

JGR Biogeosciences

RESEARCH ARTICLE

10.1029/2019JG005094

Special Section:

Water-Energy-Carbon Fluxes Over Terrestrial Water Surfaces

Key Points:

- Multiyear flux measurements show that annual CH₄ emissions from northern lakes can be dominated by emissions during ice-off in spring
- CH₄ accumulates under ice at rates exceeding summer emissions, in part because prolonged anoxia limits methanotrophy
- Under-ice carbon gas storage scales predictably with ice-cover season length, but meltwater advection or dilution can limit fluxes in spring

Supporting Information:

Supporting Information S1

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Citation:

Jansen, J., Thornton, B. F., Jammet, M. M., Wik, M., Cortés, A., Friborg, T., et al. (2019). Climate-sensitive controls on large spring emissions of CH₄ and CO₂ from northern lakes. *Journal of Geophysical Research: Biogeosciences*, 124, 2379–2399. https://doi.org/ 10.1029/2019JG005094

Received 14 FEB 2019 Accepted 19 JUN 2019 Accepted article online 29 JUN 2019 Published online 29 JUL 2019

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Climate-Sensitive Controls on Large Spring Emissions of CH₄ and CO₂ From Northern Lakes

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Abstract Northern lakes are important sources of the climate forcing trace gases methane (CH₄) and carbon dioxide (CO₂). A substantial portion of lakes' annual emissions can take place immediately after ice melt in spring. The drivers of these fluxes are neither well constrained nor fully understood. We present a detailed carbon gas budget for three subarctic lakes, using 6 years of eddy covariance and 9 years of manual flux measurements. We combine measurements of temperature, dissolved oxygen, and CH₄ stable isotopologues to quantify functional relationships between carbon gas production and conversion, energy inputs, and the redox regime. Spring emissions were regulated by the availability of oxygen in winter, rather than temperature as during ice-free conditions. Under-ice storage increased predictably with ice-cover duration, and CH₄ accumulation rates ($25 \pm 2 \text{ mg CH}_4\text{-C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$) exceeded summer emissions ($19 \pm 1 \text{ mg CH}_4\text{-C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$). The seasonally ice-covered lakes emitted 26–59% of the annual CH₄ flux and 15–30% of the annual CO₂ flux at ice-off. Reduced spring emissions were associated with winter snowmelt events, which can transport water downstream and oxygenate the water column. Stable isotopes indicate that 64–96% of accumulated CH₄ escaped oxidation, implying that a considerable portion of the dissolved gases produced over winter may evade to the atmosphere.

Plain Language Summary Northern lakes are globally significant sources of greenhouse gases methane and carbon dioxide, but the seasonal pattern of emissions from lakes that are ice covered in winter remains poorly resolved. Our multiyear, multilake study reveals the importance of emissions during the ice-off period, when carbon gas that had accumulated under ice is released. We show that more than half of the annual methane emissions and a third of the yearly carbon dioxide flux can be released at spring ice-out. Unlike emissions during summer, which tend to be closely correlated with temperature, spring emissions of both gases are in part regulated by the availability of oxygen under ice. The quantity of carbon gas accumulating under ice, and therefore the amount that can be emitted in spring, scales predictably with ice-cover duration. Parameterizations of winter and spring carbon cycling processes, such as those described in this study, may contribute to more accurate models of annual, ecosystem-level carbon fluxes and are essential tools to improve freshwater emission inventories and quantify critical Arctic warming feedbacks.

1. Introduction

Northern lakes are an important source of radiatively active carbon trace gases (Tranvik et al., 2009; Wik et al., 2016) to the atmosphere, despite being ice covered for a majority of the year (Walsh et al., 1998). A significant part of the annual flux can occur during the ice-out period in spring (Denfeld, Baulch, et al., 2018; Ducharme-Riel et al., 2015; Jammet et al., 2015; Michmerhuizen et al., 1996). Overall, emissions from northern freshwaters are projected to increase as a result of rapid Arctic warming (Thornton et al., 2015; Weyhenmeyer et al., 2015) because of a strong dependence of ecosystem-level carbon cycling on energy input (Yvon-Durocher et al., 2012, 2014), increased hydrological inputs of terrestrial carbon (Walter Anthony et al., 2016) and longer ice-free periods (Prowse et al., 2011). We may underestimate the impact of such feedbacks because the most intense Arctic warming occurs in winter months (Screen & Simmonds, 2010) and cold season emissions remain poorly represented in data sets, process-based studies, and global climate models (Tan & Zhuang, 2015; Zona et al., 2016).

The majority of lake flux studies focus on the open water period (Wik et al., 2016), which makes it difficult to identify the key climate controls on the spring and annual efflux. Functions that govern the ice-free season



flux, such as those based on temperature, cannot readily be applied to the ice-cover period when carbon cycling appears to be limited by substrate availability instead (Bertilsson et al., 2013, and references therein). Ice and snow covers shield the lake from radiative input and prevent exchange with the atmosphere (Prowse & Stephenson, 1986). This can cause rates of aerobic respiration to exceed those of oxygenic photosynthesis (Gammons et al., 2014). The resulting depletion of O_2 and other electron acceptors inhibits CH_4 oxidation at the sediment surface (Martinez-Cruz et al., 2015) while methanogenesis continues in unfrozen sediments (Zimov et al., 1997). Consequently, carbon gases accumulate in the water column (e.g. Juutinen et al., 2009; Karlsson et al., 2013) and as bubbles in the aggrading ice (Walter Anthony & Anthony, 2013; Wik et al., 2011).

Previous studies have quantified carbon gas storage before and after ice-out (Karlsson et al., 2013; Michmerhuizen et al., 1996) or have used eddy covariance (EC) techniques to estimate the spring efflux (Jammet et al., 2015). However, few winter studies include the ice-free season for comparison, and between them the spring contribution to the annual flux varies substantially: 4-74% for CH₄ and 10-55% for CO₂ (Denfeld, Baulch, et al., 2018). Because of the short duration of most flux monitoring efforts (<2 years), it is unknown whether this variability reflects spatial gradients or temporal variability. Without multiyear observations it remains unclear whether winter storage can be predicted from summer fluxes and how emissions in spring might change under future warming scenarios. This knowledge gap constitutes a major uncertainty for the freshwater carbon budget and the strength of the Arctic climate feedback and highlights the need for an improved understanding of the drivers of the spring efflux.

2. Materials and Methods

We combine multiyear measurements (2009–2018) of fluxes and storage from three small subarctic lakes in northern Sweden to assess the magnitude of CH_4 and CO_2 emissions and to infer processes driving the flux in summer and in spring.

2.1. Field Site

The studied lakes are part of the Stordalen Mire (68°21'N, 19°02'E; Figure 1), a peatland complex underlain by discontinuous permafrost in northern Sweden (Johansson et al., 2006). The catchment landscape (15 km²) consists of birch forest (58%), alpine tundra (13%), peatlands (6%; fen, bog, and palsa), and open water (5%) (Lundin et al., 2016). The 27 lakes on the Mire (350 m asl) are of postglacial origin and form part of a hydrologic network that connects Mt. Vuoskoåiveh (920 m asl) to Lake Torneträsk (341 m asl). Our study lakes, Villasjön, Inre Harrsjön, and Mellersta Harrsjön, are 0.17, 0.02, and 0.01 km² in area and have maximum depths of 1.1, 5.0, and 6.7 m, respectively (Wik et al., 2013; Table 1). Similar to many other subarctic and boreal catchments (Weyhenmeyer et al., 2015), the Stordalen lakes receive terrestrial carbon from fens, streams, and springs (Olefeldt & Roulet, 2012) and are net heterotrophic as a result (Lundin et al., 2013). In the two deeper lakes there are distinct littoral zones with emergent macrophytes (approximately ≤2-m water depth) and nonvegetated profundal zones (>2 m). Aquatic vegetation supplies organic carbon to the sediment (Wik et al., 2018), which consist of 1–3 m of carbon-rich gyttja (Kokfelt et al., 2010). The lakes are relatively clear with summer Secchi depths of 2–3 m (Karlsson et al., 2010; Wik et al., 2018).

