Methane and carbon dioxide emissions from thermokarst lakes on mineral soils

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Abstract: Thermokarst lakes are known to emit methane (CH₄) and carbon dioxide (CO₂), but little attention has been given to those formed from the thawing and collapse of lithalsas, ice-rich mineral soil mounds that occur in permafrost landscapes. The present study was undertaken to assess greenhouse gas stocks and fluxes in eight lithalsa lakes across a 200 km gradient of permafrost degradation in subarctic Québec. The northernmost lakes varied in their surface-water CO₂ content from below to above saturation, but the southern lakes in this gradient had much higher surface concentrations that were well above air-equilibrium. Surface-water CH₄ concentrations were at least an order of magnitude above air-equilibrium values at all sites, and the diffusive fluxes of both gases increased from north to south. Methane oxidation in the surface waters from a northern lake was only 10% of the emission rate, but at the southern end it was around 60% of the efflux to the atmosphere, indicating that methanotrophy can play a substantive role in reducing net emissions. Overall, our observations show that lithalsa lakes can begin emitting CH₄ and CO₂ soon after they form, with effluxes of both gases that persist and increase as the permafrost continues to warm and erode.

Key words: lithalsa, methane, permafrost, subarctic, thermokarst.

Résumé : Il est bien connu que les mares de thermokarst émettent du méthane (CH₄) et du dioxyde de carbone (CO₂), mais peu d’attention a été accordée jusqu’à présent à celles formées à la suite du dégel et de l’effondrement des lithalses, ces buttes minérales de sol riches en glace et présentes dans les paysages de pergélisol. La présente étude a pour objectif d’évaluer les stocks et les flux de gaz à effet de serre dans huit mares de lithalses sur un gradient de 200 km de dégradation du pergélisol dans le Québec subarctique. Les mares les plus septentrionales présentaient une teneur en CO₂ de surface inférieure ou supérieure à la saturation, alors que les lacs du sud présentaient des concentrations en surface beaucoup plus élevées, bien au-dessus de l’équilibre atmosphérique. Les concentrations de CH₄ dans les eaux de surface étaient au moins d’un ordre de grandeur au-dessus des valeurs d’équilibre à tous les sites, et les flux d’émission diffusive des deux gaz augmentaient du nord au sud. Le taux d’oxydation du CH₄ dans les eaux de surface d’une mare située au nord représentait seulement 10 % du taux d’émission, alors qu’à l’extrémité sud, il atteignait environ 60 % des émissions vers l’atmosphère. Ces résultats indiquent que la méthanotrophie peut jouer un rôle important dans la réduction des émissions nettes de CH₄. Dans l’ensemble, nos observations montrent que dans les mares de lithalses, le...
CH$_4$ et le CO$_2$ pourraient être émis vers l’atmosphère peu après leur formation, à des taux qui persistent et augmentent à mesure que les lacs continuent à se réchauffer et à s’éroder.

Mots-clés : lithalsa, méthane, pergélisol, subarctique, thermokarst.

Introduction

Lakes and ponds in permafrost landscapes are known to be emission sources of greenhouse gases (GHG) to the atmosphere (Tan and Zhuang 2015; Holgerson and Raymond 2016), with potentially large feedback effects on global climate (Kokelj and Jorgenson 2013; Grosse et al. 2016). Zimov et al. (1997) drew attention to the strong output of CH$_4$ from lakes in Siberia formed by thawing and collapse of ice-rich permafrost (thermokarst), and concluded that the CH$_4$ was largely derived from ancient organic carbon that had been previously stored in the frozen soils. Subsequent research suggested that this process may have accelerated the deglaciation during the early Holocene (Walter et al. 2006). A synthesis of data from boreal and Arctic lakes noted that two-thirds of the total CH$_4$ emissions from landscapes north of latitude 50°N is derived from freshwater systems, with thermokarst lakes contributing about 25% of that total (Wik et al. 2016). A constraint in defining the error in such estimates, however, is the poorly known extent of local and regional variability in GHG fluxes, with large variations among thermokarst lakes (Laurion et al. 2010; Sepulveda-Jauregui et al. 2015; Vonk et al. 2015).

Another major source of variability in GHG emissions from thermokarst lakes is that associated with landscape evolution (He et al. 2012; Allan et al. 2014; Lipson et al. 2015; Grosse et al. 2016). Fluxes of CH$_4$ to the atmosphere are thought to be especially high in newly degrading permafrost soils (Kanevskiy et al. 2014; Elvert et al. 2016), with older lakes succumbing to drainage (van Huissteden et al. 2011; Grosse et al. 2013), thereby eliminating the habitat for aquatic methanogens. Thermokarst lakes can also be subject to infilling by sediment and fen/bog vegetation, which may cause such lakes to become net sinks of carbon (Payette et al. 2004; Bouchard et al. 2017). However, the exact trajectory of geomorphological change and the associated biogeochemical effects remain uncertain in many regions of permafrost thaw and degradation.

In the subarctic region of northern Québec, Canada, two types of landscape contain permafrost mounds and associated thermokarst lakes (Allard and Seguin 1987). First, palsa landscapes occur in organic-rich peatlands, with uplifted ice-cored mounds of frozen Sphagnum and thermokarst lakes created by their permafrost thawing and collapse. The thermokarst lakes associated with palsas (hereafter, palsa lakes) are typically dark-coloured because of elevated concentrations of coloured dissolved organic matter (CDOM). Sunlight is strongly absorbed in their near-surface waters, and the lakes are highly stratified with anoxic conditions through most of the water column and during most of the year (Deshpande et al. 2017). These low or zero oxygen (O$_2$) environments are conducive to methanogenesis, and palsa lakes have strong emissions of both CH$_4$ and CO$_2$ to the atmosphere (Matveev et al. 2016). Another type of terrain occurs on mineral soils as lithalsa landscapes (Calmels et al. 2008), with frost-heaved, clayey, silt-rich permafrost mounds, and associated thermokarst lakes (hereafter, lithalsa lakes). Lithalsa lakes are more varied in colour, from blue-green to white to brown (Watanabe et al. 2011), and are also known for their stratified structure and anoxic bottom waters (Deshpande et al. 2015). Like palsa lakes, they accumulate CH$_4$ and CO$_2$ (Laurion et al. 2010) and have high rates of bacterial heterotrophic production (Breton et al. 2009; Roiha et al. 2015).

