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Ground-level concentrations of atmospheric methane in southwest Greenland evaluated using open-path laser spectroscopy and cavity-enhanced absorption spectroscopy

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Abstract

Portable open-path laser (OPL) instruments provide a way to measure real-time, in situ atmospheric methane (CH₄) concentrations at a variety of spatial and temporal scales. Our results suggest that OPL instruments may be simple and effective tools for monitoring atmospheric CH₄ dynamics near ground-level in Arctic landscapes. We used a CH₄ detecting OPL instrument at seven different field sites in southwest Greenland during the summer of 2012 to monitor atmospheric CH₄ concentrations in the presence of local CH₄ sources and sinks. Measurements with the OPL were conducted for deployments between 0.4 and 40 h over path lengths between 10 and 300 m. These measurements were checked against periodic grab samples analyzed in the field lab using cavity-enhanced absorption spectroscopy. Mean concentrations of atmospheric CH₄ measured with the OPL across all field sites ranged from 1.72 (±0.12) to 1.88 (±0.15) ppm by volume (ppmv). The median atmospheric CH₄ concentration measured using cavity-enhanced absorption spectroscopy was 1.82 ± 0.04 ppmv. Slightly elevated CH₄ concentrations were measured downwind of one lake and in a subglacial cave. OPL measurements of atmospheric CH₄ concentrations agreed with results from cavity-enhanced absorption spectroscopy (<3% difference). OPL technology may be a useful tool for extended CH₄ monitoring studies in the Arctic and may help in our understanding of atmospheric CH₄ concentrations at spatial and temporal scales not accessible to other forms of measurement.

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Introduction

Methane (CH₄) is an important greenhouse gas. One molecule of CH₄ is 20 times more effective in terms of radiative forcing than one molecule of carbon dioxide (CO₂) (Lashof and Ahuja, 1990). Average global concentrations of atmospheric CH₄ have risen from 0.75 ppm by volume (ppmv) during pre-industrial times to 1.82 ppmv in 2012 (Craig and Chou, 1982; Dlugokencky et al., 2009; Adushkin and Kudryavtsev, 2010; WMO, 2013). Over the next 100 years, CH₄ is expected to contribute 25% of the radiative forcing increase of the atmosphere (IPCC, 2013). Arctic CH₄ sources are under greater scrutiny due to the potential for increased CH₄ emissions from features such as thawing permafrost, CH₄ hydrates, and glacial margins in a warming climate (Zimov et al., 1997; Walter et al., 2006; Shakhova et al., 2009; Walter Anthony et al., 2012).

The potential for increased CH₄ emissions from Arctic environments has resulted in numerous CH₄ studies from different Arctic landscapes. Flux chambers have been used to measure CH₄ flux at spatial scales of a few square meters or less to study the influences of vegetation, water table, and soil conditions on CH₄ flux (Torn and Chapin, 1993; Schimel, 1995; Christensen et al., 2000; Turetsky et al., 2014). Eddy covariance has been used in recent years to study Arctic CH₄ fluxes at scales from hectares to km² (Friborg et al., 2000; Hargreaves et al., 2001; Wille et al., 2008; Sachs et al., 2008; Tagesson et al., 2012; Kowalska et al., 2013). A major strength of the eddy covariance method is that surface-atmospheric dynamics are not interrupted during the flux measurement. Despite the extensive data sets of atmospheric CH₄ concentrations collected during eddy covariance studies, relatively few atmospheric CH₄

concentrations from these studies have been published. The atmospheric CH₄ concentration measurements that have been published are from locations far from CH₄ source areas in the Arctic, but are critical for demonstrating a long-term increase in atmospheric CH₄ concentrations globally (Adushkin and Kudryavtsev, 2010; Dlugokencky et al., 2011; Kirschke et al., 2014).

Open-path laser (OPL) technology has proven to be a successful measurement technique for monitoring CH₄ and other biogenic gases downwind of anthropogenic sources such as confined animal feeding operations (Harper et al., 2009, 2010), and in known areas of geological CH₄ seepage (Baciu et al., 2007). OPL measurement of atmospheric CH₄ concentration can provide in situ, real-time CH₄ concentration measurements. OPL technology can also measure CH₄ concentrations at spatial scales in between those of other measurement systems, providing average atmospheric CH₄ concentrations over path lengths from 10 m to 1 km. We deployed a portable OPL to study ground-level atmospheric CH₄ in a range of environments along the ice-free margin of southwest Greenland.

As validation of the OPL method, we present results from a series of OPL atmospheric CH₄ monitoring studies in the vicinity of local CH₄ sources and sinks, complemented by other methods that work on smaller spatial and temporal scales. Study sites were selected for their potential to influence local atmospheric CH₄ concentrations. We monitored atmospheric CH₄ concentrations near lakes, in subglacial, upland, and urban environments. Micrometeorological variables were also evaluated to examine their influence on CH₄ concentrations and included air temperature, atmospheric pressure, wind speed, and wind direction.

Methods

FIELD AREA

The Kangerlussuaq region is characterized by continuous permafrost, a low Arctic continental climate, and about 160 mm yr⁻¹ of precipitation (Anderson et al., 2001, 2009; Willemse et al., 2004; Aebly and Fritz, 2009). The region is located in the rain shadow of the Sukkertoppen Ridge of the Greenland Ice Sheet, which blocks the southwesterly winds that would otherwise bring higher rainfall to the region (Ohmura and Reeh, 1991). The 180-km-long ice-free margin of West Greenland contains >20,000 lakes (Perren et al., 2012), and many have fringing wetlands.

Wetlands and lakes are the largest natural source of CH₄ to the atmosphere, and Arctic wetlands exhibit increased CH₄ emission during the spring and fall due to permafrost freeze/thaw dynamics (Mastepanov et al., 2008, 2013). The lakes in the region begin to freeze in mid-September and begin to thaw in late May to mid-June. Mean annual air temperature is -6 °C (Anderson et al., 2001), with maximum temperatures of 20 °C in June to early August when mean temperatures exceed 8 °C. The depth of the seasonally active layer, the top layer of soil above the continuous permafrost that thaws annually, ranges from 25 to 70 cm below the surface. The flora is described as an Arctic Mountain Tundra community (UNEP/GRID-Arendal, 2006).