2.2. Local Meteorology

Meteorological data were collected at three sites on the Stordalen Mire (Figure 1). At the Villasjön shore EC tower we measured air temperature and relative humidity with a HMP155 probe protected with a radiation shield (Vaisala), as well as wind speed with a R3-50 sonic anemometer (Gill Instruments). Shortwave and longwave radiation was measured at the INTERACT tower with a CNR4 radiometer (Kipp & Zonen). Snow depth was estimated with SR50 ultrasonic distance sensors (Campbell Scientific) at the INTERACT tower and at the Integrated Carbon Observation System (ICOS) site located on the fen between the three study lakes. Water temperature was measured every 5 and 15 minutes in summer and in winter, respectively, with intercalibrated temperature loggers (HOBO Water Temp Pro v2, Onset Computer) in Villasjön and at the deepest points of Inre and Mellersta Harrsjön. Sensors were mounted on mooring lines at 0.1, 0.3, 0.5, and 1.0 m (all three lakes); at 3.0 and 5.0 m (Inre Harrsjön and Mellersta Harrsjön); and 6.7-m depth (Mellersta Harrsjön). The lowermost sensors were buried in the surface sediment. MiniDOT probes (PME Systems) logged the dissolved oxygen (DO) content at 10-min intervals at 1.5 m from the water surface







Figure 1. Map of the Stordalen Mire study area. The purple-shaded area shows the ice-free season eddy covariance tower footprint at flux contribution intervals of 85%, 80%, 70%, 50%, and 10%. The Integrated Carbon Observation System (ICOS) micrometeorological tower in the center of the map supports the camera and snow depth sensor used to track snowmelt events. Filled areas in the lakes signify water depth intervals (see scale bar underneath the map). Schematics on the left show a bubble trap (top) and a floating chamber (bottom). White arrows signify hydrological flow pathways on the Mire, as described in Olefeldt and Roulet (2012).

and at 0.5 m from the sediment at the deep points of the deeper lakes (2015–2018). The DO sensors were covered with a copper antifouling mesh.

Two digital cameras took periodic photographs of the Mire throughout the study period to track the progression of ice-off and the occurrence of snowmelt events. Northward pointing cameras were mounted at the ICOS site (NetCamSC, StarDot Technologies) and 90 m south of the Villasjön EC tower (Canon G9). Due to a power failure the latter camera did not take pictures between 12 April and 6 June 2016.

We marked the start of freezing (ice-on) and thaw (ice-out), respectively, by 3-day periods with daily mean air temperatures below and above 0 °C, as well as visually during field visits. Thaw started with the stream and along the shores and transitioned into the ice-free season at the first overturn, when the daily mean water temperature gradient (0.1- to 1.0-m depth) was less than 0.1 °C (Jammet et al., 2017). Complete thaw could take up to two weeks. For the purpose of delineating the eddy covariance fluxes, we define spring as the period between the start of ice thaw and the first overturn. The lakes were ice-covered from late October to May (200 days, 2009–2018) and froze to the bottom where water depth was <80 cm. Snowmelt often occurred before complete ice-off, enabling substantial surface runoff (up to 54–63 mm/week; Olefeldt & Roulet, 2012) to enter the lakes via streams or along shores bordering thawed fens.

| Table 1 | |
|--|--|
| Morphometric, Physical, and Chemical Properties of the Studied Lakes (Mean + SE) | |

| Lake | Area (ha) | Mean/max. depth (m) | Sed. temp. ice-free (°C) | Sed. temp. ice-cover (°C) | Spec. cond. (µS/cm) | pН |
|--------------------|-----------|---------------------|--------------------------|---------------------------|---------------------|---------------|
| Villasjön | 17.0 | 0.7/1.3 | 10.0 ± 0.14 | 0.8 ± 0.04 | 28.1 ± 0.4 | 7.1 ± 0.1 |
| Inre Harrsjön | 2.3 | 2.0/5.2 | 9.3 ± 0.07 | 3.2 ± 0.02 | 56.9 ± 0.3 | 7.3 ± 0.1 |
| Mellersta Harrsjön | 1.1 | 1.9/6.7 | 8.4 ± 0.05 | 1.7 ± 0.01 | 48.2 ± 0.6 | 6.9 ± 0.1 |

Note. Seasonal mean water temperatures from continuously operating sensors at 1-m depth intervals (HOBO Water Temp Pro V2, 2009–2018) were weighted by sediment surface area using hypsographic curves (Figure 1) to obtain lake mean values. Specific conductance and pH were measured in summer 2017 (*n* = 323).



2.3. Eddy Covariance Measurements

We measured CH₄ fluxes year-round with an EC system on the western shore of Villasjön (2012–2018). The measurement setup and data processing have been described in detail in Jammet et al. (2015, 2017) and in the supporting information. In brief, we equipped a 2.92-m tall tower with a Gill R3-50 sonic anemometer and a tube inlet (6-mm ID polyethylene, 2012–2015; 8-mm ID Synflex, 2015–2018) to a closed path cavity ring-down spectrometer (Los Gatos Research). Instrumental data were sampled at 10 Hz and stored on a CR3000 datalogger (Campbell Scientific). The bimodal wind direction in the Torneträsk valley separated the fluxes from the lake and fen fetches. Raw data processing, flux calculations, and spectral corrections were done in EddyPro version 6.2 (LI-COR). We used a nonlinear parameterization based on surface sediment temperature ($R^2 = 0.95$; Figure S3) and linear interpolation to gap-fill daily mean ice-free and spring CH₄ fluxes, respectively.

2.4. Field Measurements

The CH₄ bubble flux was measured with bubble traps in the ice-free seasons of 2009–2017 (n = 14,677). Wik et al. (2013) provide a detailed description of the sampling procedure. Briefly, bubbles rising from the sediment were captured with 38–40 inverted floating funnels deployed in transects across different depth zones in each lake (Figure 1). In Villasjön the transect intersected the EC tower footprint. Every 1–3 days during the ice-free season we sampled the gas and measured the volume using polypropylene syringes equipped with 3-way gas-tight stopcocks.

Floating chambers were used to measure the diffusive CH₄ flux in 2010–2017 (n = 1,306). A total of 10 floating chambers were deployed across different depth intervals (Figure 1), approximately every week between June and October. The chambers were covered with aluminum tape to reflect incoming radiation. Underneath each chamber a shielding surface was mounted to prevent bubbles from reaching the head-space. Each chamber covered an area of 610 to 660 cm² and contained a headspace of 4 to 5 L, depending on the flotation depth. We extracted 60 mL of air from the chamber headspace at regular time intervals (2–4 times within 24 hr) using polypropylene syringes. A flux was subsequently estimated by calculating the linear rate increase of the CH₄ content within the chamber headspace. Nonlinear rate increases ($R^2 < 0.8$) were filtered out. We accounted for the decrease in the air-water concentration gradient due to CH₄ buildup in the chamber headspace (Bastviken et al., 2004); for 24-hr deployments the value of the flux correction factor was approximately 1.2. The chambers were taken out of the water and aired between deployments.

Water samples were collected weekly between June and September, and monthly during those parts of the ice-cover seasons when the ice was safe to walk on, at different depth zones (2015–2017, n = 926). Samples were collected from each lake in the littoral zone at the ends of the bubble trap transects at 0.4-m depth, and from the deep points of Inre and Mellersta Harrsjön at 0.4 m and every subsequent meter down to the sediment (Figure 1). We used a 1.2-m Tygon tube for the shallow samples, and a 7.5-m fluorinated ethylene propylene (FEP) tube at the deep points. Polypropylene syringes were first flushed three times with sampling water before a 60-mL bubble-free sample was collected. Samples were analyzed for CH₄, CO₂, and dissolved inorganic carbon (DIC) at the Abisko Scientific Research Station within 24 hr of collecting.

Sediment gas was collected by stirring up sediment with a long aluminum rod and catching the gas bubbles in a water-filled, airtight funnel capped with a three-way stopcock. Because of the disruptive nature of the collection method, we always sampled outside the bubble trap and floating chamber transects. The samples were processed in the same way as the bubble samples.

2.5. Estimation of the Ice-Free CO₂ Flux With a Boundary Layer Model

Because darkened floating chambers could have biased daytime CO_2 emissions by limiting photosynthetic uptake, we instead estimated CO_2 fluxes using pCO₂ from water samples (2015–2017) and a boundary layer model:

$$F = k (C_{aq} - C_{air,eq}), \tag{1}$$

where k is the gas transfer velocity and $C_{aq} - C_{air,eq}$ represents the concentration difference between the water in the boundary layer and at equilibrium with the air above, determined from weekly



measurements of surface water CO_2 concentrations (Figure 1) and assuming an atmospheric mixing ratio of 400 ppm. We determined *k* with a surface renewal model (Lamont & Scott, 1970):

$$k = c_1 (\varepsilon \nu)^{\frac{1}{4}} S c^{-\frac{1}{2}}, \tag{2}$$

where c_1 is a scaling parameter determined to be ~0.4 on theoretical grounds (Katul et al., 2018; Lamont & Scott, 1970) and from analysis of multiple experiments including physical measurements of turbulence and eddy covariance (Zappa et al., 2007), ν is the kinematic viscosity, *Sc* is the Schmidt number for CO₂ (Jähne et al., 1987), and ε is the dissipation rate of turbulent kinetic energy, which is driven by wind shear (u_{*w}) and the buoyancy flux under cooling (β) (Tedford et al., 2014):

$$\varepsilon = \begin{cases} 0.56u_{*w}^3/\kappa z + 0.77\beta & \text{if} \quad \beta > 0\\ 0.6u_{*w}^3/\kappa z & \text{if} \quad \beta \le 0 \end{cases}$$
(3)

Here, κ is the von Kármán constant, and z is operationally defined as 0.15 m (Czikowsky et al., 2018; Tedford et al., 2014). We used half-hourly measurements of the wind speed to compute the waterside friction velocity (u_{*w}) following the method and assumptions described in MacIntyre et al. (2010). The buoyancy flux accounts for convective mixing, for example, during nighttime surface cooling, and was computed from the effective heat flux into the water column following Imberger (1985), using half-hourly observations of the surface water and air temperature, humidity, and radiation. We assumed an attenuation coefficient of 0.72 for the visible portion of the spectrum, calculated from the Secchi depth in Inre Harrsjön (Karlsson et al., 2010) using the inverse relationship of Idso and Gilbert (1974). Here positive β implies cooling. The gas transfer velocity was calculated at half-hourly intervals. Daily mean CO₂ fluxes were calculated using daily means of k and linear interpolations of the CO₂ concentration.

