CO$_2$ and CH$_4$ emissions from streams in a lake-rich landscape: Patterns, controls and regional significance

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Abstract

Aquatic ecosystems are important components of landscape carbon budgets. In lake-rich landscapes, both lakes and streams may be important sources of carbon gases (CO₂ and CH₄) to the atmosphere, but the processes that control gas concentrations and emissions in these interconnected landscapes have not been adequately addressed. We use multiple datasets that vary in their spatial and temporal extent during 2001-2012 to investigate the carbon gas source strength of streams in a lake-rich landscape and to determine the contribution of lakes, metabolism and groundwater to stream CO₂ and CH₄. We show that streams emit roughly the same mass of CO₂ (23.4 Gg C yr⁻¹; 0.49 mol CO₂ m⁻² day⁻¹) as lakes at a regional scale (27 Gg C yr⁻¹), and that stream CH₄ emissions (189 Mg C yr⁻¹; 8.46 mmol CH₄ m⁻² day⁻¹) are an important component of the regional greenhouse gas balance. Gas transfer velocity variability (range = 0.34 to 13.5 m day⁻¹) contributed to the variability of gas flux in this landscape. Groundwater inputs and in-stream metabolism control stream gas supersaturation at the landscape scale, while carbon cycling in lakes and deep groundwaters do not control downstream gas emissions. Our results indicate the need to consider connectivity of all aquatic ecosystems (lakes, streams, wetlands and groundwater) in lake-rich landscapes and their connections with the terrestrial environment in order to understand the full nature of the carbon cycle.
1. Introduction

Aquatic landscapes are important components of regional and global carbon (C) cycles [Cole et al., 2007; Tranvik et al., 2009; Butman and Raymond, 2011]. Freshwaters transport large amounts of C in rivers and streams, store C as organic matter in lake and wetland sediments, and emit significant quantities of C to the atmosphere in the form of carbon dioxide (CO₂) and methane (CH₄). Terrestrial C input to the ocean via surface waters is a substantial global term [Hope et al., 1994; Stets and Striegl, 2012] at ~0.9 Pg C yr⁻¹ [Cole et al., 2007]. And in many instances, stream and river C efflux to the atmosphere is roughly equivalent to, or can even exceed fluvial export [Richey et al., 2002; Striegl et al., 2012]. Thus, landscape-and regional-scale C budgets that omit aquatic components may overestimate the magnitude of C storage in terrestrial ecosystems [Richey et al., 2002; Christensen et al., 2007; Jonnson et al., 2007].

The large contribution of aquatic environments to regional C balances is particularly well illustrated in the case of lake-rich landscapes. In these settings, the abundance of lakes coupled with their often-large C pools and fluxes result in a disproportionate aquatic contribution to the overall C budget [Buffam et al., 2011]. Lakes are commonly supersaturated with CO₂ [Cole et al., 1994] and many of those lakes are also net heterotrophic (i.e., organic carbon mineralization exceeds primary production [del Giorgio et al., 1997; Hanson et al., 2003] and thus C sources to the atmosphere via breakdown of terrestrial organic matter [Cole et al., 2007; Tranvik et al., 2009]. In contrast to lakes, streams in these regions have small surface areas and span short distances before intersecting lakes. Thus, one might surmise that fluvial systems make only minor contributions to the overall C balance in lake-rich regions. However, streams can have substantial interface with adjacent ecosystems and transport significant amounts of water, C, and nutrients through landscapes,
hinting that their role may be underestimated in hydrologically connected landscapes.