Atmospheric CH₄ concentrations in Greenland are routinely measured at Summit Station and currently show an intra-annual variation of about 0.05 ppmv. The highest concentrations occur in January (1.91 ppmv in 2013) and the lowest concentrations occur in July (1.86 ppmv in 2012) (NOAA, 2013). The lower concentrations during summer are due to greater hydroxyl radical production in the troposphere during Arctic summer (IPCC, 2013).

The OPL studies were conducted at seven different locations near Kangerlussuaq, Greenland (67°04.888'N, 050°21.084'W; Fig. 1) including near-lake (Sites 1, 2, 3, 4), upland (Site 6), subglacial (Site 5), and urban (Kangerlussuaq) environments. The locations were selected to represent a range in potential to serve as local CH₄ sources or sinks. Small lakes located in relatively narrow and steep-sided valleys (Fig. 2, part A) represented potential CH₄ source areas, as small lakes and fringing wetlands

can contain elevated CH₄ in sediments and water columns that lead to locally elevated flux rates (Repo et al., 2007; Bastviken et al., 2008; Juutinen et al., 2009). The narrow valleys reduced boundary layer mixing, improving the chance that the OPL would detect emitted CH₄. The subglacial site was selected because of low boundary layer mixing and reports by other investigators of methane emission from this subglacial environment (Dieser et al., 2014) (Fig. 2, part B). The upland environment was selected because of the potential for soil methanotrophic communities in drier upland soils to reduce atmospheric CH₄ concentrations (Christiansen et al., 2014). Monitoring the atmospheric CH₄ concentration in Kangerlussuaq served as a control with respect to remote field sites—the area is dominated by highly compacted soils and paved roads. The compacted soils and paved roads are stable substrates that minimize potential alignment changes in the open-path laser.

OPEN-PATH LASER

An open-path tunable diode laser for CH₄ detection (GasFinder 2.0, Boreal Laser Inc., Spruce Grove, Alberta, Canada, wavelength = 1.653 μm) was used to measure atmospheric CH₄ concentrations in the field. The OPL measures the average concentration of CH₄ in the air along the path of measurement. A retro-reflector with six corner cube mirrors was used to redirect the laser beam back to the detector. Both the OPL and retro-reflector have tripod mounts for use in portable field settings (Fig. 2).

The response time of the OPL system to increased CH₄ concentration was evaluated in the laboratory prior to field deployment. Ambient CH₄ concentration in indoor air was monitored for 18 h (data sampling rate = 0.3 to 1 s⁻¹) over a path length of 48 m. CH₄ was released into the laboratory to cause artificial spikes at approximately 3:30 p.m., 8:00 p.m., and 7:00 a.m. (steady-state concentration of each spike ~3 times ambient). The 8:00 p.m. spike consisted of a triple release of CH₄. A small increase in the baseline CH₄ concentration was observed at 1:00 a.m. The increase in CH₄ concentration observed during the night may have been the result of a natural gas release from a central steam plant located next door to the lab building. The stability of the background CH₄

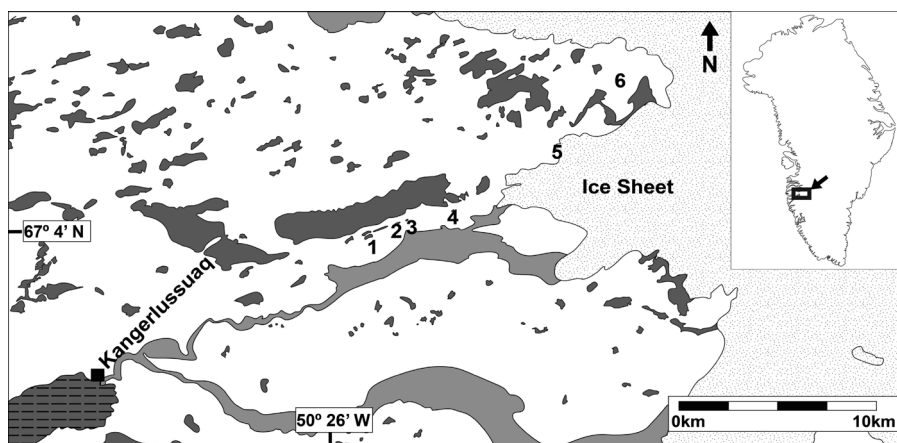


FIGURE 1. The approximate site locations of each open-path laser (OPL) time series of the summer 2012 field campaign in relation to the Greenland Ice Sheet and Kangerlussuaq. One of transects was measured in Kangerlussuaq. Other field locations are labeled by numbers. 1 = South Twin Lake, 2 = Potentilla Lake, 3 = Tear Drop Lake, 4 = Epidote Vein Valley (EVV) Lakes, 5 = Subglacial Cave, and 6 = GAP Ridge. All field site names are informal. The dark gray shapes are lakes, the light gray shapes represent glacial meltwater streams, and the dark gray shape with horizontal hatching is the northeast end of Søndre Strømfjord. Numerous smaller lakes are not depicted.

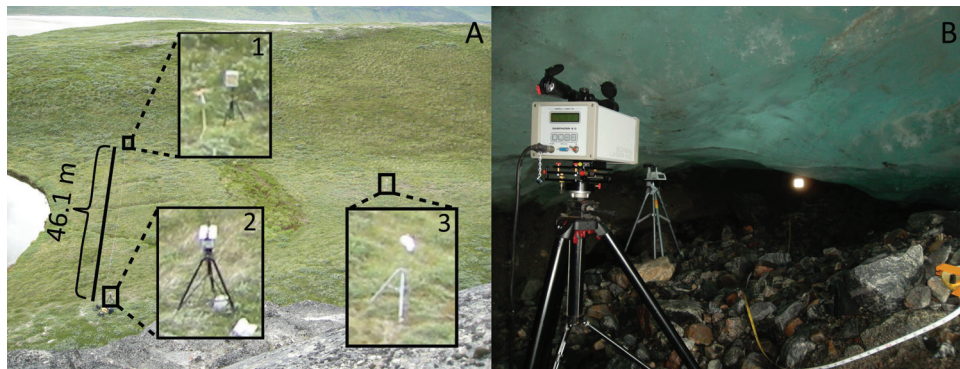


FIGURE 2. Field deployments of the OPL in (A) open-atmospheric and (B) subglacial settings. The deployment of the system in A is at Site 2. Box 1 is the retroreflector mirror, box 2 is the OPL source/detector, and box 3 is the met station. The path length of measurement is 46.1 m. Note the steep valley walls. In the subglacial setting the OPL source/detector is in the foreground, the met station is the object behind the OPL source/detector and the retroreflector mirror is the bright spot towards the right and middle of photo. The path length between the OPL and the retroreflector is 10.3 m.

concentration (1.99 ± 0.08 ppmv) was notable and the response to CH_4 spikes was less than 15 seconds (Fig. 3).