2.6. Under Ice In Situ Incubations

We performed incubations using bottles suspended in the water column to identify whether microbial processes moderated the carbon gas content in the oxygen-depleted water under ice. Specifically, we tested whether methanogenesis occurred. Lake water was transferred through a 7.5-m FEP tube into 120-mL autoclaved, N₂-filled glass vials via a stainless steel needle piercing butyl rubber stoppers. We pulled a vacuum through a second tube attached to a Nalgene PVC hand pump until the bottles were filled and no more air bubbles were visible. Four bottles (three replicates filled with lake water + one blank filled with Milli-Q water) were deployed at each of four locations at the deepest points of the deeper lakes (16 bottles total): at 2.5 and 3.5 m from the ice-water interface in Inre and Mellersta Harrsjön, respectively, and at 0.5 m from the bottom (both lakes). The bottles were deployed on 10 March 2017 and removed on 12 May 2017 (64 days), simultaneous with concentration profile measurements (section 2.4). When not in the lake we kept the bottles in a dark and cool storage container. We measured the CH₄ and DIC content of the incubated water in the same way as the water samples.

2.7. Laboratory Analyses

CH₄ concentrations in bubble and chamber samples were determined with a GC-2014 gas chromatograph (Shimadzu) at the Abisko Scientific Research Station, 10 km from the Mire. The GC was equipped with a flame ionization detector (FID) and a 2.0-m-long, 3-mm ID stainless steel column packed with 80/100 mesh HayeSep Q. For calibration of the CH₄ measurements we used standards of 2.059 ppm CH₄ in N₂ (Air Liquide) for headspace samples and 2,010 ppm CH₄ in N₂ (AGA) for bubble gas. Bubble samples—containing up to 100% CH₄—were diluted with outdoor air to better match standard concentrations. We made 10 standard measurements before and after each run. After removing the highest and lowest value, standard deviations were generally less than 0.25%. Thirty-milliliter water samples were equilibrated at room temperature with 30-mL N₂ headspace on a mechanical shaker for 10 min at 300 rpm and were analyzed for CH₄ (GC-FID) and CO₂ (LI-COR 6262 infrared gas analyzer): DIC was determined by acidifying (pH < 2) duplicate samples and analyzing for CO₂. Triplicate injections of a range of volumes of a 2,000 ppm CO₂ in N₂ standard (Air Liquide) served to create a calibration curve for the CO₂ measurements. We calculated the aqueous carbon gas quantities with the headspace method, using gas solubility constants from



Wiesenburg and Guinasso (1979) and Weiss (1974) for CH_4 and CO_2 , respectively. In 2017 we also measured the pH and conductivity of the water (S220 and S230, respectively; Mettler-Toledo).

We measured CH₄ stable isotopes (δ^{13} C, δ^{2} H) in gas bubbles stirred from the sediment (n = 52) and in a subset of water headspace samples (n = 254), as well as δ^{2} H of lake water (n = 34) at the Stable Isotope Laboratory at Stockholm University, Sweden. We used a continuous flow Gas Chromatograph Isotope Ratio Mass Spectrometer (GC-DeltaV plus, Thermo Fisher Scientific) with the standard IsoDAT software package (v3.0). High concentration samples (>5% CH₄) were injected directly into the GC, while low concentration samples were first run through a trace gas preconcentration unit (PreCon). Samples were combusted to CO₂ at 900 °C for ¹²C/¹³C ratios or pyrolized to H₂ at 1,450 °C to obtain ¹H/²H ratios. Isotopic standards (100% CH₄ [direct injections], 5 ppm CH₄ in N₂, and 100 ppm CH₄ in N₂ [PreCon], AGA) were measured frequently throughout each measurement day in order to monitor system performance and drift and to calculate delta values (δ^{13} C, δ^{2} H) from isotope ratios. δ^{2} H-H₂O was measured by Off-Axis Integrated Cavity Output Spectroscopy (Liquid Water Isotope Analyzer, Picarro).

2.8. Calculation of Carbon Gas Storage

The quantity of dissolved CO_2 , DIC, and CH_4 in the water column, the storage term, was computed from concentrations at 1-m depth intervals weighted by the water volume of each respective layer using the lakes' hypsographic curves. The volume of the surface layer was corrected for ice thickness (12–112 cm). Storage quantities in the surface and the bottom layers of the profile were estimated, respectively, with concentration measurements at 0.4- and 1-m depth, and at the sediment surface. In winter, in shallows where the ice froze close to the sediment-water interface and where we were still able to sample water, we assumed that measured gas concentrations were representative of a 25-cm deep layer of soft gyttja containing 80% porewater by volume, based on sediment cores from each of the study lakes (Wik et al., 2018) and a conservative estimate of the space between the ice-water interface and more compacted sediments (10–40 cm, measured by pushing a metal rod gently down into the sediment). We did not measure or estimate gas storage in places where the ice froze into the sediment, for example, in Villasjön during the winter of 2017–2018.

2.9. Estimation of the Quantity of CH₄ Stored in Ice-Trapped Bubbles

Gas bubbles encapsulated in the aggrading ice were clearly visible in all three lakes. They varied in size from a few millimeters (exsolution bubbles) up to a meter in diameter (trapped gas from bubble seeps). The amount of CH₄ stored in ice-trapped bubbles was estimated in two different ways to obtain an upper and lower limit value for each lake. For the lower limit, we assumed that ice bubble storage amounted to about 9% of the total annual flux. This percentage was derived from year-round flux measurements that included under-ice bubble fluxes in 19 Alaskan, nonyedoma thermokarst lakes (Sepulveda-Jauregui et al., 2015). For the upper limit we used the point source densities (seeps per square meter) from a detailed ice bubble survey of Inre and Mellersta Harrsjön in April 2009 (Wik et al., 2011), multiplied by the gas flux (milliliters per seep per day) measured with under-ice bubble traps for three different seep types from Alaskan lakes (Walter Anthony & Anthony, 2013) and the mean CH₄ content of sediment gas bubbles in the Stordalen lakes in February and May 2016 ($62 \pm 6\%$; mean \pm SE, n = 11). We further assumed that 80% of bubble gas ultimately dissolved back into the water column prior to ice melt (Greene et al., 2014). The ice-trapped bubble accumulation rates (Table 3) were calculated by dividing the storage quantity by the number of days between ice-on and the ice bubble survey. No survey was conducted in Villasjön, and only the lower limit was included in Table 3. A survey of exsolution bubbles was conducted in all three study lakes in 2008 (Boereboom et al., 2012). The concentration (<1% CH₄) and the total amount of CH₄ gas stored in this type of bubbles $(<0.08 \text{ g CH}_4 \cdot \text{m}^{-2})$ were negligible and were therefore not included in the winter CH₄ storage budget.

2.10. Computation of Annual Emissions

Bubble fluxes and diffusive fluxes can be spatially variable, even in small lakes ($<1 \text{ km}^2$) (Natchimuthu et al., 2016, 2017; Wik et al., 2013). Fluxes were therefore weighted by depth zone surface area (1-m depth intervals; Figure 1) to obtain ice-free season means (lake-integrated fluxes in Figure 2). Because ice-free monitoring usually ended before 30 September (except in 2016), we had to make assumptions about the flux prior to ice-on to calculate the total ice-free flux. We used the complete sampling season of 2016 to compare autumn emission rates with mean ice-free fluxes. Averaged over all three lakes, the flux past 30 September 2016 was 17% of the ice-free mean CH₄ bubble flux, and 30% and 43% of the ice-free mean diffusive fluxes of CH₄ and





Figure 2. Multiyear lake carbon gas emission budget. Total fluxes of CH₄ (top panel) and CO₂ (bottom panel) to the atmosphere during the ice-free season (left) and at ice-out (right). Colors signify the different lakes. Percentages denote the spring contribution to annual emissions. Fluxes were depth-integrated for each lake (I), and according to sampling location in the littoral (L; \leq 2-m water depth) and profundal (P) zones (\geq 2 m). The upper, lighter-shaded bars in the top-left panel represent the ebullition pathway; horizontally striped bars represent eddy covariance fluxes (from Villasjön only); and all other bars turbulence-driven diffusive fluxes. Error bars represent standard errors of the multiyear means.