The aim of the present study was to provide an improved understanding of GHG stocks (specifically CO$_2$ and CH$_4$) in lithalsa lakes, and of the emission fluxes from such lakes at
different stages of permafrost degradation. We hypothesized that stocks and emissions increase with increasing degree of permafrost degradation, with greatest effects at the warm southern margin of Arctic permafrost landscapes. This hypothesis implies that the northward contraction of permafrost will be accompanied by increased rates of emission, which could continue well after lake formation. We evaluated this hypothesis by making measurements at a series of lithalsal lakes across a gradient of permafrost conditions in subarctic Québec, including at the southern limit of current permafrost extent where thermokarst lakes have formed and persisted for at least many decades.

**Materials and methods**

**Study sites**

Sampling was in the western Hudson Bay area of Nunavik (Northern Quebec, Canada; Fig. 1), a region experiencing rapid warming and landscape change (Bhiry et al. 2011), and the location of multiple research sites within the program “Arctic Development and Adaptation to Permafrost in Transition” (ADAPT; Vincent et al. 2017) that this study was part of. The region spans four different permafrost zones, from continuous and discontinuous widespread permafrost in the north, to sporadic and isolated permafrost in the south (Allard and Seguin 1987; Vallée and Payette 2007), with mean annual air temperatures over that geographical range from −4.7 to −2.8 °C. Sampling of lithalsal lakes was at three sites...
across this north–south gradient (Fig. 1), namely: (a) in discontinuous widespread permafrost, north of the Nastapoka River (56.9°N, 76.3°W; NAS lakes); (b) in discontinuous permafrost, 20 km east of the village of Umiujaq (56.6°N, 76.2°W; BGR lakes); and (c) in degraded sporadic permafrost, 13 km north of the village of Whapmagoostui-Kuujjuarapik and around 200 km south of the NAS site (55.2°N, 77.5°W; KWK lakes; Supplementary Fig. S1 and associated video1; additional descriptions are given in Bégin and Vincent 2017).

Lake sampling and physical, chemical, and biological properties

In situ measurements and samples were collected from eight lakes at the three sites (Fig. 1 and Supplementary Table S11) during the summer open-water period, from 2012 to 2015. Vertical profiles of physicochemical properties were obtained from an inflatable boat transported to the sites by helicopter, with a YSI 6000 multi-probe (Yellow Springs Instruments, Yellow Springs, OH, USA) and an RBR Concerto conductivity–temperature–depth logger (RBR Ltd., Ottawa, ON, Canada). The accuracy of these measurements was ±0.15 °C, ±0.2 pH units, ±0.2 mg oxygen L⁻¹, and ±0.001 mS cm⁻¹ conductivity for the YSI; and ±0.002 °C and ±0.003 mS cm⁻¹ for the RBR. Underwater photosynthetically active radiation (PAR) irradiance was measured with a Licor submersible radiometer.

Samples for water analysis were collected at the surface and bottom of the water column, filtered at the Centre for Northern Studies (CEN) research station in Whapmagoostui-Kuujjuarapik, and then shipped to home facilities (Laval University and INRS, Québec City, QC, Canada) for laboratory analysis. Samples for analysis of soluble reactive phosphorus (SRP) were filtered through 0.2 μm cellulose acetate filters and then analyzed using a colorimetric method (Standard Methods 4500-P.E., APHA, AWWA, and WEF 1998) and a Lachat Autoanalyzer (Lachat QuikChem® 8500 Series 2 Flow Injection Analysis System, Hach Company, Loveland, CO, USA). For total phosphorus (TP), unfiltered samples were acidified with 15% H₂SO₄, digested with persulfate and analyzed for SRP as above. For dissolved organic carbon (DOC) concentrations, filtered (as above) lake water samples were acidified to remove inorganic carbon, and analyzed by high temperature catalytic combustion method with infrared detection (Standard Methods 5310 B, APHA, AWWA, and WEF 1998) in a Shimadzu VCPH analyzer (Shimadzu Scientific Instruments, Columbia, MD, USA). The total nitrogen content (TN) was measured from unfiltered water samples by alkaline digestion with persulfate, followed by analysis by the sulfanilamide colorimetric method after reduction with cadmium in a Lachat Autoanalyzer (QuikChem® Method 10-107-04-3-A). Total suspended solids (TSS) were determined by weight after filtration onto precombusted, preweighed glass fiber filters (nominal porosity of 0.7 μm). Chlorophyll a concentration (Chl-a) was measured by high-pressure liquid chromatography from pigments extracted with 95% MeOH from the above glass fiber filters kept frozen at −80 °C until analysis, as in Bonilla et al. (2005).

Automated lake surface observations

Automated cameras (Reconyx PC800, Holmen, WI, USA) were installed on the shores of three thermokarst lakes (one per study site, respectively, KWK12, BGR1, and NASa) at a distance of 5–10 m from the edge of the summer water extent. The cameras recorded six photographs per 24 h period at 1 h intervals between 1000 and 1500 (Eastern Standard Time, EST). The data were retrieved annually at the end of August each year. The complete dataset is archived in the Nordicana D data repository (Pienitz et al. 2017). These data were used to calculate the number of days of open water for each site, including for the gas flux calculations.

1Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/as-2017-0047.
**CH₄ and CO₂ measurements**

Profiles of CH₄ and CO₂ concentrations were obtained from discrete depth samples, as in Deshpande et al. (2017), and with continuous automated dissolved gas monitoring systems. The discrete depth samples were obtained in triplicate with a thin-layer laminar-flow sampler that had two plates set 63.5 mm apart (Matveev et al. 2016), at 0.1–0.5 m depth intervals. The samples were transferred with a peristaltic pump to a 2 L prerinsed, low density polyethylene bottle. The lake water was then equilibrated with a 20 mL air-filled headspace, and a 10 mL gas sample taken and injected into a 5.9 mL helium-flushed, evacuated borosilicate glass vial (Labco Exetainer®, Labco Limited, Lampeter, UK). The gas samples were subsequently analyzed for CH₄ and CO₂ by gas chromatography with flame ionization detection (Varian 3800, COMBI PAL head space injection system, CP-Poraplot Q 25 m with flame ionization detector) as in Matveev et al. (2016).