In the field, the OPL was set to record average CH_4 concentrations every 73 seconds. The duration of OPL time series ranged from 0.42 to 37.17 h, and path lengths ranged from 10.3 to 283.3 m (Table 1). The difference in path length reflects the varying width or length of study lakes or reflects the available space for measurement. The orientation of the OPL was generally perpendicular to the prevailing wind direction. A perpendicular orientation for the OPL was used to maximize the possibility of detecting CH_4 emitted from potential upwind source areas (Harper et al., 2009, 2011). In a few cases, the OPL was oriented parallel to the predominant wind direction in order to increase the path length over a potential CH_4 source. The height of the OPL above the ground or water surface was about 1 m. Atmospheric grab samples were collected at the height of the OPL laser beam during active measurement periods by pulling air into a syringe and immediately transferring it into a Tedlar bag. Air samples were analyzed for CH_4 concentrations using independent methods to check the accuracy of the OPL system.

A portable micrometeorological (met) station (Vantage Vue, Davis Instruments Corp., Hayward, California, U.S.A.) was used to record air temperature, wind speed and direction, atmospheric pressure, and relative humidity at each of the OPL field sites. The met station recorded at 1-minute intervals. The met station was placed in a location that captured the dominant wind flow patterns in the environment and was typically located within 100 m of the OPL (Table 1, Fig. 2).

CH_4 concentrations reported by the OPL are affected by changes in ambient temperature and ambient pressure. A temperature correction coefficient was calculated using:

$$T_{cc} = 0.0053T + 0.8904 \quad (1)$$

where T_{cc} is the temperature correction coefficient and T is the measured temperature in $^{\circ}\text{C}$ at the time of the OPL measurement (Boreal Laser, personal communication, 2012). A pressure correction coefficient was calculated using:

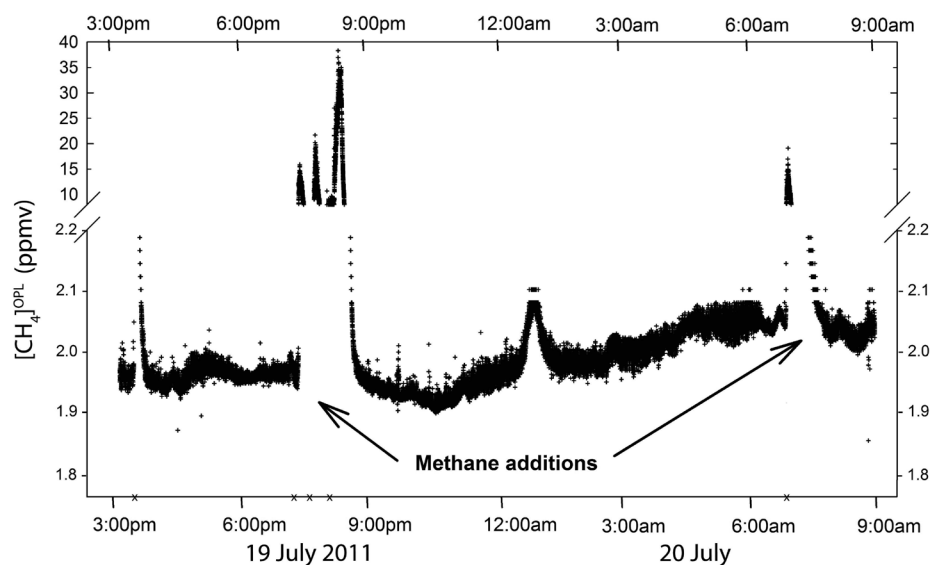


FIGURE 3. Laboratory CH_4 concentration measured with OPL ($[\text{CH}_4]^{\text{OPL}}$). The “x” symbols along the x-axis show the times of methane addition.

TABLE 1

The geographical and temporal characteristics of each open-path laser (OPL) field measurements campaign in the summer of 2012.

Location	Environment	Start date and time	End date and time	Laser coordinates	Micrometeorological station coordinates	Duration (hours)	Length (m)	% of data discarded
Kangerlussuaq	In town	12 July 2:54 a.m.	12 July 9:28 a.m.	67°00.553'N, 50°41.242'W	67°00.553'N, 50°41.238'W	6.57	54.5	4
1	Near lake	12 July 1:53 p.m.	12 July 4:25 p.m.	67°04.500'N, 50°23.370'W	67°04.522'N, 50°23.188'W	2.53	100.0	0.6
2	Near lake	13 July 11:48 a.m.	13 July 3:46 p.m.	67°04.843'N, 50°21.464'W	67°04.825'N, 50°21.520'W	3.97	46.1	9
4	Near lake	15 July 2:51 p.m.	16 July 10:19 a.m.	67°05.204'N, 50°17.587'W	67°05.186'N, 50°17.576'W	19.0	82.1	71
3	Near lake	18 July 3:25 p.m.	18 July 4:50 p.m.	67°04.927'N, 50°20.750'W	67°04.914'N, 50°20.757'W	1.42	47.0	22
5	Subglacial*	19 July 11:34 a.m.	19 July 12:38 p.m.	67°07.136'N, 50°10.017'W	67°07.136'N, 50°10.017'W	1.07	10.3	0
6	Upland Soil	19 July 3:28 p.m.	19 July 3:54 p.m.	67°09.240'N, 50°03.568'W	67°09.181'N, 50°03.440'W	0.42	121.4	27
2	Near lake	20 July 12:03 p.m.	22 July 1:13 a.m.	67°04.888'N, 50°21.084'W	67°04.850'N, 50°21.147'W	37.17	283.3	68

*Coordinates for the subglacial site are based on the opening to the cave.