 CO_2 , respectively. To calculate total ice-free season emissions in other years, we multiplied the depth-weighted ice-free mean fluxes by the number of days between ice-off and 30 September and added 30% (CH₄) and 43% (CO₂) of the emission rate for each day between 30 September and ice-on. This late-season flux contributed about 5% (CH₄) and 8% (CO₂) to total ice-free emissions. Over the same autumn gap periods EC CH₄ fluxes at Villasjön (2012–2017) show a contribution of 4.3% (2.7–6.3%) to the total ice-free CH₄ flux.

Under-ice accumulation rates were estimated with a linear regression of the depth-integrated carbon gas storage (grams per square meter) onto time (Figures 3 and S1). We limited the analysis to periods when storage increased. We compared rates of CO_2 accumulation with those of underice oxygen consumption to assess the role of aerobic respiration in winter. Dissolved oxygen drawdown rates were estimated for each MiniDOT sensor with a linear regression of the concentration onto time, from ice-on to anoxia (i.e., the sensor detection limit, 0.1 mg·L⁻¹). The volumetric DO consumption rates of the sensors (two in each of the deeper lakes) were then averaged and divided by the lake mean depths to obtain rates. Exchange with the atmosphere during the ice-cover period was assumed to be negligible. Intense, continuous bubbling in winter can prevent water from freezing (Walter Anthony & Anthony, 2013), but no such seeps were observed in the Stordalen lakes.

The potential spring efflux was calculated as the difference between depth-integrated carbon gas storage before the onset of ice thaw and after complete ice-off (usually the first open water measurement in early June). The mean spring contribution to the annual flux was computed from multiyear mean values of the total ice-free fluxes (2010–2017) and the potential spring efflux (deeper lakes, 2015–2018). For Villasjön (CH₄) we used the longer EC data set (2012–2018) rather than manual measurements. We also computed the spring contribution in individual years by comparing the (potential) spring efflux with ice-free emission of the previous year.

2.11. Flux-Temperature Relationships

We used an empirical Arrhenius function to characterize the ice-free CH_4 flux-temperature relation:

$$F = e^{-E_a'/k_BT},\tag{4}$$

where F is the CH₄ flux in milligrams carbon per square meter per day, E_a' is the empirical activation energy in electron volts (1 Ev = 96 kJ·mol⁻¹), T is temperature in degrees Kelvin, k_B is the Boltzmann constant (8.62·10⁻⁵ eV·K⁻¹). Individual flux measurements of the bubble flux (2009–2017, n = 14,677) and turbulence-driven diffusive flux (2010–2017, n = 1,306) were binned (1 °C bins) according to mean surface sediment temperatures during bubble trap and chamber deployment periods in each lake. The activation energy was computed from the linear regression of the natural logarithm of the flux onto the inverse of the temperature (Figure S4). CO₂ fluxes computed with the boundary layer model (2015–2017, n = 129) were similarly binned according to surface sediment temperature (1 °C bins).

2.12. Stable Isotopic Composition of CH₄

In this study we use stable isotopes to distinguish between microbial CH_4 production and removal processes. There are two primary CH_4 production pathways that can be distinguished isotopically, using either acetate $(CH_3CO_2^-)$ or CO_2 and H_2 as substrate(s) (Whiticar, 1999):







Figure 3. Functional relationships of the CH₄ and CO₂ flux. (Left panels) Flux-temperature relationships of ice-free CH₄ diffusion (open circles) and ebullition (closed circles) and under-ice CH₄ accumulation rates (open triangle; means of the three lakes; a) and the ice-free CO₂ flux (circles) and under-ice CO₂ accumulation rates (triangles; c). No floating chamber measurements were available for bins $\geq 18^{\circ}$ C. R^{2} values refer to linear regressions used to derive the activation energy (shown in Figure S4) and *p* values test the significance of the slope coefficient. Ice-free fluxes in panels (a) and (c) were averaged into 1 °C bins. Error bars represent 95% confidence intervals of the binned means. (Right panels) Multiyear time series of volume-integrated CH₄ (b) and CO₂ (d) storage. Closed symbols represent increasing carbon gas content and these data were used to calculate the mean under-ice accumulation rate (solid lines in panels b and d; triangles in panels a and c). Open symbols represent decreased carbon gas content during the snowmelt, ice thaw, and ice-free periods. Dotted lines represent 95% confidence intervals of the linear regressions. Regression slopes were used to compute the accumulation rates (Table 3). Figure S1 shows for extended time series of CH₄, CO₂, and DIC.

$$CH_3CO_2^- + H_2O \rightarrow CH_4 + HCO_3^-$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O_3^-$$

In lakes that remain oxygenated throughout the ice-free season the majority of methane oxidation takes place via the energetically favorable aerobic oxidation pathway:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2$$

Alternative electron acceptors such as nitrate and sulfate can drive anaerobic methane oxidation in freshwater environments (Segarra et al., 2015), albeit at lower rates (Deutzmann & Schink, 2011). Because of the microbial preference for isotopically lighter substrates, net methane production generally leads to an isotopic depletion of the (aquatic) CH₄ pool, while net oxidation to CO₂ results in isotopic enrichment of the remaining CH₄ pool. This isotopic fractionation between precursor and product is thought to be distinct for each reaction, and pathway-specific isotopic signatures have been identified in laboratory and field experiments (Bastviken et al., 2002; Chanton et al., 2006; Whiticar, 1999). We corrected for the δ^2 H signature of precursor H₂O, which tends to be depleted at high-latitude sites (Chanton et al., 2006).

2.13. Isotope Fractionation Models

We used open and closed system isotope fractionation models (Bastviken et al., 2002) to compute the CH_4 fraction oxidized in summer and at ice-off, respectively. The open system model (Happell et al., 1994) is



only valid in steady state conditions and assumes equal rates of addition (production) and removal (evasion + oxidation):

$$f_{ox} = \left(\delta_{aq} - \delta_{sed}\right) / (\alpha - 1), \tag{5}$$

where the numerator represents the isotopic signature difference between sediment gas and aqueous CH₄ and α the fractionation factor, a measure of the microbial preference for lighter over heavier isotopologues (we assume $\alpha = 1.020$; Bastviken et al., 2002). We further assumed that fractionation due to transfer across the water-air interface was negligible ($\alpha \leq 1.001$; Whiticar, 1999). The oxidation rate (J_{ox}) was then calculated using the diffusive fluxes from floating chambers, F_{ch} (Bastviken et al., 2002):

$$J_{ox} = F_{ch} \times f_{ox} / (1 - f_{ox}). \tag{6}$$

In spring rapid evasion invalidates the steady state assumption, and we applied a closed system model, which describes a removal process acting at different rates on two constituents (e.g., the microbial preference for lighter over heavier isotopologues) of a single enclosed reservoir (e.g., a quantity of CH_4) (Liptay et al., 1998):

$$\ln\frac{R}{R_0} = (\alpha - 1)\ln\frac{C}{C_0},\tag{7}$$

where R/R_0 represents the ratio of final over initial isotope ratios, for example, $R(^{12}C/^{13}C)$, calculated here as $[\delta^{13}C_{june}/\delta^{13}C_{may}]$, and C/C_0 is the ratio of final over initial reservoir size (e.g., concentrations), equal to the fraction remaining after oxidation $(1-f_{ox})$. We can thus rewrite equation (7) as

$$f_{\alpha x} = 1 - \exp\left[\ln\frac{R}{R_0}/(\alpha - 1)\right].$$
(8)

A key assumption of the closed system model is that the reservoir is affected only by a single removal process with negligible external inputs. Though production was likely ongoing in spring, the marked CH₄ concentration decrease during ice-off indicated that removal rates far exceeded production rates. However, we could not easily distinguish between microbial and physical removal processes in spring. We therefore used the fraction oxidized (equation (8)) to estimate upper and lower limits of the quantity oxidized (C_{ox}). For the upper limit we assumed that microbial oxidation acted on the large reservoir prior to ice-off in May ($C_0 = C_{May}$ in equation (7) and computed $C_{ox,up} = f_{ox} \times C_{May}$. For the lower limit we assumed that the concentration in June represented the remaining fraction ($C = C_{June}$ in equation (7)) and that most CH₄ had been emitted before oxidation started ($C_0 < C_{May}$), using $C_{ox,low} = C_{June}/(1 - f_{ox})$. We assumed that the remainder ($C_{May} - (C_{ox} + C_{June})$) was emitted to the atmosphere without affecting δ^{13} C values.