In this study we address the question: What are the patterns, controls, and regional significance of stream gas efflux in Wisconsin’s Northern Highlands Lake District (NHLD), a lake-rich region in the northern U.S. temperate zone? There were three key motives for asking this question. First, we wanted to resolve the apparent contradiction between streams as minor contributors to regional C emissions in a lake-rich landscape [Buffam et al., 2011] versus their sometimes substantial role revealed in watershed-scale studies (described earlier). Second, because lakes are defining features of these landscapes, we wanted to understand how lakes influenced stream C gas concentrations and fluxes and how this influence compared with two other major influences on gas dynamics: groundwater inputs and in-situ metabolism. Finally, while CO₂ dominates aquatic gas efflux, CH₄ can also be present in streams draining catchments with C-rich soils or sediments [Hope et al., 2001]. Given the amplified greenhouse warming potential of this gas relative to CO₂, even small fluxes may lead to an important role for streams as a regional greenhouse gas source [Baulch et al., 2011; Striegl et al., 2012; Crawford et al., 2013].

To answer our overarching question, we took multiple approaches that varied in their temporal and spatial scale in order to: (1) establish patterns of stream gas concentrations and efflux in the NHLD, (2) assess the relative importance of different drivers in shaping the observed patterns, and (3) generate a regional estimate of stream C gas emissions.

2. Site Description

This study was conducted in the Northern Highlands Lake District (NHLD) (area ~6400 km²) of north central Wisconsin and Michigan, U.S. We intensively studied five small streams, which are part of the U.S. Geological Survey Water, Energy and Biogeochemical Budgets Program (WEBB) in the Trout Lake catchment, as well as six other streams in adjacent catchments. We also include previously unpublished data from a regional stream
survey [Lottig et al., 2011], an extensive groundwater chemistry dataset, as well as a high resolution metabolism dataset (timing and locations are given in Table 1). The NHLD has thousands of kettle lakes formed from the last glacial period, but streams are also present and cover approximately 0.5% of the total surface area (lakes cover 13%) [Buffam et al., 2011]. The geology of the NHLD is distinct relative to other glacial drift lake districts of the Midwest and Canada [Walker et al., 2003]. There is 30 to 50 m of unconsolidated sand and gravel overlying Precambrian igneous bedrock [Okwueze, 1983; Attig, 1985]. Notably, the glacial drift is believed to be essentially free of carbonates [Kenoyer and Bowser, 1992].

Stream flow is a mixture of groundwater and surface flows from lakes, but is typically dominated by longer groundwater flowpaths due to variable hydraulic conductivity of the sand aquifer [Okwueze, 1983; Hunt et al., 1998]. Permeable sands and extensive peats [Buffam et al., 2010] limit surface runoff and impart a hydrologic regime to streams characterized by low variability and atypical channel geomorphology [Watters and Stanley, 2007].

3. Methods

3.1 Temporal and spatial gas concentrations and fluxes

3.1.1 Temporal dynamics

Determinations of gas partial pressures and gas transfer velocities were done once per week at five WEBB stream sites (Mann Creek, Allequash Lower, Allequash Middle, Stevenson Creek, North Creek) that drain into Trout Lake, one of the region’s larger lakes. Samples were all collected on the same day from May 2012 to September 2012. These data were used to establish variability in gas transfer rates for the basin and to investigate spatiotemporal patterns of concentrations and fluxes.

We measured stream water mole fraction of CO₂ using a modified hand-held Vaisala CARBOCAP CO₂ meter positioned just below the water surface [Johnson et al., 2010]. CO₂
mole fraction was converted to $p$CO$_2$ (µatm) by multiplying by barometric pressure. Surface waters were sampled for $p$CH$_4$ using a headspace equilibration method [Striegl et al., 2012].

Gas efflux from the stream surface was measured weekly at these same five WEBB sampling locations using a suspended chamber technique, a technique that has shown agreement with tracer gas studies with respect to gas transfer velocities [Crawford et al., 2013]. CO$_2$ concentration of the chamber air was recorded every 2 seconds for 5 minutes using a PP Systems EGM-4 infrared gas analyzer. CO$_2$ fluxes ($J_{CO2}$) were measured in triplicate at each site, and calculated using Equation 1:

$$J_{CO2} = \frac{dC}{dt} \times h$$

(1)

where $dC/dt$ is the CO$_2$ concentration change in the chamber air (mol m$^{-3}$ air) over the deployment time, and $h$ is chamber height (m). When combined with stream $p$CO$_2$ data, the gas transfer velocity ($K_{CO2}$) can be calculated from flux measurements by rearranging Fick’s Law (Equation 2):