The surface fluxes of CH₄ and CO₂ were calculated from the dissolved gas concentrations at the air–water interface as in Matveev et al. (2016). We used a wind-based model, with correction for turbulence and low-solubility gases as in Vachon et al. (2010). The gas flux $F_i$ for each gas $i$ was expressed assuming molecular diffusion as

$$F_i = k_i K_{Hi} \Delta P_i$$

where $K_{Hi}$ is the Henry Law constant, $k_i$ is the gas transfer velocity, and $\Delta P_i$ is the gradient of the gas partial pressures at the air–water interface.

Two automated systems were used, depending on sampling conditions: (1) a “CO₂-box” continuous GHG monitoring system that simultaneously measured dissolved CO₂, CH₄, and O₂ contents in a gas stream continuously equilibrated with the source water (Carignan 1998, details in Laurion et al. 2010) and (2) a Franatech METS system composed of an infrared-CO₂ sensor and a semi-conductor CH₄ sensor (Franatech GmbH, Lüneburg, Germany) in separate housings and assembled on a flow-through chamber with a constant water flow produced with a submersible pump (model SBE-5T, Sea-Bird Electronics, Inc., Bellevue, WA, USA). The two instruments were cross-calibrated and the datasets combined (an example of the consistency among methods is given in Supplementary Fig. S2).

Gas concentrations in the littoral zone were measured with the CO₂-box deployed from the shore (KWK12 and BGR1), whereas concentrations in the deepest offshore water and for the NASa transect were measured with the Franatech METS instrument deployed from the boat. The intake of the CO₂-box was submerged to 5–10 cm from the surface, with the peristaltic pump located inside the instrument housing; the METS intake was a 15 cm tube connected to a submersible Seabird pump, and the entire instrument was submerged at around 10 cm depth from the surface for surface samples.

Ebullition of CH₄ and CO₂ was assessed at KWK and BGR sites by collecting gas samples with submerged, opaque, inverted cones, with a 0.5 m² opening at the bottom and a syringe equipped with a valve at the top (details in Matveev et al. 2016). Two to three gas traps per lake were installed for 1–30 days, depending on ebullition rates and logistic constraints. The gas samples were stored in 12 mL or 5.9 mL Labco Exetainer® vials, prepared as above. Sampling dates and numbers of ebullition samples for each lake are given in Supplementary Table S2, which also provides the sampling dates for dissolved gas concentrations measured by the headspace, CO₂-box, and METS profiler methods, as described above.

The CH₄ oxidation rates were calculated as a linear regression from concentrations measured every 3 h by subsampling a closed vessel containing 20 L of surface lake water connected to the CO₂-box. The incubations were performed in the laboratory under ambient temperature (ca. 15 °C) and low light (<50 μmol photons m⁻² s⁻¹).
Isotopic composition and radiocarbon

Samples for CO₂ and CH₄ radiocarbon dating (¹⁴C isotope) were collected in helium-flushed, evacuated 50 mL serum bottles (Wheaton, IL, USA) from two gas ebullition samples collected from funnels installed in lake BGR1 in 2014. The ¹⁴C content of CO₂ and CH₄ was measured by accelerator mass spectrometry in the Keck Carbon Cycle AMS Facility of the University of California Irvine (Irvine, CA, USA), as in Matveev et al. (2016). The ¹⁴C ages were expressed as fractions of the modern standard (Δ¹⁴C) following Stuiver and Polach (1977), with all results corrected for isotopic fractionation.

The δ¹³C isotopic fractionation was assessed in the ebullition and the discrete depth samples, all collected in triplicates by the headspace method and stored in 12 mL Exetainer® vials, prepared as above. The δ¹³C in CH₄ and CO₂ was measured at the GRIL-UQAM facility (Montreal, QC, Canada) by continuous-flow cavity ring-down spectroscopy (CRDS) with near-infrared laser source method, using a Picarro (Picarro Inc., Santa Clara, CA, USA) “G2201-i δ¹³C in CH₄ and CO₂ Gas Analyzer” (<0.12‰ δ¹³C-CO₂ and <0.4‰ δ¹³C-CH₄ precision at 1-σ, 1 h window, 5 min average). The results were expressed as the δ¹³C ratio of a sample relative to the Vienna Pee Dee Belemnite (VPDB) international measurement standard (Coplen 2011). The isotope separation factor between δ¹³C-CO₂ and δ¹³C-CH₄ (ε₉) was calculated according to Whiticar (1999).

ε₉ = δ¹³C-CO₂ − δ¹³C-CH₄

The δ¹³C-CO₂ − δ¹³C-CH₄ carbon isotope partitioning resulting from microbial CH₄ production and oxidation was further expressed as a combination plot of the δ¹³C-CO₂ versus δ¹³C-CH₄, as in Fig. 8 of Whiticar (1999).

Results

Morphometry
The lithalsa lakes were all shallow, with an average (±SD) depth of 2.7 (±1.1) m (Supplementary Table S1¹), and a distinct morphometry with steep, eroded shores (Supplementary Fig. S2¹). The maximum depths were relatively stable among sampling years at KWK and NAS from 2012 to 2015, but BGR1 increased by 0.6 m to a maximum of 4.4 m, while BGR2 increased by 0.25 m to a maximum of 1.55 m. The mean surface area of the studied lakes averaged 942 m² with large variations among sites (coefficient of variation (CV) = 94%), but much less between lakes within each site (average CV = 19%). Within this limited data set, the average lake area per site decreased as a function of distance (R² = 0.88 for the linear regression) southwards in the study region (Supplementary Fig. S3 and Table S1¹). There were no observed changes during the period of observation in lake area at KWK and NAS sites, but the BGR site showed further evidence of rapid landscape change. Some of the lithalsa mounds experienced thawing and collapse (thermokarst), producing new lithalsa lakes (e.g., BGRb), and there were also increases in area of some lakes (e.g., BGR1 and BGR2) and fusing of adjacent water bodies (Fig. 2).