2.14. Statistical Analysis

Uncertainties of seasonal total fluxes were calculated from the standard deviations of individual flux measurements using the delta method for propagation of errors (Rice, 2007). Uncertainties of multiyear means were calculated from annual totals. Comparisons between mean values were performed with an unpaired *t* test (for two groups) and analysis of variance (for more than two groups). A paired *t* test was used to assess the significance of the concentration changes in the bottle incubations. For the linear regressions we used the ordinary least squares method (OLS) and tested whether the slope was significantly different from zero using the standard error of the slope. All statistical tests used a significance level of 0.05. Statistical calculations were done with Paleontological Statistics software package (Hammer et al., 2001).

3. Results

3.1. Annual Budget and the Contribution of the Spring Efflux

The three lakes were sources of CH_4 and CO_2 to the atmosphere year-round. Ice-free CO_2 emissions were the largest component of the carbon flux—especially in stream-fed Mellersta Harrsjön. In the other two lakes, however, the radiative forcing of annual emissions of CH_4 was greater than that of CO_2 (100-year global



Table 2

Total Annual Emissions (Multiyear Means \pm SE) of CH₄ and CO₂ and the Relative Annual Contributions of Each Emission Pathway

| Total annual emissions | Villasjön | Inre Harrsjön | Mellersta Harrsjön |
|---|--------------------------|------------------|--------------------|
| CH_4 annual flux (g C·m ⁻² ·year ⁻¹) | 5.0 ± 0.8 | 3.7 ± 0.5 | 4.9 ± 1.0 |
| $CH_4 GWP^a (g CO_2 - C eq. m^{-2} year^{-1})$ | 170.6 ± 28.6 | 125.7 ± 18.5 | 166.3 ± 33.7 |
| % Diffusion (ice free) | 12 % (7–16) | 21 % (18–27) | 20 % (15–26) |
| % Ebullition (ice free) | 62 % (59–68) | 20 % (14–23) | 40 % (33–44) |
| % Storage (spring efflux) | 26 % (6–54) ^D | 59 % (46-71) | 40 % (20–67) |
| CO_2 annual flux (g C·m ⁻² ·year ⁻¹) | 78.0 ± 16.6 | 89.5 ± 17.7 | 261.3 ± 24.0 |
| % Diffusion (ice free) | 85 % (78–94) | 70 % (67–73) | 82 % (73–88) |
| % Storage (spring efflux) | 15 % (6–22) | 30 % (27-33) | 18 % (12–27) |

Note. Estimates are multiyear means. Ranges of individual years are given in parentheses. The contribution of the spring efflux was computed as a percentage of the total flux that includes the ice-free season of the previous year. GWP is the global warming potential.

^aThe long-term radiative forcing effect of emitted CH_4 was estimated by converting into CO_2 -equivalent emissions, assuming a 34 times greater GWP for CH_4 over a 100-year time scale (Myhre et al., 2013). ^bEddy covariance observations were used to compute the spring efflux contribution in Villasjön.

warming potential; Table 2). Annual CH_4 emissions were highest in Villasjön and Mellersta Harrsjön and lowest in Inre Harrsjön. About two thirds of open water CH_4 emissions occurred via the ebullition pathway (Table 2). Bubbling was observed in all depth zones and was most important in the two high-emitting lakes (Figure 2). In winter the upper estimate of the under-ice bubble flux was lower than the estimated CH_4 accumulation rates in the water column (Table 3).

The contribution of the spring efflux to the annual flux was significant in all three lakes (Figure 2; Table 2). In shallow Villasjön the multiyear mean spring contribution was 15% for CO_2 (manual observations) and 26% for CH_4 (EC). The potential spring contribution in the two deeper lakes was larger for both CO_2 (18–30%) and CH_4 (40–59%). The latter number could be as high as 66–71% if ice-trapped bubbles were included (upper estimates in Table 3), but this quantity is highly uncertain because bubble CH_4 concentrations and volumes are unknown (Wik et al., 2011). We found that the (potential) spring CH_4 efflux could exceed multiyear mean ice-free emissions in Villasjön (in one out of five measurement years), Inre Harrsjön (three out of four), and Mellersta Harrsjön (two out of four).

3.2. Relationships With Environmental Covariates

Under-ice CH₄ accumulation rates ($25 \pm 2 \text{ mg CH}_4\text{-}\text{C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, mean \pm SE; Figure 3b) were higher than the 9-year three-lake mean ice-free flux ($19 \pm 1 \text{ mg CH}_4\text{-}\text{C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, ebullition plus diffusion; unpaired *t* test, *p* < 0.01). This seasonal difference was greatest in the deeper lakes (Table 3). Moreover, while ice-free CH₄ emissions were strongly correlated with sediment temperature and closely fitted an Arrhenius function,

Table 3

| Multiyear Mean Rates of Lake CH ₄ and CO ₂ Emission, Removal, and Under-ice Accumulation | | | | | | | |
|--|----------------------------------|-----------------|--------------------|----------------|--------------------|--|--|
| Rates (mg $C \cdot m^{-2} \cdot day^{-1}$) | | Sampling years | Villasjön | Inre Harrsjön | Mellersta Harrsjön | | |
| CH ₄ | | | | | | | |
| Ice free | Ebullition | 2009-2017 | 21.2 ± 2.6 | 5.3 ± 0.8 | 13.7 ± 1.8 | | |
| | Diffusion | 2010-2017 | 4.4 ± 0.8 | 5.0 ± 0.3 | 6.0 ± 0.5 | | |
| | Oxidation | 2015-2017 | -1.2 ± 0.1 | -7.3 ± 0.6 | -10.7 ± 0.8 | | |
| Ice cover | Ice-trapped bubbles ^a | 2009 | 1.8 | 0.8 -7.5 | 1.4 - 19.0 | | |
| | Under-ice accumulation | 2009, 2015-2018 | 17.8 ± 6.9^{b} | 23.0 ± 2.7 | 21.3 ± 2.0 | | |
| CO ₂ | | | | | | | |
| Ice free | Diffusion | 2015-2017 | 458 ± 68 | 446 ± 113 | 1,485 ± 47 | | |
| Ice cover | Under-ice accumulation | 2015-2018 | 94 ± 34 | 107 ± 20 | 149 ± 21 | | |
| DIC | | | | | | | |
| Ice cover | Under-ice accumulation | 2015-2018 | 132 ± 50 | 226 ± 31 | 252 ± 40 | | |

Note. Comparison between multiyear ice-free and ice-cover seasons (mean \pm SE). The summer CH₄ oxidation rate was calculated as the oxidized fraction of the multiyear mean turbulence-driven diffusive flux (equation (6)).

^aRange represents upper and lower limits of the ice-trapped bubble accumulation rate (see section 2.9). ^bData available for 2015–2016 only.





Figure 4. Seasonal evolution of CH₄ (a) and CO₂ (b) storage, O₂ saturation (c) δ^{13} C-CH₄ (d), and water temperature (e–g). (a and b) In the deeper lakes the lake mean storage (solid lines) was calculated from samples collected at 1-m intervals at the deepest location (representative of the profundal zone: ≥ 2 -m depth) and in the shallows (plotted separately as dotted lines, representative of the littoral zone: ≤ 2 -m depth). Error bars are smaller than symbol sizes. (c) Dissolved oxygen saturation from MiniDOT probes deployed 0.5 m above the sediment surface (solid lines) and 1.5 m below the water surface (dashed lines). No sensors were deployed in Villasjön and in Inre Harrsjön in summer 2016. (d) δ^{13} C of aqueous CH₄. Squares on the left represent the sediment bubble signature. Error bars represent the standard error of the mean. Shaded areas in panels (a)–(d) represent snowmelt events (solid dark gray) and the ice-cover period—from ice-on to the start of ice-off (solid light gray) via thaw (dashed light gray) to the first overturn (dashed black). (e–g) Water temperatures from HOBO sensors with 0 °C isotherm (dotted line) and ice cover thickness (solid line) in Villasjön (e), Inre Harrsjön (f), and Mellersta Harrsjön (g). Temperatures between March and June 2017 are from the MiniDOT probes. Dots on the depth axes indicate sensor deployment depths.

under-ice accumulation rates far exceeded the predicted ice-free flux at 0–4 °C (triangle vs. yellow line in Figure 3a). Conversely, under-ice CO_2 accumulation rates were consistent with the ice-free flux-temperature relationships (Figure 3c) and did not exceed mean ice-free fluxes (Table 3). In contrast to the ice-free CH_4 fluxes, which were highest in the shallow lake and depth zones, we measured the largest under-ice carbon gas quantities in the deeper lakes and depth zones (Figure 2).

