$-depletion events (Supplementary Fig. S3) that occur at the ice–water interface in spring[22]. There were less prominent but still distinctive cases of non-combustion CH$_4$ sources observed near the surface on 21 November 2009 (Fig. 1b). A possible occurrence of CH$_4$ release, masked with high CO, was seen on 13 January 2009 (Fig. 1c). In contrast, we saw no CH$_4$ enhancements other than those associated with excess CO on 26 March 2010, when ice coverage was highest and lead areas lowest.

The boundary-layer enhancements we see are unlikely to originate from oil and gas extraction in the Arctic. Back trajectories for most boundary-layer observations do not track directly back to Prudhoe Bay (Supplementary Fig. S5; refs 23,24), home to the world's largest gas facility. Flights over this facility show enhancements of CH$_4$ correlated with CO. This CH$_4$ originates from leaks and the CO from collocated combustion activity. The absence of CO in our data indicates that leaks from the Prudhoe Bay area cannot explain our observations. Leaks elsewhere in the gas system removed from CO sources are possible, but these air masses would not be depleted in O$_3$, as we see frequently in our profiles. We also see enhanced boundary-layer CH$_4$ on many profiles across the Arctic (Fig. 2), making it unlikely for all the signals to be explained by sporadic transport from localized lower-latitude sources, such as Prudhoe Bay or Arctic lakes. Finally, the variability of CH$_4$ we see within the boundary layer at very high latitudes, correlated with other trace gases, is strongly indicative of a local source (Supplementary Figs S4 and S5).

Inspection of individual profiles clearly shows the influence of CH$_4$ flux from the ocean surface. The first profile offshore on 2 November 2009 occurred over open ocean, adjacent to the advancing edge of the sea ice at ~74° N (Fig. 2a). This profile had a well-developed planetary boundary layer of depth 930 m, probably maintained by sensible heat from the open water below, containing a distinctive CH$_4$ enhancement of 3.2 ppb correlated with mole fraction of water and negatively correlated with CO. Subsequent profiles occurred over sea ice, but leads were ubiquitous even at the highest latitudes (Fig. 3). CH$_4$ enhancements were frequently restricted to very shallow layers over sea ice (0.1–0.4 km, Fig. 2b–d). In autumn, when increased CH$_4$ concentrations were observed over ice interspersed with leads, concentrations correlated strongly with water vapour; maximum CH$_4$ was seen at the lowest altitude that the aircraft reached (~0.15 km). The correlations of high CH$_4$ and high H$_2$O (for example Supplementary Fig. S2) clearly point to the leads as the source. Some of these CH$_4$ signals show strong simultaneous covariance with H$_2$O, CO$_2$ and O$_3$ (Supplementary Fig. S2). In spring, the surface sea ice acts as a strong sink to water vapour, eliminating the positive correlation seen in the autumn. However, a strong correlation with O$_3$-depletion events is evident

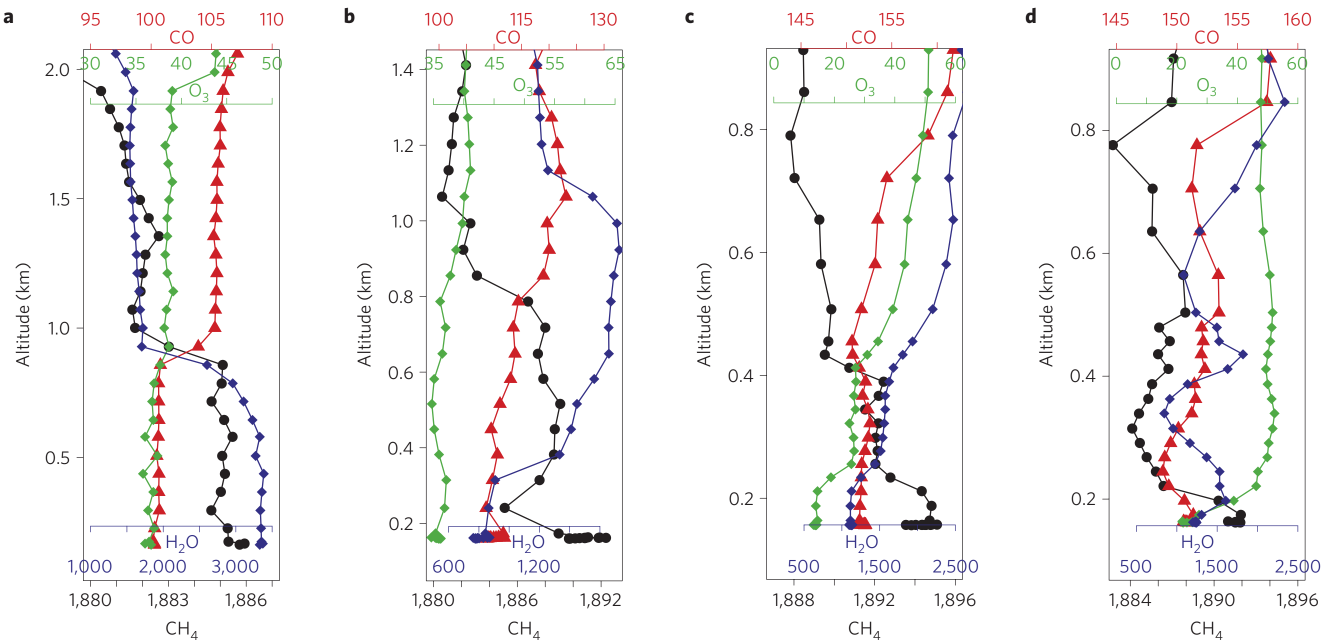

Figure 2 | Vertical profiles of 10 s average data. Observations from **a**, 2 November 2009 at 74° N; **b**, 21 November 2009 at 77° N; **c**, 15 April 2010 at 79° N; and **d**, 15 April 2010 at 82° N showing atmospheric enhancements associated with CH_4 emissions from the surface of the Arctic Ocean proximate to sea ice. CH_4 (black), CO (red) and O_3 (green) are reported in ppb, H_2O (blue) in ppm.