Ice regime and winter snow accumulation
The automated camera records showed the lakes were ice-covered for around eight months each year. At the lake NASa (site NAS), the lake ice formed at the beginning of November (2014), with an overlying layer of snow that accumulated to a maximum thickness of 0.8 m (winter 2015). The ice first broke up during the last week of April (2015), but quickly reformed, with final break-up and disappearance during the first 2 weeks of June (2015). At the BGR site, the lake ice broke up on lake BGR1 during the last week of May.
(2015), and the open-water period extended from the first week of June to the second week of October (2016). The maximum winter snow accumulation was around 0.7 m (winter 2016). The ice-free period recorded at the lake KWK12 (in the southern KWK valley) was about 2 weeks longer than in BGR (from the last week of May to the third week of October 2016), with a maximum winter (2016) snow accumulation of ca. 0.6 m. None of the three lake ice records showed any evidence of persistent gas bubbling (“bubbling hot-spots” as in Wik et al. 2011) on images with clear ice during its formation and break-up.

**Limnological properties**

All of the lithalsa lakes were thermally stratified during the period of observation, with the shallowest thermocline occurring at 0.5 m depth in NASa (Fig. 3a), possibly linked to the strong light attenuation in its turbid waters (surface TSS = 319 mg L\(^{-1}\), Table 1). The surface mixing zone was 2 and 1.5 m deep in the lakes BGR1 and KWK12, respectively (Figs. 3d, 3g). The depth of the euphotic zone (1% of surface PAR) similarly varied among the lakes, from 0.55 m in NASa to 4.1 m (to the lake bottom) in BGR1 (Figs. 3a, 3d, 3g). The pH was close to neutral in most lakes of NAS and BGR sites (Figs. 3b, 3e), while it was significantly lower in KWK lakes \((p < 0.0001\) in two-way ANOVA per site comparison), falling to acidic values of 4.6 at the bottom of KWK12 (Fig. 3h). Specific conductivity values varied from 2.7 to <15 mS m\(^{-1}\) in most lakes of different permafrost regions, typically increasing with depth by about 50% (Figs. 3b, 3h), with the exception of BGR1, where it sharply increased up to 40.1 mS m\(^{-1}\) below the mixing zone (Figs. 3d, 3e).

TN and TP concentrations were variable among lakes in all sites (Table 1), with no significant difference between the top and bottom of the water column \((p > 0.1, \text{Wilcoxon’s test})\). SRP averaged high values (3.5 μg P L\(^{-1}\)) but was similarly variable in all lakes \((CV = 85\%)\), and with no significant difference between the top and bottom of the water column \((p = 0.12, \text{Wilcoxon’s test})\). The lakes had substantial concentrations of TSS in their bottom waters, with exceptionally high values throughout the water column of NASa (Table 1). DOC concentrations (all depths combined) were significantly higher \((p = 0.007, t\text{ test})\) in
the southern KWK lakes versus northern lakes (BGR and NAS, Table 1), averaging 14.5 and 4.9 mg C L\(^{-1}\), respectively. Chl-\(a\) concentrations (all depths combined) were also significantly higher (\(p = 0.025\), \(t\) test) in the southern (mean of 16.9 \(\mu\)g L\(^{-1}\)) versus northern (mean of 2.5 \(\mu\)g L\(^{-1}\)) lakes.

**Dissolved gas concentrations**

Dissolved O\(_2\) concentrations were typically at saturation at the surface of all lakes, with undersaturation at depth, whereas CH\(_4\) and CO\(_2\) concentrations varied considerably among sites, lakes, and lake depths (Fig. 4). CO\(_2\) concentrations increased toward the bottom in all lakes. CH\(_4\) concentrations also increased with depth in KWK and BGR lakes (Figs. 4c–4f), but were similar throughout the water column in NAS lakes (Figs. 4a, 4b).

Unlike other lakes, the surface waters of lake NAS\(_a\) were undersaturated in CO\(_2\) to the depth of 1 m (Fig. 4a) and this gas was in low concentration to 3 m in NAS\(_h\) (Fig. 4b). In lakes of the BGR site, surface CO\(_2\) values varied from 29.9 \(\mu\)mol L\(^{-1}\) in BGR1 and 20.5 \(\mu\)mol L\(^{-1}\) in...
BGR2, to 42.5 μmol L⁻¹ in the newly formed lake BGRb (Table 2). All these were above the air-equilibrium value of about 16.7 μmol L⁻¹ (Fig. 5). Surface CO₂ concentrations were less variable and generally higher in KWK lakes relative to those in the north, averaging 45.4 ± 13.2 μmol L⁻¹ (Table 2), all at least an order of magnitude above the air-equilibrium value of about 0.0031 μmol L⁻¹ (Fig. 5). The CH₄ concentrations in BGR lakes were much higher, from 0.35 to 0.80 μmol L⁻¹ (Figs. 4c, 4d), and averaged 0.41 μmol L⁻¹ (Table 2). KWK lakes also had high surface CH₄ concentrations averaging 0.43 μmol L⁻¹, including the highest encountered in this study, and large variability among lakes (CV = 78%).

The bottom waters of all lakes were supersaturated in CH₄ and CO₂, with concentrations 2–3 orders of magnitude higher than at the surface (Figs. 4, 5). The vertical gradients were much steeper in KWK lakes compared with those in NAS lakes and in some of the BGR lakes (Fig. 4); BGR1 (Fig. 4c) and the newly formed BGRb (Supplementary Fig. S4) also had steep gradients in CO₂ and CH₄ concentrations towards the bottom. The bottom concentrations of CH₄ and CO₂ were one or more orders of magnitude higher in the lakes of the southern KWK site (mean ± SD: 1259 ± 1066 μmol CO₂ L⁻¹ and 310 ± 281 μmol CH₄ L⁻¹) relative to those of the northernmost NAS site (120 ± 58 μmol CO₂ L⁻¹ and 0.14 ± 0.08 μmol CH₄ L⁻¹). Values at the BGR sites (1081 ± 1402 CO₂ L⁻¹ and 162 ± 165 μmol CH₄ L⁻¹) were similar to or below those at KWK; however, the lake-to-lake variability at all sites was considerable, as shown by the large SD values.

To examine lateral variations in GHG concentrations, we sampled one of the larger lakes (NASa) in duplicate at the surface and below the surface (0.7–1.0 m depth) at five stations extending from one side of the lake to the other (Fig. 6). The variation in CH₄ concentrations was small, with CVs of 8% (surface) and 9% (subsurface). The CO₂ variation was slightly larger, with CVs of 23% (surface) and 20% (subsurface), with the lowest concentrations measured in the littoral zone at each end of the transect.