Seasonal changes in carbon gas storage paralleled those of dissolved oxygen. The deeper lakes Inre and Mellersta Harrsjön were oxygenated in summer and stratified and oxygen-depleted for most of the ice-cover period, starting with the hypolimnion in December (Figures 4c, 4f, and 4g). Over a 2-month transition period, the buildup of CO₂ and CH₄ tracked the upward migration of the oxycline from the sediment to the ice-water interface (Figure S2). The increase of CH₄ storage during the anoxic period was linear (OLS; $R^2 \ge 0.90$, $p \le 0.01$; Figure 3b), and the accumulation rate did not vary significantly between years (analysis of variance; $p \ge 0.20$, n = 3). Under-ice inorganic carbon accumulation showed a different pattern (Figure 3d). Initially, CO₂ accumulation rates mirrored the O₂ consumption rate (10.9 ± 0.9 mmol CO₂·m⁻²·day⁻¹; -10.6 ± 1.5 mmol O₂·m⁻²·d⁻¹, mean ± SE) but slowed in February when O₂ levels dropped below 0.1 mg·L⁻¹





Figure 5. Concentrations of aqueous CH_4 (left panels) and dissolved inorganic carbon (DIC; right panels) in lake water (solid lines) and in situ incubated bottles (dotted lines) in Inre Harrsjön (top panels) and Mellersta Harrsjön (bottom panels). Final bottle concentrations (12 May 2017) are three-bottle means; data labels represent the concentration change. The lake water concentrations were extrapolated from 12 May 2017 to approximate ice-out on 1 June 2017 (dashed lines).

(Figures 4b and 4c). However, the total depth-integrated amount of DIC accumulated under ice in Inre Harrsjön (2.7–3.0 mol·m⁻² DIC) and Mellersta Harrsjön (2.8–4.1 mol·m⁻² DIC) exceeded the amount of dissolved oxygen available at ice-on (0.8–0.9 mol·m⁻² O₂), while DIC production from acetoclastic methanogenesis was negligible (<0.2 mol·m⁻² DIC).

3.3. Seasonal Dynamics of Carbon Gas Production and Removal

Using CH₄ stable isotopes, we can qualitatively assess how these seasonally distinct oxygen regimes affected CH₄ storage. With equation (5) we estimated that in the open water season, $24 \pm 10\%$ of the aquatic CH₄ pool was oxidized in Villasjön and $62 \pm 5\%$ and $64 \pm 8\%$ in Inre and Mellersta Harrsjön, respectively (mean \pm SE). In spring, between May and June, an isotopic enrichment of CH₄ accompanied reoxygenation and the concentration decrease in the deeper lakes (Figures 3a and 3d). With equations (7) and (8) we computed a lower limit of the fraction oxidized ($f_{ox} = C_{ox,low}/C_{May}$) at $4 \pm 2\%$, and an upper limit ($f_{ox} = C_{ox,up}/C_{May}$) at $36 \pm 17\%$ (mean \pm SE) in the deeper lakes, lower than values obtained there in summer. Ice-free CH₄ oxidation rates were about an order of magnitude lower than CO₂ accumulation rates (Table 3).

The isotopic composition of CH₄ in sediment gas bubbles was similar in summer ($\delta^{13}C = -70 \pm 8\%$, $\delta^{2}H = -308 \pm 43\%$) and winter ($\delta^{13}C = -68 \pm 6\%$, $\delta^{2}H = -301 \pm 12\%$). The signature fell within the approximate range of the acetoclastic methanogenesis pathway; $\delta^{13}C = -80$ to -40%, $\delta^{2}H = -400$ to -275% (Whiticar, 1999), corrected for the H₂ precursor effect assuming 1/4th of CH₄ hydrogen was derived from lake water ($\delta^{2}H$ -H₂O = -93.1 \pm 1.1\%) and 3/4th from the methyl group in acetate (Whiticar et al., 1986; Figure 6). CH₄ in the water column was isotopically enriched compared to the sediment bubbles, except in April in the deeper lakes (Figures 4d and 6).

In situ incubations did not yield evidence of net methanogenesis in the anoxic water column (Figure 5). Instead, bottle CH₄ concentrations decreased 1–30% over the deployment period. DIC increased 6–18% but did not exceed DIC buildup in the water column over the same period. All concentration changes were statistically significant (paired *t* test, p < 0.05) and were most pronounced in the incubations with hypolimnetic water. Neither CO₂ nor CH₄ was detected in the bottles used as blanks.



3.4. Interannual Variability of the Spring Efflux

The quantity of carbon gas accumulated under ice scaled predictably with days after ice-on (closed symbols in Figures 3b and 3d), and storage peaked in years with a longer ice-cover season as a result. However, concentrations of both CH_4 and CO_2 could decrease during the snowmelt and ice thaw periods prior to the spring overturn (open symbols in Figures 3b and 3d). Similarly, the oxygen and temperature sensors in the deeper lakes showed that reoxygenation at the ice-water interface and breakup of stratification could occur well before ice-off and after snowmelt events (dark gray bars, Figures 4c and 4e–4g). The concentration decreases started in the shallow zones and were most pronounced in Villasjön and in Mellersta Harrsjön when the stream and shores were ice-free (e.g., in May 2016; Figures 4a, 4b, and S2). Unlike the constant accumulation rates the concentration decreases did not recur consistently each year.

Multiyear eddy covariance measurements of CH₄ emissions from shallow lake Villasjön (2012–2018) showed substantial variability in the spring efflux (Figure 7b); it varied an order of magnitude between years $(0.2-2.5 \text{ g CH}_4\text{-}C\cdot\text{m}^{-2}\cdot\text{year}^{-1}, n = 5)$ and contributed between 6% and 54% of annual emissions (Table 2). In years with a reduced spring efflux (2016, 2017), CH₄ and CO₂ concentrations below the ice decreased before ice-off, and similar to the deeper lakes this decrease occurred after periods of extensive snowmelt (Figures 4a and 4b). Conversely, the highest spring CH₄ emissions in the Villasjön EC dataset (2013 and 2018) were preceded by single snowmelt events (Figure 7c). We tested whether the magnitude of the Villasjön spring efflux could be predicted from the length of the preceding ice-cover season, but we found no significant correlation (OLS; $R^2 = 0.09$, p = 0.62). Instead, spring emissions appeared to be negatively correlated with the total EC CH₄ flux of the preceding ice-free season (OLS; $R^2 = 0.55$, p = 0.15) and the number of snowmelt events in the preceding winter (OLS; $R^2 = 0.77$, p = 0.05).

4. Discussion

Our multiyear measurements revealed distinct environmental drivers for CH_4 and CO_2 cycling during icefree and ice-cover periods. In the following sections we discuss the seasonal controls on lake carbon cycling processes and the patterns of storage and flux variability that emerge from them.

4.1. Controls on Ice-Free Carbon Gas Emissions

Thermal energy input is a potential master proxy of ice-free lake CH_4 emissions (Aben et al., 2017; Thornton et al., 2015). Empirical activation energies were 1.00 ± 0.17 eV for diffusion, similar to ecosystem-level estimates for wetlands and aquatic environments (0.96 ± 0.10 eV) (Yvon-Durocher et al., 2014) and 1.37 ± 0.10 eV for ebullition (mean \pm 95% confidence interval). Ebullition rates were highest in shallow Villasjön and the littoral areas of Mellersta Harrsjön (Figure 2), perhaps because a larger fraction of insolation reaching the bottom led to warmer sediments in shallow (≤ 2 m) compared to deeper zones (Bastviken et al., 2008; Wik et al., 2013), and/or because of more labile carbon input from macrophytes (Marinho et al., 2015) and runoff (Olefeldt & Roulet, 2012).

Compared to CH_4 , ice-free CO_2 emissions were not strongly coupled to temperature-dependent biotic processes (Figures 3a and 3c). This suggests that the CO_2 emissions were largely driven by terrestrial dissolved organic carbon (DOC) export from the Mire into the lakes (estimated at 7.0–8.1 g DOC-C·m⁻²·year⁻¹ from the fen into the stream feeding Mellersta Harrsjön; Olefeldt & Roulet, 2012) or external inputs of inorganic carbon (Maberly et al., 2012; Weyhenmeyer et al., 2015). Indeed, elevated emissions in stream-fed lake Mellersta Harrsjön coincided with a lower pH (Table 1) and higher CO_2 concentrations in the stream feeding the Mire compared to the lakes (Lundin et al., 2013).