$$P_{cc} = - \frac{0.329}{\frac{4p^2}{b} - \left[\left(\sqrt{2} + \frac{2\sqrt{2p^2}}{b} \right) * \left(2 + \frac{2b}{p^2} \right)^{\frac{1}{2}} * \left(1 + \frac{b}{p^2} \right)^{-1} \right]} \quad (2)$$

where P_{cc} is the pressure correction coefficient and p is the atmospheric pressure in kPa, and b is a constant equal to 28291.072 as determined by Boreal Laser during their measurements of the OPL's response to differing pressures (Boreal Laser personal communication, 2012). Typically, concentrations of atmospheric CH_4 reported in the literature are measured in air samples that have been stripped of their water vapor (Dlugokencky et al., 1994). Since OPL measurements were made in open atmosphere, ambient water vapor was unavoidable during the measurement. In order to compare OPL measurements with published values from dry air, we corrected OPL measurements for the presence of ambient water vapor using a water vapor correction coefficient V_{cc} as follows:

$$V_{cc} = p (p - P_{H_2O})^{-1} \quad (3)$$

where P_{H_2O} is the partial pressure of water vapor in the atmosphere in kPa at the time of the OPL measurement. The corrected CH_4 concentration, $[\text{CH}_4]_c$, was calculated by taking the product of the correction coefficients and the OPL reported CH_4 concentration, $[\text{CH}_4]_m$ (ppmv), as follows:

$$[\text{CH}_4]_c = T_{cc} * P_{cc} * V_{cc} * [\text{CH}_4]_m \quad (4)$$

Data quality also varied with instrumental parameters in addition to atmospheric conditions. Data collected when light levels were outside of this optimal range recommended by Boreal Laser (<2000 or >12,000 relative light units—the unit of infrared light intensity that is measured by the Boreal Laser) were discarded. The OPL reports an instrument R^2 , a measure of how well the absorption spectrum of the atmospheric measurement matches the absorption spectrum of the internal CH_4 calibration cell; the reported R^2 values corresponded to a percent uncertainty, a , associated with all $[\text{CH}_4]_i$. We eliminated all $[\text{CH}_4]_i$ with an a of >2%. Furthermore, if a period of data contained at least 25% of a values >2%, that portion of a time series was also discarded. High frequency variations in the R^2 value corresponded with anomalous CH_4 measurements. Data obtained during these oscillations were also discarded from analysis (Fig. 4). The amount of data discarded from each analysis ranged from 0% to 68% (Table 1).

LAKE WATER AND SEDIMENT METHANE

Dissolved methane concentrations were measured in water samples collected from lakes within or bordering OPL study sites. Adapting common headspace equilibration methods (McAuliffe, 1971; Fendinger and Adams, 1986), a 500 mL aliquot of lake water from a Kemmerer bottle was transferred to a 1 L Erlenmeyer flask fitted with a three-way luerlock inlet and three-way luerlock valve attached to a stopper. The stopper was affixed to the flask, the valves were closed, and the flask was shaken vigorously for 1 minute to partition the dissolved gases into the headspace. Headspace gases were then displaced into an attached Tedlar bag by injecting water through the three-way valve into the flask. The concentration of dissolved CH_4 in the water samples was calculated by adding the CH_4 concentration of the headspace gas to the amount of CH_4 remaining in the aqueous phase after

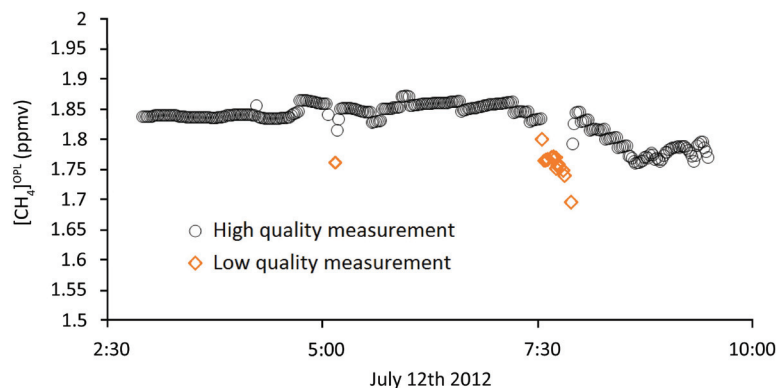


FIGURE 4. OPL time series from Kangerlussuaq (Site 1) showing both high quality (black circles) and low quality data (orange diamonds) obtained with the OPL. Low quality data were removed prior to analysis.

gas stripping, which was calculated by applying Henry's Law and correcting gas solubility for temperature (Lide and Frederikse, 1995).

Entrained methane gas in littoral sediments was sampled by stirring the sediments and trapping emitted bubbles in a large plastic funnel outfitted with a gas-tight sampling tube and three-way luer-lock valve affixed to the neck. Gas samples were transferred from the funnel into Tedlar bags using a gas-tight syringe. Air samples were generally analyzed within 24 hours at the field laboratory.

SOIL METHANE

CH₄ in dry and water-saturated soils within OPL study sites was sampled with a soil gas sampling probe (Retract-A-Tip, AMS, American Falls, Idaho, U.S.A.). Samples were withdrawn from the base of the active layer, just above the permafrost. In dry soils, sampling syringes were flushed three times with their total volume of soil pore gas before the sample was injected into a 1 L Tedlar bag. In water-saturated soils, dissolved methane from soil pore-water was collected by stripping 70 mL of water with 70 mL of air. The syringe was shaken vigorously for 1 minute to extract the dissolved gas. The sample gas was then transferred to a 1 L Tedlar bag. The dissolved concentration of CH₄ in the saturated soil samples was calculated using the same procedure for calculating dissolved CH₄ in lake water.

ANALYTICAL METHODS

Cavity-Enhanced Absorption Spectrometry

The CH₄ concentrations of collected gas samples were analyzed in a laboratory at the Kangerlussuaq International Science Support center using a cavity-enhanced, near-infrared tunable diode laser absorption spectrometry system (Methane Carbon Isotope Analyzer [MCIA]) produced by Los Gatos Research Inc., Mountain View, California (Mortazavi et al., 2013). The MCIA uses a laser operating near 1.656 μm and measures the concentration of CH₄ in air by summing the ¹²C and ¹³C isotopologues of CH₄. A pretreatment station removes CO₂ and water vapor prior to the gas entering the cavity. The MCIA was calibrated at a concentration of 50 ppmv using a well-characterized laboratory standard.

Gas Chromatography

To determine the validity of CH₄ measurements made with the MCIA, a subset of CH₄ samples was analyzed on a gas chromatograph. About 50 to 60 mL of gas were transferred to an evacuated

50 mL glass serum vial from Tedlar bags for measurement of CH₄ concentration using a Varian 450 gas chromatograph with a flame ionization detector (GC-FID) produced by Agilent Technologies, Palo Alto, California. Samples were carried by helium (15 mL min⁻¹) onto a HayeSep Q column (80/100 mesh, 1.22 m by 0.16 cm).