$$K_{CO2} = \frac{J_{CO2}}{(CO_{2\text{stream}} - CO_{2\text{atm}})}$$

(2)

where $K_{CO2}$ is the gas transfer velocity (m d$^{-1}$), $CO_{2\text{stream}}$ is the CO$_2$ concentration of stream water (mol m$^{-3}$), and $CO_{2\text{atm}}$ is the CO$_2$ concentration of water in equilibrium with the atmosphere corrected for temperature induced changes in solubility according to Henry’s Law (mol m$^{-3}$, assuming constant atmospheric partial pressure of 396 µatm) [Wanninkhof, 1992]. Methane fluxes were measured similarly to $J_{CO2}$ by collecting four discrete air samples over a 15 minute deployment (one every 5 minutes) from the return line of the IRGA and analyzed using gas chromatography [Crawford et al., 2013].
3.1.2 Regional Survey

Stream $pCO_2$ and $pCH_4$, water chemistry, land cover, and channel morphology were determined as part of a larger survey of 52 NHLD streams [Lottig et al., 2011]. All sites were in separate drainages and selected at random using a stratified design based on the presence or absence of an upstream lake. Sites were sampled between May and August 2006; further details about site selection and methods are described in Lottig et al., [2011]. Stream $pCO_2$ and $pCH_4$ were determined using a headspace equilibration method [Cole et al., 1994]. We modeled gas concentrations from the survey dataset with multiple linear regression (discussed further below) using the following as potential predictor variables: discharge, water temperature, conductivity, pH, acid neutralizing capacity, calcium, $CH_4$, dissolved organic carbon, $CO_2$, iron, potassium, magnesium, manganese, ammonium, nitrate, sulfate, soluble reactive phosphate, total dissolved nitrogen, total nitrogen, total phosphorus, watershed area, % cover water, % cover forest, % cover wetland, % cover shrubland, % cover natural grassland, % cover urban, and % cover agriculture.

3.2 Influences on stream gas concentrations

3.2.1 Lake and groundwater effects

We took two approaches to test for the effects of upstream lakes on stream $pCO_2$ and $pCH_4$. First, we compared gas concentrations in streams with and without upstream lakes from the regional survey. Second, we sampled longitudinal transects of streams draining lakes and streams with no upstream lake on five occasions approximately every three weeks beginning in May 2012. Streams with lakes (Lost, White Sand, Aurora) were sampled starting at the approximate lake outlet and along a 2000 m transect (0 m, 250 m, 500 m, 1000 m, 2000 m). The epilimnia of upstream lakes were also sampled during late July or early August 2012 at the lake center to allow for a direct comparison with streams. Streams without
upstream lakes (Stella, Mud, and North) were sampled at an arbitrary upstream location (0 m) and followed the same sampling progression as streams with lakes.

We estimated the residence time of CO₂ in streams using two similar equations. First, the length at which ~95% of excess CO₂ in streams is lost to the atmosphere (Length 95%) was calculated according to Chapra and DiToro [1991] (Equation 3)

\[
\text{Length 95\%} = \frac{3v}{K_f}
\]  

(3)

Where \( v \) is the stream velocity (m sec\(^{-1}\)), \( K_f \) is the gas transfer coefficient (sec\(^{-1}\)). Second, we modeled the concentration of CO₂ along our stream transects assuming first order decay of an initial CO₂ pool that was not replenished by any new sources with Equation 4

\[
C(d)=C_0e^{-\lambda d}
\]

(4)

Where \( C(d) \) is the gas concentration at distance \( d \), \( C_0 \) is the concentration at \( d=0 \), and \( \lambda \) is the rate of gas loss (m\(^{-1}\)) calculated from the gas transfer velocity and measures of mean stream depth and velocity determined from field measurements.