4.2. Controls on Under-ice Carbon Gas Production, Removal, and Storage

Carbon gas storage increased with the length of the ice-cover season (Figure 3b), indicative of continuous production or release from sediment storage. The lack of methanogenesis in the water column, as shown by the in situ incubations (Figure 5), indicates that the sediment was an active source of CH_4 throughout the ice-cover period. This notion was further supported by an increase of $113 \pm 19\%$ (mean \pm SE) in ice bubble area between October and April 2009 (Wik et al., 2011). However, whereas in summer ebullition was higher in the shallows (Wik et al., 2013), the ice bubble surveys showed no significant difference in bubble coverage between depth zones (Wik et al., 2011).





Figure 6. Co-isotope plot of CH_4 stable isotopologues of water column aqueous CH_4 in winter (n = 77, dots) and of sediment gas samples in winter (n = 14, black triangles) and in summer (n = 37, gray triangles). Blue and green areas mark the approximate signature ranges of different production pathways as defined in (Whiticar, 1999; dotted lines) and corrected for the depleted signature of precursor H_2 (filled areas), assuming lake water contributes 100% of the hydrogen in CH_4 generated via the carbonate reduction pathway, and 25% in CH_4 formed through acetate fermentation. Depth profiles of CH_4 stable isotopologues are shown in Figure S2.

Under-ice carbon gas accumulation concentrated in the deeper areas of the lakes where surface CH_4 emissions were lowest in summer (Figure 2). This pattern may have resulted from redistribution by respiration-driven density currents, which can occur when addition of heat and mineralization products to waters near the sediment in the productive littoral zones increases its density and initiates a downslope flow (MacIntyre et al., 2018; Mortimer & Mackereth, 1958). Under-ice circulation could also explain why DIC accumulation rates exceeded respiration rates in the in situ incubations and why the difference was greatest in the hypolimnion (Figure 5).

More CO₂ can accumulate in deeper than in shallow lakes (Figure 2; Ducharme-Riel et al., 2015; Karlsson et al., 2013) due to a greater watercolumn integrated quantity of available electron acceptors. We found that only 25–30% of accumulated inorganic carbon could be explained by O₂ consumption, corresponding to a respiratory quotient (Δ DIC/ Δ O₂) of 3.3–4.0. A value of 0.85 would be expected for aerobic respiration (Wetzel & Likens, 2000). Such excess DIC production is generally assumed to be accounted for by anaerobic respiration (Mattson & Likens, 1993; Rich & Wetzel, 1978). Here, an odor of hydrogen sulfide in water samples from >3-m depth (March and April) pointed to sulfate reduction, but other electron sinks, such as organic matter, could also have supported anaerobic decomposition (Mattson & Likens, 1993;

Wilson et al., 2017). Active anaerobic metabolism, including anaerobic oxidation of methane, is not uncommon in ice-covered lakes (Kankaala et al., 2006; Rich, 1979; Wand et al., 2006) and could explain the accumulation of DIC and decrease of CH_4 in the in situ incubations.

Aspects of the lakes' seasonal redox dynamics remain poorly understood. After ice-on CH_4 in the water column was highly enriched with heavy isotopes (Figures 6 and S2) compared to the ice-free season (Figure 2d), which indicates CH_4 removal by methanotrophs. While this result corroborates reports of elevated relative abundance, biomass, and activity of aerobic methanotrophs at low temperatures in ice-covered lakes (Samad & Bertilsson, 2017; Sundh et al., 2005), the biogeochemical conditions that enable this peak have not been identified. It also remains unclear why microbial activity appears to be elevated in the anoxic bottom waters (bottle incubations; Figure 5).

4.3. Enhanced Carbon Gas Production Under Ice?

The temperature proxy based on ice-free CH₄ emissions greatly underestimated under-ice CH₄ accumulation rates calculated from storage (Figures 3a and 3b). Moreover, the abundance of ice-trapped bubbles (Wik et al., 2011) suggests a resurgence of bubbling in winter after minimal emission rates in the fall (Jammet et al., 2015; Wik et al., 2013). Low winter methanogenesis rates could have been compensated by reduced methanotrophy in the O₂-limited redox regime (Bastviken et al., 2008; Denfeld et al., 2016; Huttunen et al., 2003; Juutinen et al., 2009). While the gradual isotopic depletion of CH₄ in winter indeed suggests that gas mixed in from the sediment was not significantly affected by oxidation (Figure 6), an absence of oxidation would account for <78% of the below-ice CH₄ buildup rate, and only if we assume diffusion continued at summer rates (F_{ch}+|J_{ox}lin Table 3). CH₄ from bubbles trapped at the base of the ice will diffuse back into the water column (Greene et al., 2014), but this effect is limited to the ice-water interface due to the slowness of diffusive transport and cannot explain elevated CH₄ concentrations at greater depth (Figure S2). Accumulation rates of CO_2 under ice (94–149 mg CO_2 -C·m⁻²·day⁻¹; Table 3) were higher than those reported for oligotrophic arctic lakes of similar size (<50 mg CO₂-C·m⁻²·day⁻¹; MacIntyre et al., 2018) and larger, mesotrophic boreal and temperate lakes (13-86 mg CO₂-C·m⁻²·day⁻¹; Ducharme-Riel et al., 2015). Consequently, processes unique to the ice-cover season may have increased carbon mineralization rates.

Enhanced production of CH_4 and CO_2 under ice could result from thermal inertia of the lake sediments (Golosov & Kirillin, 2010), especially deeper in the lakebed where the sediment is cohesive enough for



bubble formation (Scandella et al., 2011). Furthermore, fresh detritus from aquatic plants may have contributed to elevated rates of aerobic respiration and methanogenesis (Marinho et al., 2015). The main CH₄ production pathway in the lake sediments suggested by the isotope analysis, acetoclastic methanogenesis (Figure 6), has been associated with inputs of easily degradable organic carbon (Hodgkins et al., 2014; McCalley et al., 2014; Schulz & Conrad, 1995) and the C:N ratio of organic carbon in the lake sediments matched that of aquatic vegetation (Wik et al., 2018). In late winter the contribution of acetoclastic methanogenesis appeared to be higher in aqueous CH_4 (deeper lake hypolimnion) than in sediment gas bubbles (Figures 6 and S2). Dieback of macrophytes in the fall and subsequent degradation under ice could provide a surplus of fresh organic substrate that drives diagenesis as well as the rapid drawdown of O_2 after ice-on. The least-degraded material sits at the sediment surface, where rates of methanogenesis are highest (Borrel et al., 2011). We therefore hypothesize that in winter, anoxic bottom waters allow the CH₄ production zone to migrate closer to the sediment-water interface, increasing methanogenesis rates.

4.4. The Impact of Snowmelt Events on the Spring Efflux

Interannual variability of the spring efflux emerged from two distinct factors. While under-ice carbon gas storage scaled with ice-cover season length (Figures 3b and 3d), the Villasjön EC data suggest that the fraction of stored carbon emitted in spring was linked to snowmelt events (Figure 7c; section 3.4).

Snowmelt affects under-ice carbon gas storage in different ways. A buoyant meltwater plume will either displace some of the near-surface water (Cortés et al., 2017) and transport stored carbon out of the lake and/or introduce oxygen which, when mixed downward, enables microbial oxidation of the accumulated substrate. Both processes could reduce the spring CH_4 efflux. Contrastingly, in boreal lakes rapid increases in pelagic DOC, DIC, and CH_4 concentrations after snowmelt have been attributed to terrestrial inputs and could dominate the spring efflux (Denfeld, Klaus, et al., 2018; Miettinen et al., 2015). In snow-covered peatlands such as the Stordalen Mire carbon degradation and emission continue in winter (Jammet et al., 2017; Melloh & Crill, 1996), and annual peaks of DOC export accompany snowmelt events (Finlay et al., 2006; Olefeldt & Roulet, 2012). Timing is important; winter melt can mobilize concentrated solutes via subsurface flow, but spring discharges occur also via surface runoff and can have both a mobilizing and a diluting effect (Laudon et al., 2007).

On the Stordalen Mire runoff enters the lakes through streams and fens (Olefeldt & Roulet, 2012) that remain partially unfrozen in winter under an insulating snow cover (Figure 7a). Most of the snowmelt occurred at the end of the ice-cover season (Figure 7a), and dilution and/or advection appeared to be the primary result. Though we observed some isotopic enrichment of CH_4 associated with reoxygenation in spring (Figures 4c and 4d), the calculated fraction oxidized was lower than in summer. Our findings corroborate low fractions oxidized ($f_{ox} = 7\%$) observed after ice-out in temperate lakes by Michmerhuizen et al. (1996; in situ incubations), and could be explained by slow initial growth of methanotroph communities (Krüger et al., 2008). A simultaneous decrease in CO_2 concentrations and the lack of CH_4 isotopic enrichment in Villasjön further support the notion that transport processes, such as meltwater advection or emission via thawed shore areas and ice cracks, were the main drivers of carbon gas depletion following extensive snowmelt.