Peak areas for the GC-FID were converted to concentrations using two linear least squares regression equations, one for samples <100 ppmv and another for samples >100 ppmv. Measured CH₄ concentrations by MCIA and GC-FID yielded similar results ($[\text{CH}_4]^{\text{GC}} = 1.008[\text{CH}_4]^{\text{MCIA}} - 0.1671$, $r^2 = 0.998$) (Fig. 5). All results reported for discrete field samples will be based upon MCIA analyses conducted in the field laboratory.

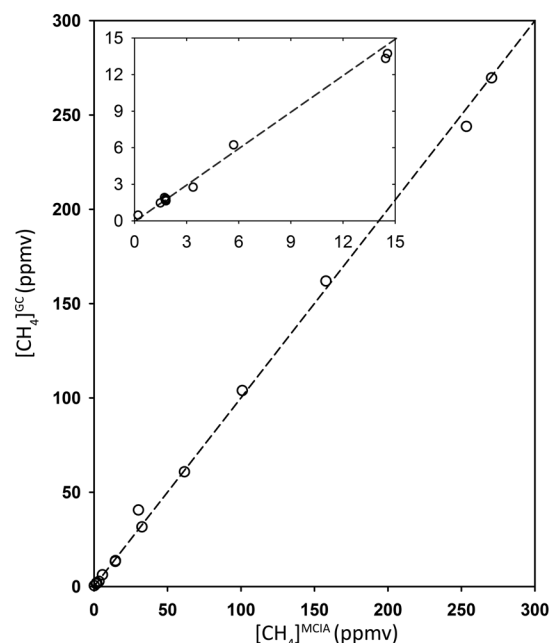


FIGURE 5. Methane concentrations measured with the gas chromatograph ($[\text{CH}_4]^{\text{GC}}$) versus methane concentrations measured with the methane carbon isotope analyzer ($[\text{CH}_4]^{\text{MCIA}}$). The independent measurements show a high degree of agreement. The inset graph shows the relationship between measurements for concentrations less than 15 ppmv. The linear least squares regression equation that related CH₄ concentration measurements from the Methane Carbon Isotope Analyzer (MCIA) to the gas chromatograph with a flame ionization detector (GC-FID) was $y = 1.008x - 0.1671$ and had an r^2 of 0.998.

The uncertainty of individual methane concentrations obtained with the OPL, e , was assessed using

$$e = a [\text{CH}_4]_i + m[\text{CH}_4]_i L^{-1}, \quad (5)$$

where e is the uncertainty associated with the corrected CH_4 concentration, $[\text{CH}_4]_i$, m is the uncertainty in the path length of the OPL, and L is the measured path length in meters. The uncertainty of the path length of the laser was assessed by repeatedly measuring the distance with a measuring tape, a laser range finder, or by determining distance using precise locations in Google Earth. The detection limit for the open-path laser is 1 ppmv times meters divided by L : (ppmv \cdot m) L^{-1} . A longer path length improves the sensitivity of the measurement and minimizes the uncertainty associated with the path length. However, longer path lengths also average the CH_4 concentration in a larger parcel of atmosphere, which dilutes the influence of point source CH_4 emissions. The average uncertainty, U , of the average CH_4 concentration, $[\text{CH}_4]$, for a time series was calculated by summing the average e and twice the standard deviation of the $[\text{CH}_4]_i$. We calculated a U of ± 0.08 ppmv or $\pm 4\%$ of the $[\text{CH}_4]$ during the test of the OPL under ideal conditions in the laboratory (Fig. 3).

The met station and the OPL recorded data at different rates. This prevented direct ordered-pairs statistical analysis on the raw data. Therefore, linear interpolation of the met station data was used to create an ordered pair of met station data and OPL data for statistical analysis. In time series analyses, the correlation of a parameter of interest with time may cause a false correlation with another parameter of interest that may or may not be correlated with time. A way to prevent false relationships from obscuring actual relationships in parameters of interest is to examine the rate of change of the parameters with respect to time. Linear regression models were used to assess the relationships between the changes in atmospheric CH_4 concentration with respect to time for consecutive measurements ($\Delta[\text{CH}_4]_i \Delta t^{-1}$) and the change in atmospheric parameters with respect to time for consecutive measurements (temperature, $\Delta T \Delta t^{-1}$; wind speed, $\Delta W \Delta t^{-1}$; atmospheric pressure, $\Delta p \Delta t^{-1}$). Wind direction was relatively constant for the individual time series and did not factor into potential changes in CH_4 concentrations.

Results

Corrected atmospheric CH_4 concentrations, $[\text{CH}_4]_r$, measured by OPL for all time series in the study ranged from 1.58 (± 0.04) to 1.98 (± 0.04) ppmv (Fig. 6). Different time series exhibited different amounts of variation in the measured $[\text{CH}_4]_i$. For example, a time series exhibiting limited variation was obtained on 12 July between two buildings in Kangerlussuaq (Fig. 6, part A). In contrast, we observed large variations in $[\text{CH}_4]_i$ on 20 and 21 July at Site 2 (Fig. 6, part H).

$[\text{CH}_4]_r$ measured by the OPL were generally in agreement with the MCIA measurements of discrete air samples collected at the same time and place (mean difference $< 3\%$). The methane concentrations measured with the MCIA showed a high degree of consistency between field sites with a median concentration of 1.82 ± 0.04 ppmv (Fig. 6). The mean of the absolute difference between the OPL and MCIA from all sites was 0.04 ppmv (standard deviation = 0.05 ppmv; $n = 10$). CH_4 concentrations measured by MCIA and OPL were similar at Tear Drop Lake (Site 3, MCIA 1.81 ± 0.04

ppmv vs. OPL 1.82 ± 0.04 ppmv and MCIA 1.80 ± 0.04 ppmv vs. OPL 1.82 ± 0.04 ppmv; Fig. 6, part E) and the Subglacial Cave (Site 5, MCIA 1.90 ± 0.04 ppmv vs. OPL 1.90 ± 0.08 ppmv; Fig. 6, part F). OPL time series with large variations in $[\text{CH}_4]_i$ exhibited larger disagreements with MCIA results (Fig. 6, parts D and H). The average absolute difference between the MCIA and OPL results from 20 and 21 July was 0.10 ppmv. Eliminating low confidence data from these time series yielded a mean absolute difference between the OPL and MCIA of 0.02 ppmv (standard deviation = 0.04 ppmv; $n = 7$; Fig. 7).