Figure 3 | Leads overflown at high latitudes on 15 April 2011 ∼82° N. Photo provided by NCAR Earth Observing Laboratory under the sponsorship of NSF (http://data.eol.ucar.edu).

(Supplementary Fig. S3), with maximum CH_4 seen at lowest altitudes, again indicating emissions from the surface ocean proximate to sea ice.

Using the approach outlined in the Methods section, we estimate eddy diffusivities and fluxes for two profiles (Fig. 2b,d) with favourable atmospheric structure for flux estimation. In both cases we estimate a CH_4 flux of 2 mg d^{-1} m^{-2}, with upper and lower bounds placed at 8 and 0.5 mg d^{-1} m^{-2}. If we assume that similar eddy diffusivities applied for other profiles we would retrieve fluxes within this range. Given the Gulfstream V's average speed of ∼900 km h^{-1}, and the time spent on the bottom of dips (200–300 s) , the extent of these fluxes reaches over at least 50 km. These emission rates are comparable to those found from the eastern Siberian Arctic shelf[10] (11.8 mg d^{-1} m^{-2}), attributed to subsea permafrost degradation.

These observations show a clear signature of CH_4 emissions from surface water distributed across the Arctic Ocean north of the Chukchi and Beaufort seas, spanning many months of the year. Signatures of surface emissions are present on most profiles on 2 November 2009, 21 November 2009 and 15 April 2010. On 13 January 2009 and 26 March 2010, the flight dates with most solid sea-ice coverage, emissions were weak to non-existent, although some efflux may have been masked by CO-related emissions (Fig. 1, flights in January may also fail to find evidence of emissions owing to not fully penetrating into the Arctic boundary layer). There seems to be a correlation between the presence of open water/leads and emissions. Our results are consistent with observations of strong correlations between CH_4 supersaturation in surface water and increased fractional ice cover in the presence of open water (up to 80%; ref. 25), indicating that open water adjacent to sea ice may be most hospitable to CH_4 production. This apparent coupling raises the possibility of production increases with increasing areas of seasonal sea-ice melt.

We observed CH_4 enhancements in the atmosphere at very high latitudes, as far as 82° N. These profiles were taken over deep water far removed from shallow continental shelves that hold vulnerable CH_4 hydrates; decomposition of hydrates, or other sedimentary sources, are unlikely to explain our measurements, as oxidation through the water column would prevent much CH_4 from reaching the atmosphere[26]. We cannot completely exclude a potential contribution from continental shelves—if supersaturated in CH_4, water is quickly advected to high latitudes and vertically mixed, and oxidation rates in the water parcel are very low—but previous work has asserted that this is unlikely[4].

HIPPO flights over Arctic sea ice and adjacent waters found atmospheric evidence of strong CH_4 emissions. The areal extent and spatial–temporal variability of this source are largely unknown. Further studies are needed to better understand the emissions processes and therefore be able to accurately extrapolate to an annual total for the Arctic. Given the large areal extent of the Arctic subject to seasonal melting of sea ice (∼10 million km^2), the emissions rate we encountered (2 mg d^{-1} m^{-2}) could present a source of global consequence. The association with sea ice makes this CH_4 source likely to be sensitive to changing Arctic sea-ice cover and dynamics, providing a hitherto unrecognized feedback process in the global atmosphere/climate system.

Methods

To estimate CH_4 fluxes we assumed that vertical transport was associated with eddy-scale processes and estimated the flux (F) from the eddy diffusivity (K_z), and the observed gradient[27] (dCH_4/dz, where z is altitude):

$$F = -K_z \times dCH_4/dz$$

We employed two simple approaches to estimate the eddy diffusivity. In two of the observed profiles (Fig. 3b,d), we encountered very high wind speeds near the surface ($>12\,m\,s^{-1}$) and an Ekman spiral was apparent (Supplementary Fig. S6). From the thickness of the observed Ekman layer ($z \sim 200$ m) and the latitude of the observations (77° and 82° N) we can then calculate the eddy diffusivity by solving for K_z (ref. 27):

$$K_z = f/(2 \times (\pi/z)^2)$$

where f is the Coriolis parameter ($2 \times \Omega \times \sin(\text{latitude})$). Ω is the angular rotation of the earth, $7.27 \times 10^{-5}\,rad\,s^{-1}$. For both profiles this returns an eddy diffusivity of $0.3\,m^2\,s^{-1}$.

To get an independent estimate of K_z and also place upper and lower bounds on potential flux values, we refer to a variety of one-dimensional model predictions[27]. For a stable boundary layer in the Arctic with a height exceeding 200 m, various models find eddy diffusivities at a height of 150 m ranging from $\sim$0.1 to $1\,m^2\,s^{-1}$(ref. 27). In our analysis, for profiles in Fig. 3b,d we use the Ekman-derived K_z to obtain the estimated flux and the model range in K_z to place upper and lower bounds on that estimate.

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Author contributions

E.A.K. collected the CH_4 data, noted the Arctic features, carried out analysis and wrote the manuscript. S.C.W. led the HIPPO campaign and guided both analysis and writing. B.C.D. and R.J. collected CH_4 data. R.S.G. and J.R.S. collected O_3 data. M.D., J.W.E., E.J.H., D.F.H., F.L.M and M.A.Z. collected water vapour data. All authors discussed results and commented on the manuscript.

Additional information

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