While our results show order of magnitude variability of the spring efflux between years, it may be more consistent in lakes less affected by snowmelt. In deeper and hydrologically isolated lakes (such as Inre Harrsjön), ice-cover season length could be an accurate proxy, but longer time series are needed to evaluate this hypothesis. Differences in land cover type could explain some of the local and regional variability of late-winter carbon gas storage (Juutinen et al., 2009; Sepulveda-Jauregui et al., 2015). For example, spring under-ice CH_4 storage can be substantially lower in lakes situated in forest versus mire-dominated parts of the catchment (Denfeld, Klaus, et al., 2018; Karlsson et al., 2013), possibly because more snow accumulating in sheltered forests (Larsen et al., 2007) results in greater runoff volumes. Villasjön may be particularly sensitive to snowmelt, as it is bordered by birch forest upstream (Lundin et al., 2016) that could retain a deep snowpack. More work is needed to identify relations between catchment hydrology and cold season carbon gas emissions, and the fate of the advected gas.

4.5. Method Validation and Bias

 CH_4 fluxes obtained with the EC technique closely matched the quantity and timing of manually measured emissions on daily (Figure 7d), seasonal (Figure 7b), and interannual time scales (Figure 2; Jammet et al.,



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Figure 7. Time series of local meteorology of the Stordalen Mire (a) and CH_4 flux measurements in Villasjön (b–d). (a) Snow depth (black line) and air temperature (blue area) at the Stordalen ICOS site (Figure 1). The dark blue line shows the peat temperature at 25-cm depth (T107 temperature probe (Campbell Scientific) 3 m from the EC tower). (b) Comparison between total CH_4 fluxes from manual measurements (bubble traps, floating chambers, and under-ice storage) and the eddy covariance system. Ice-free totals were calculated from gap-filled daily means and integrated over the manual flux measurement period (green areas). Error bars show the standard error (manual observations) and the gap-filling bias (eddy covariance), which was largest for seasons with low data coverage (labels). (c and d) half-hourly and daily mean eddy covariance fluxes (small and large green triangles, respectively), daily mean bubble fluxes (red line). Panel (d) zooms in to the period April–November 2016 on panel (c). The ice-cover and thaw periods are marked by solid and dashed light gray areas, respectively. Dark gray areas represent snowmelt events (air temperatures above 0 °C and a decrease in the snow depth). Black lines (c) and the dashed black area (d) mark the spring overturn and the start of the ice-free season.

2017). Even though the mean ice-free season EC data coverage was limited to 21% of half-hourly fluxes (2012–2017), the robust flux-temperature relationship (Figure S3) made the gap-filling method sufficiently accurate. While both EC observations and manual measurements indicate a reduced spring efflux in 2016 and 2017 (Figure 7b), additional parallel observations during a high efflux event would be needed to test and improve the gap-filling method used for this time of year.

Carbon gas concentrations and fluxes can peak at nighttime if wind speeds are low throughout the day (Czikowsky et al., 2018; Liu et al., 2016; Natchimuthu et al., 2017). While our 24-hr chamber deployments captured this diel variability for CH_4 , we may have underestimated ice-free CO_2 emissions by taking daytime water samples only, in which case we overstated the annual importance of the CO_2 spring efflux.

5. Summary and Implications

In this study we used an extensive multiyear data set to evaluate ice-free emissions, winter under-ice accumulation, and the spring efflux of CH_4 and CO_2 from three subarctic lakes. We found that spring emissions can contribute significantly to the annual flux and are not regulated by the same biogeochemical drivers that



govern ice-free emissions. While temperature and external carbon inputs controlled emissions in summer, winter accumulation was in part regulated by the availability of oxygen and other electron acceptors, and by the length of the ice-cover season. The substantial interannual variability of the spring efflux from shallow waters was associated with snowmelt events through the process of meltwater advection or dilution under ice.

Synthesis studies suggest that the mean spring contribution in seasonally ice-covered lakes (45–75°N) is \leq 27% for CH₄ and 17% for CO₂ (Denfeld, Baulch, et al., 2018; Wik et al., 2016). This is lower than the 40–59% (CH₄) and 18–30% (CO₂) we observed in the deeper lakes and the 37–54% (CH₄) observed at Villasjön with the EC technique in years minimally affected by snowmelt (2013, 2018). Previous studies may have underestimated carbon emissions at and immediately following ice-off if only surface gas concentrations are considered and hypolimnetic or ice reservoirs are neglected. Because carbon gas storage increased with ice-cover duration (Figures 3b and 3d) differences with previous studies can partly be explained by the longer winter at our high-latitude study site (Walsh et al., 1998). Indeed, the contribution of the spring efflux appears to be higher in the Arctic compared to boreal and temperate regions (Denfeld, Baulch, et al., 2018; Huttunen et al., 2003; Juutinen et al., 2009; Michmerhuizen et al., 1996; Sepulveda-Jauregui et al., 2015; Zimov et al., 1997).

Postglacial lakes comprise approximately 80% of northern lake surface area >50°N (Wik et al., 2016); therefore, our findings could be representative of a majority of northern lakes. Like Inre and Mellersta Harrsjön, the vast majority of lakes are small (\leq 0.1 km²) but deep enough to maintain an unfrozen hypolimnion (\leq 2.6-m mean depth; Cael et al., 2017), and north of 50°N, these lakes are ice-covered for more than 5 months of the year (Walsh et al., 1998). Small lakes such as the ones studied here tend to be more susceptible to anoxia (Deshpande et al., 2015) and could, collectively, emit more CH₄ in spring than larger, deeper lakes that remain partially oxygenated (Ducharme-Riel et al., 2015; Juutinen et al., 2009; Michmerhuizen et al., 1996). Winter anoxia prevailed in surveys of 200+ Finnish boreal (Juutinen et al., 2009) and 40 Alaskan lakes (Sepulveda-Jauregui et al., 2015) and was common even in oligotrophic and mesotrophic systems. The widespread drawdown of oxygen implies that spring CH₄ emissions are significant on an annual basis throughout the Arctic today. Annual spring contributions of more than 40% (Table 2) may not be exceptional. The most recent CH₄ emission estimate for northern lakes (Wik et al., 2016), 12.4 ± 6.9 Tg CH₄-C·year⁻¹ (mean ± 0.5 interquartile range), which assumes a spring contribution of 23%, should therefore be considered conservative. Instead, our results support the implicit assumption made in global upscaling efforts (Bastviken et al., 2011; DelSontro et al., 2018) that net sedimentary CH₄ production under ice continues at ice-free rates.

Future carbon gas emissions from seasonally ice-covered lakes cannot be predicted from ice-free parameterizations alone. Current Arctic warming has opposing effects on winter and summer drivers of the flux; higher temperatures and longer ice-free seasons will likely increase CH_4 emissions in summer (Thornton et al., 2015) while shorter ice-cover periods (Prowse et al., 2011) and more frequent winter warming events (Graham et al., 2017) may reduce emissions in spring. Recurring snowmelt can transport more carbon gas out of lentic systems to evade downstream and, when oxygen is introduced and mixed downward, reduce the fraction of carbon emitted as CH_4 . While more work is needed to quantify this potential offset, the exponential temperature-sensitivity of freshwater organic matter cycling is likely to drive substantial increases in total carbon emissions (Figure 3a; Davidson et al., 2018; DelSontro et al., 2018; Yvon-Durocher et al., 2017) that ultimately accelerate climate change.

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Acknowledgments

This work was funded by the Swedish Research Council (VR) with grants to P. Crill (2007-4547 and 2013-5562), the DEFROST Nordic Center of Excellence under the Nordic Top-Level Research Initiative, the European Commission Seventh Framework Programme project PAGE21 (ref. 282700), and by the Danish National Research Foundation (CENPERM DNRF100). Contributions of S. MacIntvre and A. Cortés were funded by the U.S. National Science Foundation Arctic Natural Sciences Grants 1204267 and 1737411. The authors declare no competing financial interests. We thank the staff at the Abisko Scientific Research Station (ANS) and H. Siegmund of the Stockholm University Stable Isotope Lab (SIL) for logistic and technical support, and our field assistants for their help in the field. We thank H. Crill and J. Melack for valuable comments on the manuscript. Eddy covariance observations can be obtained via www.europe-fluxdata.eu (site SE-St-1), and manually collected and auxiliary data are available at the Bolin Centre website (www.bolin.su.se/ data/).



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