In order to evaluate the relative influences of surface versus groundwater flow along these transects, we sampled the \(^{18}\text{O}/^{16}\text{O}\) isotope ratio of water (\(\delta^{18}\text{O}\)-H\(_2\)O) which is an established tracer of groundwater and surface water hydrology in the NHLD [Walker et al., 2003]. Samples were collected by filtering stream water in the field using 0.45 µm syringe filters (Whatman) and collected in bubble-free 10 mL glass vials. Isotope samples were analyzed using a Liquid Water Isotope Analyzer (Los Gatos Research). \(\delta^{18}\text{O}\)-H\(_2\)O (per mil, ‰) is expressed relative to Vienna Standard Mean Ocean Water (VSMOW). Water isotopes were collected less frequently than gases at our transect locations.

We also measured potential hydrologic exchange between the stream and underlying
sediments in August 2012 at 17 of the 30 transect sites using a portable mini-piezometer and manometer [Rosenberry et al., 2008]. The potential vertical advective velocity of water flowing through the hyporheic zone was calculated using Darcy’s Law (Equation 5)

\[ v = -K_2(h_1/l) \]  

(5)

where \( v \) is the velocity of water discharging into the stream (upwelling) or stream water discharging into the hyporheic zone (downwelling), \( K_2 \) is the hydraulic conductivity (fine sand= 0.1 cm s\(^{-1}\) [Domenico and Schwartz, 1990], \( h_1 \) (cm) is the hydraulic head difference between the sediment and the water interface at the piezometer depth (usually 30 cm), and \( l \) (cm) is the distance between the piezometer and the sediment water interface.

We investigated the potential contribution of groundwater to stream CO\(_2\) pools by sampling from a series of wells along a pair of hillslope transects at the Allequash Middle site at 4 to 6 week intervals for 1 year in 2001-2002 using a headspace equilibration method on bubble-free water [Kling et al., 1992; Finlay, 2003]. Walker et al. [2003] and Pint et al. [2003] elucidated groundwater sources and flowpaths for these wells, and water origins were confirmed here by comparing groundwater δ\(^{18}\)O-H\(_2\)O to these published studies. Groundwater sources included (n = 3 for all categories): lake recharge, deep hillslope (precipitation) recharge, shallow hillslope (precipitation) recharge, and the water table in riparian soils. We assume that these sites were representative of the groundwater conditions in the region’s relatively homogeneous glacial sand (see section 2).

3.2.2 In-stream metabolism

We deployed a dissolved oxygen (DO) and CO\(_2\) sensor package for 3-23 days on 4 of the 5 WEBB streams (the lower Allequash Creek reach was not included) between July and September 2001 to evaluate temporal changes in dissolved gases related to metabolism.

Details about sensor design and calibration are reported in Hanson et al. [2003]. We ©2014 American Geophysical Union. All rights reserved.
calculated in-stream metabolism for Allequash Creek (which had the most data points (n=23 days)) to evaluate the contribution of internal processes to potential CO₂ emissions. Net ecosystem production (NEP) was estimated from daily changes in DO and CO₂ using the single station method [Hauer and Lamberti, 2007] using $K_{O2} = 4.8 \text{ m d}^{-1}$ which was selected to match the values measured with the chamber technique at the site (see section 3.1.1).

3.3 Up-scaling technique

We used a common Monte Carlo simulation approach [Beck, 1987; Wallin et al., 2012; Crawford et al., 2013; Striegl et al., 2012] to calculate total CO₂ and CH₄ fluxes (and uncertainty) from stream surfaces in the NHLD. We chose this technique because of a lack of clear spatial patterns or predictive power from multiple linear regressions. We simulated fluxes by combining bootstrapped observations of stream surface area (lengths derived from geographical information system and surveyed stream widths), stream $p_{CO2}$ and $p_{CH4}$, and gas transfer velocities calculated from our 2012 field campaign. We conservatively assumed 200 days of open water. Simulations were repeated 1000 times and we estimated uncertainty by calculating the median and 95% quantiles of the final modeled distributions. The CH₄ gas transfer velocity was estimated according to Equation 6:

$$K_{CH4} = K_{CO2} (Sc_{CH4}/Sc_{CO2})^n$$

(6)