Changes in CH_4 concentrations over the course of a time series showed limited relationships with changes in nearby micrometeorological conditions (all r^2 values < 0.18). The change in corrected CH_4 concentration measurements with time ($\Delta[\text{CH}_4]_i \Delta t^{-1}$) vs. air temperature with time ($\Delta T \Delta t^{-1}$), and wind speed with time ($\Delta W \Delta t^{-1}$) was statistically significant in three of the OPL time series performed and was not significant in the others (Table 2). The change in corrected CH_4 concentration measurements with time ($\Delta[\text{CH}_4]_i \Delta t^{-1}$) vs. the change in atmospheric pressure with time ($\Delta p \Delta t^{-1}$) was not significant at any site. In the Kangerlussuaq time series, the observed relationship between the CH_4 concentration change and the wind speed change was significant ($\Delta[\text{CH}_4]_i \Delta t^{-1} = -0.003 \Delta W \Delta t^{-1}$). At Site 4 (Epidote Vein Valley, EVV), the relationships between the CH_4 concentration change and the wind speed change and the CH_4 concentration change and the temperature change were both significant ($\Delta[\text{CH}_4]_i \Delta t^{-1} = 0.0013 \Delta W \Delta t^{-1}$; $\Delta[\text{CH}_4]_i \Delta t^{-1} = 0.0102 \Delta T \Delta t^{-1}$).

Average atmospheric CH_4 concentrations, $[\text{CH}_4]$, from all sites ranged from 1.72 to 1.88 ppmv (Table 3). These results are consistent with the mean atmospheric CH_4 concentration for July 2012 of 1.86 ppmv measured at Summit Station, Greenland (NOAA, 2013). Note that Summit Station is the only source of year-round data for trace gas concentrations in Greenland. The average OPL uncertainty, U , associated with six of the time series was within 0.04 ppmv of the OPL U of ± 0.08 ppmv observed under ideal conditions in the laboratory. In the other two studies, the OPL U was twice that observed in the laboratory (± 0.15 ppmv or 8% of the $[\text{CH}_4]$, and ± 0.16 ppmv or 9% of the $[\text{CH}_4]$). $[\text{CH}_4]$ from the subglacial cave, upland, and urban environments showed no difference from near-lake and near-wetland environments (two-tailed t-test, $t = 0.77$, $p = 0.48$, $df = 4$).

The CH_4 concentration in gas bubbles collected from littoral sediments near OPL transects ranged from 32% to 38% by volume (320,000 to 380,000 ppmv) and occasional ebullition was observed during July sampling periods. All nearby lakes were thermally stratified at the time of the study. CH_4 concentrations in the well-mixed surface (epilimnetic) waters of the study lakes ranged from 2.5 to 26 μM (60 to 620 ppmv equivalents). The active layer of upland soils was unsaturated with water, and CH_4 concentrations obtained from upland soil gas samples were all below 1.86 ppmv, the mean concentration of tropospheric methane reported at Summit Station for this time of year (NOAA, 2013). Wetland soils were all saturated with water, and CH_4 concentrations in the soil-pore water were elevated compared to water in equilibrium with the atmosphere (0.003 μM) and ranged from 0.09 to 3.2 μM (2.2 to 77 ppmv equivalents).

Discussion

Despite evidence of active CH_4 production and consumption in close proximity to OPL time-series measurements, strong deviations in atmospheric CH_4 concentrations (> 2.5 ppmv) were not