### CH₄ and CO₂ fluxes

The diffusive CO₂ flux from Nunavik lithalsa lakes gradually increased towards the south in the region of study (Table 3). The values ranged from a net sink of −1.7 mmol CO₂ m⁻² day⁻¹ (in lake NASa) to a source of up to 30.8 mmol CO₂ m⁻² day⁻¹ in lake KWK12.

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**Table 1.** Biogeochemical properties of the studied lakes, including total nitrogen (TN), total phosphorus (TP), soluble reactive phosphorus (SRP), chlorophyll a (Chl-a), total suspended solids (TSS), dissolved organic carbon (DOC), and dissolved CO₂ and CH₄ concentrations.

| Lake    | TN (mg N L⁻¹) | TP (mg P L⁻¹) | SRP (μg P L⁻¹) | Chl-a (μg L⁻¹) | TSS (mg L⁻¹) | DOC (mg C L⁻¹) | CO₂ (μmol L⁻¹) | CH₄ (μmol L⁻¹) |
|---------|---------------|---------------|----------------|----------------|--------------|----------------|----------------|---------------|
| Surface |               |               |                |                |              |                |                |               |
| KWK1    | 1.08          | 0.47          | 5.0            | 8.7            | 14           | 17             | 32             | 0.1           |
| KWK11   | 1.01          | 0.12          | <3             | 24             | 8.3          | 27             | 42             | 0.13          |
| KWK12   | 0.41          | 0.02          | 0.4            | 5.6            | 2.4          | 6.3             | 44             | 0.9           |
| BGR1    | 0.24          | 0.01          | 0.4            | 1.0            | 2.0          | 2.4             | 30             | 0.8           |
| BGR2    | 0.43          | 0.04          | 3.3            | 0.9            | 5.9          | 10             | 20             | 0.5           |
| BGRb    | 0.11          | 0.01          | 4.1            | —              | 10           | 4.1             | 43             | 0.4           |
| NASa    | 4.22          | 0.13          | 2.9            | 3.0            | 319          | 3.0             | 15             | 0.13          |
| NASb    | 0.60          | 0.03          | 6.2            | 3.6            | 18           | 4.1             | 30             | 0.19          |
| Bottom  |               |               |                |                |              |                |                |               |
| KWK1    | 0.94          | 0.05          | 11             | 19             | 188          | 12             | 807            | 190           |
| KWK11   | 0.57          | 0.02          | <3             | 39             | 27           | 18             | 731            | 40            |
| KWK12   | 0.63          | 0.07          | 1.8            | 5              | 6            | 8               | 762            | 710           |
| BGR1    | 0.51          | 0.06          | 2.1            | 4.6            | 14           | 3               | 382            | 197           |
| BGR2    | —             | —             | —              | —              | 31           | 10              | 193            | 3             |
| NASa    | 4.14          | 0.18          | 19             | 2              | 810          | 2               | 97             | 0.02          |
Fig. 4. Gas concentration profiles in representative lakes from each of the three study sites located in the discontinuous widespread (NAS profiles from 7 August 2012), discontinuous (BGR profiles from 9 August 2012), and sporadic (KWK profiles from 25 August 2015) permafrost.

(Table 4), with an intermediate value of $8.1 \pm 7.7 \text{ mmol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$ on average in BGR lakes. Although the CO$_2$ flux at NAS was on average negative, it alternated between positive and negative values both within one lake and between the lakes of this site at different visits ($CV = 168\%$). The average diffusive flux of CO$_2$ from the southern KWK lakes ($20.2 \pm 7.1 \text{ mmol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$) was more than double that from BGR, and an order of magnitude greater than from NAS lakes. There was no significant correlation between the concentrations of DOC and CO$_2$ in these lakes (Table 1; $r = 0.33$, $p = 0.42$ for surface waters; $r = 0.63$, $p = 0.2$ for bottom waters). The diffusive CO$_2$ fluxes were several orders of magnitude greater than the CO$_2$ ebullition fluxes, the latter only measured in BGR and KWK lakes.
However, the CO₂ ebullition flux was an order of magnitude greater at the BGR site (0.01 mmol CO₂ m⁻² day⁻¹) relative to KWK (0.006 mmol CO₂ m⁻² day⁻¹).

The positive southward gradient was also observed in the CH₄ diffusion rates from these Nunavik lakes (Table 3). The diffusive CH₄ fluxes at the NAS site were always positive (0.12 ± 0.03 mmol m⁻² day⁻¹), and with low variability between the lakes (CV = 25%). Diffusive emissions from BGR lakes averaged 0.45 ± 0.06 mmol CH₄ m⁻² day⁻¹, in the same order of magnitude than from KWK lakes that showed greater variability (0.47 ± 0.33 mmol CH₄ m⁻² day⁻¹). Similar to the observations for CO₂, the mean CH₄ ebullition from the BGR site on discontinuous permafrost (0.26 mmol CH₄ m⁻² day⁻¹) was an order of magnitude greater than that from the KWK site in the largely degraded isolated permafrost region (0.016 mmol CH₄ m⁻² day⁻¹). Overall, the observed total CH₄ fluxes from the studied lakes were within the range of values observed in other thermokarst lakes in the circumpolar region, and the CO₂ fluxes were at the upper limit or above the values reported elsewhere (Table 4).

Isotopic fractionation and ¹⁴C-dating of GHG

In general, the δ¹³C isotopic signatures in dissolved gases were similar in surface waters of the lithalsa lakes (Table 5), with the exception of a low δ¹³C-CH₄ value in the surface water.
Fig. 6. Dissolved gas concentrations measured along the south–north transect crossing lake NASa on 24 August 2014 at the surface and at 1 m depth. The bottom panel shows the bathymetry (from Proult 2014) and corresponding stations on the lake.