Where $K_{CO2}$ is the CO₂ gas transfer velocity (m d⁻¹), $Sc_{CH4}$ and $Sc_{CO2}$ are the Schmidt numbers for CH₄ and CO₂, respectively, at standard temperature and pressure [Jähne et al., 1987] and $n$ is a coefficient which describes the nature of the water surface. We chose $n$ to equal 0.5 to represent an uncontaminated, moderately turbulent surface [Macintyre et al., 1995]; however, others have reported values for rivers closer to 0.7 (e.g. [Striegl et al., 2012]).
3.4 Statistical Analysis

All statistical analyses were performed using the statistical programming language R [R Core Team, 2012]. In order to test for the effects of lakes on downstream gas concentrations we used two similar models on both the transect dataset and the regional survey dataset. For the transect dataset we used a repeated measures ANOVA to test for the effects of distance downstream and presence of upstream lakes. For the regional survey data, we used a two-way ANOVA to test for the effect of lakes and distance downstream. To assess landscape and chemical influences on $pCO_2$ and $pCH_4$, we used multiple linear regressions on the survey dataset and used backwards and forwards model selection procedures (function ‘regsubsets’, ‘leaps’ package) and the Bayesian Information Criteria ($pCO_2$ and $pCH_4$ were transformed by their natural logarithm). To analyze the relationship between CO$_2$ and O$_2$ saturation time series we fit “Deming” type least squares regressions using the package ‘MethComp’ [Deming, 1943], and we report regression coefficients along with boot-strapped 95% confidence intervals.

4. Results

4.1 Temporal and spatial concentrations and fluxes

Stream $pCO_2$ was highly variable but consistently supersaturated at the five WEBB streams in the Trout Lake watershed (Figure 1a). Mean $pCO_2$ was 3960 µatm (n = 93), but varied between 40 and 12040 µatm (CV = 0.59). There were no clear temporal trends over the growing season, although higher concentrations typically followed rain and increases in discharge. As with $pCO_2$, $pCH_4$ values from the weekly dataset were consistently supersaturated and highly variable (Figure 1b) (mean = 100.2 µatm, range = 21.8 to 191.8, CV = 1.09).

Streams were consistent sources of CO$_2$ to the atmosphere, as expected given their supersaturated status (Figure 2a). Streams had variable $K_{CO2}$ (mean = 3.85 m d$^{-1}$, range =
0.34 to 13.45, CV = 0.58) (Figure 2c) but were not statistically different among our weekly sampling sites (ANOVA, p>0.05). CO₂ fluxes ranged from -0.05 to 2.03 mol m⁻² day⁻¹ and averaged 0.51 mol m⁻² day⁻¹ (n = 93, CV = 0.92). We only measured slight net CO₂ uptake for three of the 93 measurements. All chamber deployments showed linear patterns for dC/dt and the r² values for concentration vs. time used in Equation 1 were typically >0.88. The mean CH₄ flux from our weekly sampling was 8.46 mmol m⁻² day⁻¹ and was highly variable (n = 42, range = 0-60.1 mmol m⁻² day⁻¹, CV = 1.26) (Figure 2b). Like CO₂, there were no clear temporal patterns but CH₄ flux varied among sites (ANOVA, p<0.01), with Allequash Middle having the highest mean flux (18.6 mmol m⁻² day⁻¹). We did not detect net CH₄ uptake during any of our chamber deployments, nor did we observe non-linearity in dCH₄/dt.

Measured pCO₂ from the 52 stream survey was similar to the distribution measured in the 2012 intensive weekly sampling, although with a slightly higher average concentration (mean = 4950 µatm, range = 201-15550 µatm, CV=0.72) (data not shown). Linear models developed from the 52 stream survey showed no significant predictive power based on landscape variables, but relatively strong relationships with chemical variables. The top performing model for regional pCO₂ (natural log transformed) included pH, acid neutralizing capacity (ANC) and calcium (r²=0.86, p<0.01, Table 2). Other high-performing models substituted calcium for sulfate, and iron, respectively, with lower predictive power. Regional pCH₄ (natural log transformed) was best predicted by CO₂, DOC, and water temperature (r²=0.56, p<0.01, Table 2), and less well predicted in model configurations including ANC and calcium.