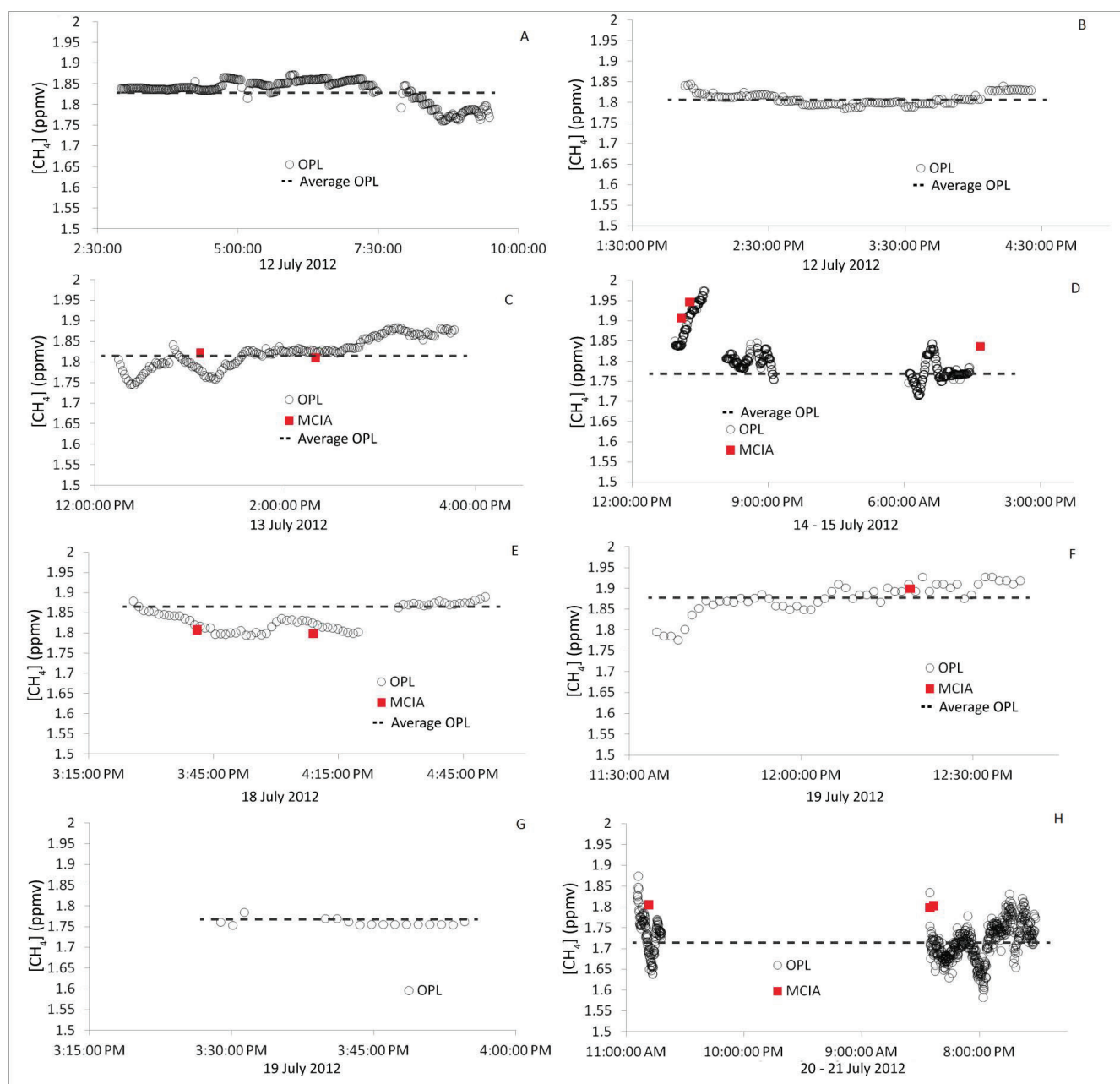


FIGURE 6. $[\text{CH}_4]$ for the following OPL campaigns: (A) Kangerlussuaq, (B) Site 1, (C) Site 2, (D) Site 4, (E) Site 3, (F) Site 6, (G) Site 7, and (H) Site 2. Gaps in the OPL time series are due to losses of data fidelity. Circles represent OPL $[\text{CH}_4]$, squares represent concentrations of methane in independent onsite air samples measured by MCIA (MCIA precision = 0.04 ppmv), and the dashed lines indicate the average of the measurements collected with the OPL. The uncertainty associated with each measurement for each time series is as follows: (A) $a = 0.04$ ppmv, (B) $a = 0.07$ ppmv, (C) $a = 0.04$ ppmv, (D) $a = 0.04$ ppmv, (E) $a = 0.04$ ppmv, (F) $a = 0.08$ ppmv, (G) $a = 0.07$ ppmv, and (H) $a = 0.04$ ppmv.

measured in our OPL time-series studies. Ground-level CH_4 concentrations were determined by OPL in southwestern Greenland for a variety of Arctic landscapes using path lengths ranging from 10 to 280 m and time periods between 0.4 and 37 h. All OPL measurements of ground-level methane concentrations were consistent with the mean value of 1.84 ppmv CH_4 reported by others for Arctic air samples (Dlugokencky et al., 2009; Adushkin and Kudryavtsev, 2010), and with the mean CH_4 concentration reported for July 2012 at Summit Station, Greenland, of 1.86 ppmv (NOAA, 2013). Measurements made with OPL also were in good agreement with

independent measurements of samples collected on-site and analyzed using cavity-enhanced laser absorption spectrometry and gas chromatography.

Field deployments of the OPL generally yielded comparable uncertainty over the duration of the time-series (U) to its performance under laboratory conditions. However, for some field deployments, the OPL instrument was susceptible to changes in operating conditions. At site 2 on 20 July, the temporal variation in recorded methane concentration caused the U for the time series to increase by a factor of about two compared to optimal performance

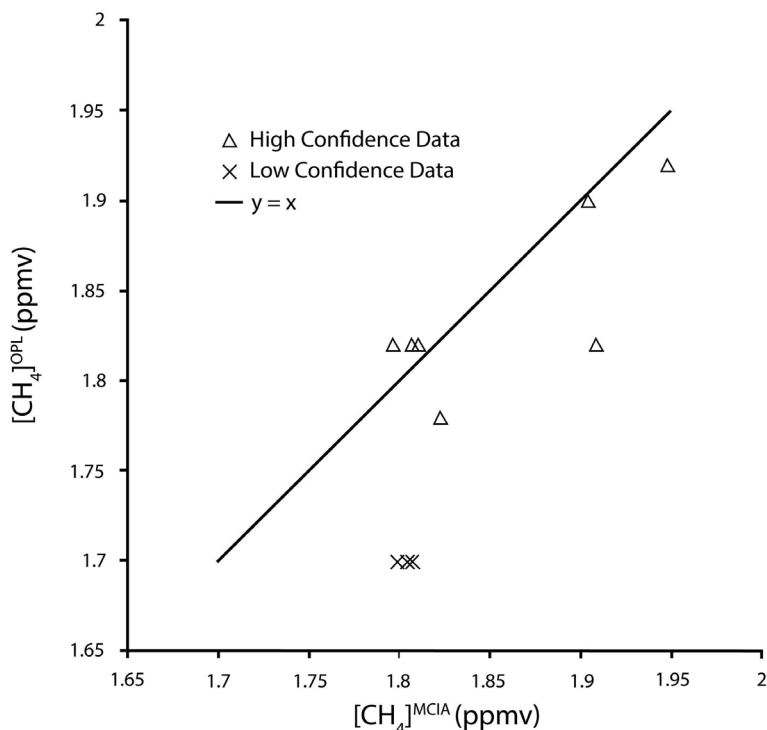


FIGURE 7. Methane concentrations measured with open-path laser ($[\text{CH}_4]^{\text{OPL}}$) versus methane concentration measurements made with the MCIA ($[\text{CH}_4]^{\text{MCIA}}$). Triangles and crosses represent high and low confidence data, respectively. The line represents the expected 1:1 relationship between the two independent measurements.

under laboratory conditions ($U = 0.08$ ppmv). An important source of variability may be the instability of the tundra soil surface as a platform to conduct open-path optical measurements. Peat-rich tundra soils can deform under load, causing shifts in tripod mounting systems and changes in alignment between the OPL laser/sensor relative to the retro-reflector mirror.

Variability in micrometeorological conditions such as air temperature, wind speed, and wind direction increased with longer time series, likely contributing to greater variability in OPL stability for the longer time series. Increases in variability of environmental factors may affect the stability of the OPL system in complex ways causing shifts in alignment between the OPL laser/sensor and

retro reflector mirror. These small changes in alignment may have added noise to the measurement system above the baseline noise determined for laboratory time series. Longer deployments have a greater probability of being subjected to factors that cause shifts in alignment and consequent drift in OPL response as environmental variables exhibited greater variability in longer time series than in shorter time series ($0.50 \leq r^2 \leq 0.96$). OPL instability also increased as the duration of the monitoring increased. For example, two of the four time series with U above 0.10 ppmv were from time series of longer duration (Sites 2 and 4, Table 4). It is interesting to note that the long-duration time series from Kangerlussuaq exhibited greater stability than the other long-duration time series, suggest-

TABLE 2
Summary statistics for linear regression analyses for each OPL time series.