CH₄ oxidation rates
Concentrations of CH₄ during the two laboratory incubations of lake water decreased linearly with time over the 27–48 h duration of the experiments, while CO₂ concentrations increased (Fig. 8). These net CH₄ consumption rates were an order of magnitude higher for...
Table 3. Average (summer 2012–2015) CO₂ and CH₄ flux (diffusion and ebullition) and their greenhouse gas forcing per study site (given as CO₂-equivalent*).

| Gas flux     | Study site | NAS  | BGR  | KWK  |
|--------------|------------|------|------|------|
| CO₂ ebullition | Mean rate (mmol m⁻² day⁻¹) | —    | 0.1  | 0.006|
|              | Mean rate (mg CO₂ m⁻² day⁻¹) | —    | 0.4  | 0.26 |
|              | Coefficient of variation (%) | —    | 132  | 116  |
|              | Number of measurements (n) | —    | 2    | 2    |
| CO₂ diffusion | Mean rate (mmol m⁻² day⁻¹) | 3.4  | 8.1  | 20.2 |
|              | Mean rate (mg CO₂ m⁻² day⁻¹) | 150  | 357  | 889  |
|              | Coefficient of variation (%) | 169  | 95   | 35   |
|              | Number of measurements (n) | 6    | 6    | 6    |
| CH₄ ebullition | Mean rate (mmol m⁻² day⁻¹) | —    | 0.26 | 0.016|
|              | Mean rate (mg CO₂ eq m⁻² day⁻¹)* | —    | 117  | 7    |
|              | Coefficient of variation (%) | —    | 136  | 132  |
|              | Number of measurements (n) | —    | 2    | 2    |
| CH₄ diffusion | Mean rate (mmol m⁻² day⁻¹) | 0.12 | 0.45 | 0.47 |
|              | Mean rate (mg CO₂ eq m⁻² day⁻¹)* | 54   | 202  | 211  |
|              | Coefficient of variation (%) | 25   | 12   | 70   |
|              | Number of measurements (n) | 6    | 6    | 6    |
| Total greenhouse gas forcing | Per study region (mg CO₂ eq m⁻² day⁻¹) | 204† | 676  | 1108 |
|              | Average lake area (m²) | 2035 | 728  | 427  |
|              | Open water period (days) | 133  | 134  | 145  |
|              | Per lake per open water period (kg CO₂ eq year⁻¹) | 5 5† | 66   | 68   |

Note: Yearly estimates are for the open water period, as determined from the automated camera images.
*For methane, CO₂-equivalent (CO₂-eq.) = CH₄ (mg CH₄ m⁻² day⁻¹) × 28, to consider its global warming potential over 100 years, as in Myhre et al. (2013).
†Diffusion only.

Table 4. The diffusive and ebullition flux of CH₄ and CO₂ from lithalsa lakes (2012–2015 average) compared with other lakes in the circumpolar region.

| Site [Ref.*] | Canada | Finland | Alaska | Siberia |
|--------------|--------|---------|--------|--------|
| Latitude (°N) | Lihalsal (mineral) [1] | Palsa (peatland) [2] | Tundra lakes [3] | High Arctic [4] | Permafrost boreal [5] | Continuous yedoma [6] | Tundra (peatland) [7] |
| 55-57 | 55-57 | 73 | 82 | 61.5 | 60-68 | 65 |
| CH₄ ebullition | Mean rate (mmol m⁻² day⁻¹) | 0.1 | 0.2 | 16.9 | 0.001 | 0.9 | 5.5 | 0.2 |
|              | Range | <0.01-0.8 | 0.00-535 | 0.00-0.01 | 0.2-1.5 | 2.2-7.2 | 0.04-0.3 |
| CH₄ diffusion | Mean rate (mmol m⁻² day⁻¹) | 0.4 | 3.3 | 0.8 | 0.7 | 0.7 | 0.9 | 0.4 |
|              | Range | 0.07-0.8 | 0.01-12.8 | 0.03-5.8 | 0.00-1.34 | 0.1-2.0 | 0.6-1.1 | 0.2-0.6 |
| CO₂ ebullition | Mean rate (mmol m⁻² day⁻¹) | 0.1 | 0.01 | 0.7 | 0.002 | 0.3 | 0.11 | 0.005 |
|              | Range | 0.006-0.2 | 0.001-0.1 | 0.00-16.3 | 0.00-0.01 | 0.002-0.5 | 0.01-0.14 | 0-0.03 |
| CO₂ diffusion | Mean rate (mmol m⁻² day⁻¹) | 12.3 | 58.3 | 8.7 | 7.2 | 17.0 | 133.9 | 34.1 |
|              | Range | -17 to 30.8 | 4-242 | -12 to 65 | 0.00-165 | 9-25 | 4.6-263 | 11.4-59 |

*References in the table: [1] This study, [2] Matveev et al. 2016, [3] Bouchard et al. 2015, [4] Emmerton et al. 2016, [5] Huttunen et al. 2003, [6] Sepulveda-Jauregui et al. 2015, and [7] Repo et al. 2007.
Table 5. Isotopic fractionation $\delta^{13}$C of CH$_4$ and CO$_2$ dissolved in surface and bottom waters at KWK and BGR sites (August 2015), and the separation factor $\varepsilon_C$ in these lakes ($\delta^{13}$C versus VPDB, mean ± SD, $n = 3$).

| Lake  | $\delta^{13}$C-CH$_4$ (±SD) (%) | $\delta^{13}$C-CO$_2$ (±SD) (%) | $\varepsilon_C$ (%) |
|-------|---------------------------------|---------------------------------|-------------------|
| Surface KWK1 | $-45.7$ (0.5) | $-14.8$ (0.3) | 30.9 |
|       KWK11 | $-46.2$ (0.0) | $-16.2$ (0.0) | 30.0 |
|       KWK12 | $-47.0$ (0.1) | $-14.2$ (0.3) | 32.8 |
|       Average | $-46.3$ (0.2) | $-15.1$ (0.2) | 31.2 |
| Bottom KWK1 | $-66.1$ (0.0) | $-17.4$ (0.0) | 48.7 |
|       KWK11 | $-56.6$ (0.8) | $-18.1$ (0.5) | 28.4 |
|       KWK12 | $-67.0$ (1.6) | $-22.3$ (1.7) | 44.8 |
|       Average | $-63.2$ (0.8) | $-19.3$ (0.7) | 44.0 |
| Surface BGR1 | $-47.9$ (0.5) | $-13.8$ (1.3) | 34.1 |
|       BGR2 | $-48.2$ (4.1) | $-16.1$ (2.7) | 32.1 |
|       BGRb | $-30.7$ (0.3) | $-15.8$ (0.3) | 14.9 |
|       Average | $-42.3$ (1.6) | $-15.2$ (1.4) | 27.1 |
| Bottom BGR1 | $-55.2$ (3.7) | $-13.6$ (1.8) | 41.6 |
|       BGR2 | $-47.1$ (0.2) | $-17.7$ (1.0) | 29.4 |
|       BGRb | $-51.8$ (0.7) | $-12.1$ (1.7) | 39.7 |
|       Average | $-51.4$ (1.5) | $-14.5$ (1.5) | 36.9 |

Note: VPDB, Vienna Pee Dee Belemnite.