4.2 Influences on stream gas concentrations

4.2.1 Lake effects

Our first approach to test for lake effects on stream gases was to compare streams with and without upstream lakes across the NHLD. We found no significant effects of

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upstream lake presence or distance from the lake outlet on stream $CO_2$ or $CH_4$ from the 52 stream survey (2-way ANOVA, $p>0.05$ for both gases). Similarly, we did not find that lake presence was a significant landscape predictor of regional stream $pCO_2$ or $pCH_4$ using multiple linear regression. Next, examination of longitudinal profiles also provided little evidence of a persistent influence of lakes on stream gases. Effects of lake and distance on $pCO_2$ or $pCH_4$ along stream reaches with and without upstream lakes were not significant (2-way ANOVA with repeated measures, $p>0.05$). Mean partial pressure of both $CO_2$ (2218 μatm, CV=0.94) and $CH_4$ (157 μatm, CV=1.56) in streams draining lakes overlapped substantially with reference sites lacking upstream lakes (2852 μatm $CO_2$, CV=0.92; and 81 μatm $CH_4$, CV=1.26). Longitudinal patterns of $pCO_2$ were relatively consistent from week to week along each stream regardless of the presence of an upstream lake, showing distinctive site-specific patterns (Figure 3). For example, $pCO_2$ in both Stella (no lake) and Lost (lake present) Creeks increased to a local maximum at 1000 m, then subsequently declined at 2000 m, while $pCO_2$ in Mud Creek was low at 500 m then increased with distance downstream on all sample dates. Average $pCO_2$ was lower, although not significantly so ($p > 0.05$), at 0 m stations (approximate lake outlet) in streams with upstream lakes on most dates. However, comparison of concentrations between mid-lake epilimnetic water and 0 m stations provided ambiguous results. Lost Lake had higher $pCO_2$ than its recipient stream (830 μatm in the lake vs 240 μatm at 0 m), White Sand lake and stream concentrations were similar (310 vs 260 μatm, respectively), and Aurora Lake $pCO_2$ was notably lower than its stream (960 vs 5180 μatm). $pCH_4$ profiles did not follow such strong patterns relative to $pCO_2$ (Figure 4) and were characterized by higher spatial and temporal variance within and among streams. Concentrations both increased and decreased with downstream distance and were similar at 0 m stations for both stream types.
Mean CO₂ residence length (calculated using gas transfer velocities and a distribution of measured stream velocities) was 1400 m. Therefore, only ~5% of the gas in a given parcel of water (e.g., water from a lake outlet) would be present 1400 m downstream. This result is also demonstrated as part of Figure 3 (dashed lines), where the initial pCO₂ is assumed to undergo first order decay solely as a result of emission to the atmosphere with no additional biological or chemical uptake. The same pattern is evident for pCH₄ where the initial CH₄ pool is depleted over relatively short distances (Figure 4).

4.2.2 Groundwater Effects

Despite similarities in C gases for the two stream types, δ¹⁸O-H₂O clearly differentiated lake-drained streams from non lake-drained streams (Figure 5). In general, streams draining lakes had enriched δ¹⁸O-H₂O signatures (-4.5 to -9 ‰) indicating contributions from evaporated epilimnetic lake waters (-4.4 to -5.5‰), whereas streams without upstream lakes had more negative values (-6.5 to -11.5‰) indicating more contribution from terrestrial recharge (-11 to -12‰) [Walker et al., 2003]. Vertical hydraulic gradient measures demonstrated that all streams were likely receiving groundwater discharge. Gradients across the stream hyporheic zone were almost always positive indicating upwelling potential, with only one measurement indicating weak downwelling potential. The mean head difference between streams and the stream bed was 19.6 cm resulting in a mean advective velocity of 5.76x10⁻² cm s⁻¹.