Location	Start date	Regression analysis					
		$\Delta[\text{CH}_4]_i \Delta t^{-1}$ vs. $\Delta W \Delta t^{-1}$		$\Delta[\text{CH}_4]_i \Delta t^{-1}$ vs. $\Delta T \Delta t^{-1}$		$\Delta[\text{CH}_4]_i \Delta t^{-1}$ vs. $\Delta P \Delta t^{-1}$	
		r^2	p	r^2	p	r^2	p
Kangerlussuaq	12 July	0.01*1	0.03	0.005	0.18	0	0.66
1	12 July	0.01	0.18	0	0.93	0	0.93
2	13 July	0	0.75	0	0.86	0.02	0.75
4	15 July	0.01	0.04	0.01	0.04	0.001	0.44
3	18 July	0.04	0.12	0.17	0.18	0.002	0.72
5	19 July	—*2	—	0.02	0.32	0	0.98
6	19 July	—	—	—	—	—	—
2	20 July	0	0.51	0	0.72	0	0.81

*1Bolted numbers indicate significant results ($p < 0.05$).

*2Dashes indicate that no linear regression was performed due lack of changes in wind speed (location 5) or due to small sample size (location 6).

TABLE 3

The average CH₄ concentration and error of the average CH₄ concentration, *U*, associated with each OPL time series.

Location	Start date	[CH ₄] (ppmv)	<i>U</i> (ppmv)
Kangerlussuaq	12 July	1.83	0.10
1	12 July	1.81	0.10
2	13 July	1.82	0.12
4	15 July	1.77	0.16
3	18 July	1.86	0.10
5	19 July	1.88	0.15
6	19 July	1.77	0.08
2	20 July	1.72	0.12

ing that deployment of the OPL on less stable peat soil was a large contributor to instrumental noise.

Time series of longer duration also are more likely to capture real variations in local CH₄ concentrations. At Site 4 (EVV), we observed a short-term increase in OPL-based CH₄ concentration values above 1.90 ppmv that was also observed in independent air samples measured by MCIA (Fig. 6, part D). The highest CH₄ concentration measured by the OPL during this time series was 1.98 ppmv and could be related to ebullition of CH₄ from the littoral sediments of the nearby EVV lakes.

We evaluate sediment degassing at EVV as a potential factor affecting local ground-level CH₄ concentrations by determining the dimensions of a CH₄ plume generated from sediment degassing that could account for the elevated [CH₄]_{*i*} observed at this site. The width of a plume of CH₄-enriched air that results in the observed [CH₄]_{*i*} can be calculated as follows:

$$l = ([CH_4]_i L - CL)(c - C)^{-1} \quad (6)$$

where *l* is the width of the plume in meters, *c* is the CH₄ concentration of the plume, and *C* is the atmospheric background CH₄ concentration. CH₄ concentration in a plume of air downwind of sediment gas ebullition was measured at one of the field sites, and ranged from 2 to 12 ppmv (Christensen, unpublished data, 2013). In order to measure 1.98 ppmv CH₄ in air downwind of EVV, *l* would range from 1.1 m to 71 m if we assume plume CH₄ concentrations of 12 ppmv to 2 ppmv, respectively, and a background CH₄ concentration of 1.84 ppmv. The plume of CH₄ that could cause elevated CH₄ concentrations at EVV was likely broad and diffuse (71 m × 2 ppmv) given the well-mixed boundary layer. This is also consistent with the CH₄ concentrations measured in the independent discrete air samples collected at EVV (1.91 and 1.95 ppmv) during the same time period as the OPL measurements. The calculated plume width seems physically reasonable, and the combination of plume width and plume concentration can generate the observed deviations from the expected background CH₄ concentration. These calculations are consistent with the idea that sediment ebullition may have caused the departures from background CH₄ concentrations measured at EVV.

Several studies have demonstrated that sediments in shallow areas of lakes are a significant source of CH₄ to the atmosphere during summer months (Casper et al., 2000; Bastviken et al., 2008;

Repo et al., 2007). Yet, average ground-level CH₄ concentrations downwind of lakes were not significantly higher than values from sites distant from lakes and wetlands. Based upon the OPL time series collected downwind of lakes in this study, localized emissions appear to be rapidly obscured by boundary-layer mixing (Liss, 1973).

For two of the three OPL time series longer than 8 h, Kangerlussuaq and EVV, we observed significant relationships between CH₄ and at least one of the micrometeorological parameters. The other study of longer duration (Site 2, 20–21 July) suffered from high instrumental noise, which probably masked any relationships with micrometeorological parameters. However, the correlations were weak (*r*² ≈ 0.01), suggesting that micrometeorological effects on ground-level methane concentrations are insufficiently dynamic to be detected by the OPL.

The slightly elevated CH₄ concentrations in a subglacial cave suggest a local methane source associated with water within the glacial system. We are cautious about the interpretation of these results given that the [CH₄]_{*i*} of 1.90 ± 0.08 ppmv and the MCIA measurement of 1.90 ± 0.04 ppmv inside the glacial cave are close to the concentrations of 1.82 ± 0.04 ppmv measured by MCIA at our other field sites nearby. However, our interpretation is supported by recent reports of elevated CH₄ concentrations and methanogenic Archaea in the discharge waters emanating from this same subglacial cave (Dieser et al., 2014). Other studies also report evidence for subglacial methane emissions (Walter Anthony et al., 2012; Boyd et al., 2010; Wadham et al., 2008; Christner et al., 2012). Further study of CH₄ concentrations and stable isotopic analyses of subglacial air are in progress and should yield valuable insight into CH₄ dynamics in the interior and at the base of ice sheets.

Conclusions

A portable OPL system measured accurate ground-level CH₄ concentrations over a range of spatial and temporal scales and a variety of landscape types during summer field surveys in southwestern Greenland. Slightly elevated CH₄ concentrations were observed in near-lake and subglacial environments. However, no differences from known background CH₄ concentrations were observed in upland environments or in Kangerlussuaq. The similarity between our local ground-level CH₄ concentrations and those measured for the same period at Summit Station, Greenland, suggests that local sources and sinks of CH₄ were not strong enough to cause deviations from regional atmospheric CH₄ concentrations on a time scale of days. However, slight positive deviations from regional atmospheric CH₄ concentrations were observed downwind of a lake source and in a subglacial setting. We suggest that OPL systems can serve as a robust measurement technology for year-round monitoring of atmospheric CH₄ concentrations in the Arctic when mounted to a stable platform and may be able to fill spatial gaps in atmospheric CH₄ monitoring strategies.

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