Fig. 7. Isotopic fractionation $\delta^{13}$C of CO$_2$ and CH$_4$ in surface and bottom waters of the lakes sampled at KWK and BGR sites, and the separation factor $\varepsilon_C$ in these lakes (data from August 2015).
KWK (0.38 ± 0.02 μmol CH₄ L⁻¹ day⁻¹, R² = 0.92) compared with NAS (0.016 ± 0.002 μmol CH₄ L⁻¹ day⁻¹, R² = 0.94). These values corresponded to 5.7% (KWK) and 0.8% (NAS) of the measured net CO₂ production rates.

Discussion

Landscape changes in the region of the present study were most evident in the BGR area, with deepening, expansion and fusion of lakes, and the creation of new lakes (Fig. 2). These effects of the northward contraction and rapid degradation of permafrost have been well documented at BGR (Calmels et al. 2008). Changes of similar origin and scale were observed in the past at the southern end of our sampling region, the KWK valley site, during the period 1930–1960 (Allard and Seguin 1987). Over more recent decades, however, the total areal extent of lithalsa lakes in degraded permafrost region has remained relatively constant (Bouchard et al. 2014). Despite the older age, the KWK lakes continued to retain water up to a depth of almost 3 m, with strong stratification and anoxic bottom layers indicating intense microbial activity.

The diffusion rates of both CO₂ and CH₄ were much greater in the KWK lakes than at the more northerly sites where permafrost was less degraded, particularly relative to the NAS lakes. The rates of high diffusion exceeded those for ebullition at all measured sites. This contrasts with many reports for thermokarst lakes elsewhere, where ebullition was the dominant flux (Casper et al. 2000; Bastviken et al. 2011; Wik et al. 2013; Sepulveda-Jauregui et al. 2015). It remains possible that our limited sampling of ebullition missed important periods and places of intense ebullition, and that the values presented here are underestimates. The largest ebullition fluxes that have been observed elsewhere are persistent point sources (“seeps” and “hotspots”, as in Anthony et al. 2010), which are identifiable in the lake ice-cover (Wik et al. 2011; Lindgren et al. 2016). However, our continuous automated camera imaging of the lake surfaces did not reveal any persistent point ebullition in these lakes, nor were such hotspots observed during the sampling campaigns in four consecutive years. Thus, the undersampling error in our estimates of the ebullition flux seems unlikely to be large. It is possible, however, that our estimates of diffusion flux may have included quasi-stable microbubbles of gas (Prairie and del Giorgio 2013) that form in the supersaturated bottom waters and rise up through the water column (Matveev et al. 2016).

The total CH₄ efflux rates varied among sites and, to a lesser degree, among years and month of sampling, but at all locations the rates were substantial (Table 3). The maximum combined emission rate per unit area of 1.2 g CO₂-eq m⁻² day⁻¹ was observed in the KWK site experiencing accelerated permafrost degradation. However, the larger northernmost
lakes of the NAS site were emitting a similar amount of gas per lake, even although only diffusive fluxes were measured there (Table 3). The KWK lithalsa lakes, which lie in the most degraded permafrost region, had minimal ebullition rates (7.2 mg CO₂-eq m⁻² day⁻¹ versus rates of 2450 mg CO₂-eq m⁻² day⁻¹ for lakes elsewhere reported in Wik et al. 2016), and were the smallest of all the studied lithalsa sites in terms of lake area (Supplementary Table S1). Despite these features, they still emitted an estimated 72.3 kg CO₂-eq year⁻¹, as high as the recently formed BGR. The camera images also indicated that they had a two-week longer open-water period, which would favour a more prolonged period of emission.

Although these rates generally fall within the range of emissions reported elsewhere, they are less than those of palsa lakes in the same region (Table 4). Palsa lakes show similar pattern of emissions dominated by diffusion, but their organic-rich nature and intense bacterial activity (Deshpande et al. 2016) creates anoxic conditions through most of the water column (Deshpande et al. 2017), with abundant methanogenic communities (Crevecoeur et al. 2016) and thus high rates of methanogenesis. Even the oxygenated strata of these waters may be sites of methanogenesis, as recorded in oxic environments elsewhere (Bogard et al. 2014), and CH₄ production may be favoured by anoxic microenvironments within the organic particles that occur in high concentration in these waters.

The gas concentrations and emission rates measured here were made during the summer period of open water, and future studies will need to consider the full annual cycle. Continuous oxygen data from these subarctic waters indicate prolonged anoxia under the winter ice-cover, with mixing of the water column that may be delayed until convective overturn in autumn (Deshpande et al. 2015, 2017). Additional CH₄ and CO₂ sampling would therefore be of particular interest during the late winter ice-cover, spring ice-out, and fall cooling periods. Variations are also likely at much shorter timescales. The lithalsa lakes contain moderate Chl-a levels (Table 1), and phytoplankton as well as aquatic macrophytes may cause diurnal fluctuations in O₂, CO₂, and possibly also CH₄. Previous studies with the CO₂-box on the KWK lakes, for example, have provided initial indications of such diurnal cycles in all three gases (see Fig. 7c in Laurion et al. 2010). Nocturnal cooling and convective mixing may also influence emission rates (Anthony and MacIntyre 2016).