Groundwater pCO₂ in the Allequash Creek basin varied between the various source categories (Figure 6). pCO₂ in relatively old groundwater derived from lake recharge was consistently <2000 µatm, and thus lower than typical stream water concentrations. Deep groundwater derived from hillslope recharge was even more distinct in terms of its highly depleted concentrations (20-85 µatm), suggesting near complete CO₂ consumption during
weathering. CO₂ in younger, precipitation-derived shallow groundwater was variable but consistently supersaturated, ranging between 3520 and 15400 µatm. Groundwater collected from near-stream organic riparian soils demonstrated further enrichment, averaging between 12266 and 22975 µatm over the year (range =5242-50118 µatm).

**4.2.3 In-stream metabolism**

CO₂ and O₂ saturation varied widely among the four stream sites, but O₂ was consistently undersaturated and CO₂ was supersaturated (Figure 7). Slopes of O₂/CO₂ saturation were either steeper than (Stevenson and Allequash Creeks), indicating greater change in O₂ relative to CO₂, or flatter than the idealized case of -1 (North, Mann) due to greater change in CO₂ than O₂ (Table 3). None of the 95% confidence intervals overlapped -1, and slopes appeared to become flatter (less negative) at low O₂ saturations. In all cases, intercepts were significantly greater than zero, consistent with the expectation of additional inputs of CO₂ from external sources.

NEP was negative at Allequash Creek (-479 mmol O₂ m⁻³ d⁻¹ and 647 mmol CO₂ m⁻³ d⁻¹) based on estimates of both O₂ and CO₂ diurnal changes, respectively (Table 4). The CVs of the NEP estimates were 0.31 and 0.27, for O₂ and CO₂, respectively. No clear trends in NEP were apparent across the 23 days of deployment.

**4.3 Upscaling gas fluxes**

Assuming 200 days of open water, we estimate that NHLD streams emit 23.4 Gg C yr⁻¹ to the atmosphere as CO₂ (95% CI = 0.20-310 Gg C yr⁻¹). Median CO₂ efflux calculated from the survey dataset (0.49 mol m⁻² day⁻¹) was nearly equivalent to the mean of weekly chamber measurements (0.51 mol m⁻² day⁻¹). Regional CH₄ emissions were significantly lower (in terms of C) relative to CO₂. We estimate that streams emit 189 Mg C yr⁻¹ as CH₄ to the atmosphere (95% CI=7.1-8510 Mg C yr⁻¹). Since CH₄ has 25 times the radiative forcing of CO₂ over 100 years (kg CH₄:kg CO₂) [Forster et al., 2007], we converted CH₄ to CO₂.
equivalents. CH₄ emissions were 6.30 Gg CO₂-eq, which is 26% of the total estimated CO₂ flux. Normalized to the area of the NHLD, streams emit 3.74 g C m⁻² yr⁻¹.

5. Discussion

5.1 Overview of basic patterns

Streams in the NHLD were consistently supersaturated with, and a net source of CO₂ both within and between years and across a broad range of sites, as has been reported in other studies [Richey et al., 2002; Christensen et al., 2007; Jonsson et al., 2007; Teodoru et al., 2009; Butman and Raymond, 2011; Humborg et al., 2010; Striegl et al., 2012; Wallin et al., 2012; Juutinen et al., 2013]. pCO₂ values in NHLD streams (40-12040 µatm) were typical of temperate and boreal zone streams (360-24000 µatm; see comparisons by Crawford et al. [2013] and Wallin et al., [2012]), and means and ranges were consistent across years despite the temporal separation and small differences in gas collection methods. Streams were also consistent sources of CH₄. pCH₄ and CH₄ fluxes also fell within the range of reported values for aquatic systems, but the paucity of data currently prohibits broad scale comparisons. We found no strong landscape predictors of pCO₂ or pCH₄ (Table 2), which suggests that adjacent landscapes or perhaps in-stream processes are more important than average basin landcover (cf. Lauerwald et al., 2012). Strong relationships between CO₂ and pH, acid neutralizing capacity, and calcium were detected which are consistent with the acid-base dynamics of CO₂ in the freshwater carbonate system [Stumm and Morgan, 1996]. Given that these constituents are widely used to estimate pCO₂ when direct measurements are unavailable, this result is somewhat trivial. Models of regional pCH₄ were weak and somewhat ambiguous as pCO₂ was a significant predictor of pCH₄, but not vice versa. Instead, we show (below) that groundwater discharge and stream metabolism, but not the presence of lakes, can explain the patterns observed for both gases.
5.2 Controls on stream C gas concentrations