**CH₄ oxidation**

Our laboratory experiments indicate active methanotrophy taking place in these waters under oxygenated conditions, as was expected from previous 16S RNA analyses showing the presence of abundant methanotrophs in these waters (Crevecoeur et al. 2015). In both the KWK and NAS lakes this contributed a small fraction (around 1%–6%) of the total microbial respiration rate, consistent with the high rates of bacterial heterotrophy in thermokarst waters (Roiha et al. 2015; Deshpande et al. 2016). It is also consistent with the ¹⁴C data that showed large differences in age between the two GHG because CO₂ derived from CH₄ oxidation would yield the same age (see below). The CH₄ oxidation rates (0.016 and 0.38 µmol CH₄ L⁻¹ day⁻¹, respectively, for NAS and KWK lakes) are at the low end of the range reported in other environments, for example 0.02–1.3 µmol CH₄ L⁻¹ day⁻¹ in the surface waters of a boreal lake in Finland (Kankaala et al. 2006). Much higher rates (1.2–33.8 µmol CH₄ L⁻¹ day⁻¹) were reported from Alaskan lakes across a range of landscapes in summer, however these estimates were derived from longer term (10–12 days) incubations after CH₄ enrichment (Martinez-Cruz et al. 2015). The CH₄ oxidation rates observed in the present study also imply that methanotrophy in lithalsa lakes is a much slower loss process than efflux to the atmosphere: the turnover time for CH₄ in KWK12 based on these measured oxidation rates would be 4.4 days, but only 2.8 days based on emission to the atmosphere from the upper 1 m of the water column; the equivalent turnover rates for NASa would be 8.1 (CH₄ oxidation) and 0.9 days (efflux). Rapid production and diffusion of
CH₄ from deeper waters and sediments to the surface waters of the lake would be needed to maintain the CH₄ concentrations above air-equilibrium, and seems unlikely to be a limiting factor for methanotrophy in these waters, where inorganic nutrient supply may impose a greater constraint.

**Isotopic signatures**

The analysis of isotopic signatures of CH₄ and CO₂ in lithalsa lakes showed large variability in their emission sources. The ¹⁴C dating of ebullition samples indicated that microbial community in at least one of these lakes has access to an ancient (mid-Holocene) carbon source, probably of the same postglacial origin as in the other lithalsa lakes in the region (Bouchard et al. 2014). The Δ¹⁴C values of CO₂ emitted by ebullition from lake BGR1 varied by a factor of two, with a maximum age of around 6000 years. The Δ¹⁴C values of CH₄ in the same samples from BGR1 also varied by about a factor of two, but corresponded to more modern ages (100–320 years B.P.). This divergence in Δ¹⁴C signatures, with values corresponding to a much older age of the CO₂ carbon versus that of CH₄, implies at least partial separation of the pathways for production of the two gases. It is important to note however that the CO₂ ebullition flux measured at BGR is only about 4% of CH₄ ebullition flux (about 37% at KWK), so this old carbon source may have a negligible impact in terms of greenhouse effect. Differences in age have been found in other studies in the region and further north in the Canadian Arctic (Negandhi et al. 2013; Bouchard et al. 2015; Matveev et al. 2016), and sometimes with the reverse trend showing older CH₄ associated with methanogenesis based on old organic carbon released from degrading permafrost (Matveev et al. 2016). The older CO₂ measured here could potentially be derived from subsurface flows into the lake that pick up this gas from soil decomposition processes, including from thermokarst organic soils as described in the Alaskan tundra by Kling et al. (1991). Younger CH₄ could be derived from vegetation that occurs at the edge of and within the lithalsa lakes, and that is broken down by anaerobic processes in the bottom waters and sediments. However, the data are limited and will require corroboration with more extensive sampling and analyses.

The analysis of the δ¹³C signatures showed a marked difference between the lithalsa lakes in discontinuous permafrost (BGR) versus those in the largely degraded permafrost (KWK). This difference was especially apparent in the bottom waters, which, in most of these lakes, would be little affected by aerobic oxidation of CH₄ that would deplete the δ¹³C of the remaining CH₄. More depleted (i.e., more negative) values of δ¹³C-CH₄ have been attributed to the differential use of lighter substrate carbon by methanogens (Whiticar 1999; Conrad 2005; Sanci and Panarello 2015). This also leads to carbon isotope separation between CH₄ and CO₂, which can indicate the methanogenic pathways that predominate (Whiticar 1999; Galand et al. 2010). In particular, Whiticar (1999) showed that carbon isotope separation factor εC [eq. (2)] in the range of 40‰–55‰ is most commonly associated with methylated substrate fermentation prevailing in freshwater environments, whereas higher and lower values were linked to acetoclastic (AM) and hydrogenotrophic (HM) pathways of CH₄ production, respectively, with some overlap on both sides (Galand et al. 2012; Vaughn et al. 2016). The εC values observed in the lithalsa lakes mostly fall at the edge between the ranges associated with HM and AM. This is in line with the analysis of archaeal 16S rRNA in these lakes (Crevecoeur et al. 2016), which found methanogens of the orders Methanomicrobiales (hydrogenotrophic) and Methanosarcinales (multiple pathways) to co-occur in abundance as the dominant Archaea. The lower εC values observed in the surface waters of the lithalsa lakes relative to those in the bottom waters (Table 3) could potentially be linked to CH₄ oxidation in the oxygenated epilimnion. The more depleted
δ¹³C-CH₄ values observed in the bottom of the KWK lakes (Table 5) may be linked to a greater degree of the substrate depletion by the methanogens.

**Conclusions**

Our subarctic observations indicate that lithalsa lakes begin emitting CH₄ and CO₂ as soon as they are formed. These emissions are through ebullition and diffusion pathways, and are liable to continue and accelerate, particularly via diffusive fluxes, as the permafrost continues to warm and erode. CH₄ oxidation appears to have a variable effect in reducing the stocks and therefore diffusive transfers of this gas to the atmosphere; at NAS the oxidation rates were a factor of 10 less than emission rates (11% of the calculated efflux from the upper metre of the water column to the atmosphere), but at KWK the oxidation rates were equivalent to around 63% of emissions, indicating a substantive reduction of potential emission rates by methanotrophy. Despite this effect of CH₄ oxidation, the KWK lakes were stronger emitters of CH₄ than at northern sites, and also emitted more CO₂ per unit area. Detailed surveys of lake sizes and density distributions will be needed to fully extrapolate these findings to the landscape scale. However, if the southern KWK lakes can be considered a space for time proxy for future change (Blois et al. 2013), these observations imply that thermokarst development in the lithalsa dominated landscape will be accompanied by increased GHG emissions, and that the lakes will persist as strong sources for at least many decades.

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