5.2.1 Lake Influence

Several lines of evidence indicate that upstream lakes did not substantively influence CO$_2$ or CH$_4$ concentrations in NHLD streams. First, we did not detect significant differences in stream CO$_2$ or CH$_4$ among sites with and without upstream lakes in our spatially extensive survey. Second, repeated measures along stream reaches with and without upstream lakes also failed to reveal a significant lake effect for either CO$_2$ or CH$_4$. Although data directly comparing CO$_2$ in lakes and their recipient streams were limited, stream CO$_2$ concentrations were approximately an order of magnitude higher (ca. 2500-5000 µatm) than summertime lake values in the NHLD (lake mean = 465 µatm from Hope et al. [1996]; undersaturation detected in 10 NHLD lakes [Striegler et al. 2000]), suggesting that lake outflows are incapable of supporting high stream concentrations.

Currently, there is limited information available for extensive comparison of the limited lake effect observed in the NHLD with other regions. Two studies of lake influence on stream CO$_2$ found comparable stream concentrations in close proximity to lake outfalls in lake-rich landscapes of Canada [Teodoru et al., 2009] and Sweden [Ingvarsson, 2008]. However, this effect persisted only for short distances (<500 m) below lakes before being over-ridden by effects of C loading from the surrounding watershed. Given lower lake pCO$_2$ relative to streams in the NHLD, we expected to see some concordance between lake and stream gas concentrations at least at the head of the drainage stream transects. However, transitions between lacustrine and fluvial habitats are not always distinct in this low-relief region. Lake outlets are often shallow, macrophyte-rich habitats that transition gradually into recognizable channels. These conditions may favor localized CO$_2$ accumulation either from focused groundwater discharge (e.g., Lowry et al. [2009]) or enhanced metabolic activity in
transitional zones.

5.2.2 Groundwater

Evidence of a substantial role for groundwater discharge in dictating stream gas concentrations in the NHLD comes from multiple sources. Our model of downstream gas concentration change indicated that without any additional inputs stream CO₂ would decline to a point of almost complete depletion within 1400 m (but would stabilize at atmospheric equilibrium before) (Figure 3). The elevated pCO₂ requires new inputs such as in-stream respiration or influxes of high pCO₂ water, regardless of the presence or absence of an upstream lake. The importance of groundwater as a major CO₂ source is first suggested by the spatial and temporal consistency of longitudinal gas patterns along these transects, coupled with positive vertical hydraulic gradients and stream water isotope values indicative of groundwater discharge. Spatially and temporally consistent gas concentrations due to groundwater upwelling have been reported across diverse geographic settings, including an upland catchment of boreal Alaska, U.S. [Crawford et al., 2013], Danish lowland streams [Sand-Jensen and Staehr, 2012], an upland Scottish peatland stream [Hope et al., 2001], and in a Vermont, U.S. temperate forest stream [Doctor et al., 2008].

For groundwater to support persistently supersaturated stream pCO₂ and pCH₄ levels, discharging waters must be highly enriched in these gases. However, pCO₂ is lost to weathering along groundwater flowpaths, and in the NHLD, gas concentrations can be depleted to near-detection levels [Kenoyer and Bowser, 1992], as we observed for deep groundwaters approaching Allequash Creek. Hence, deep groundwater discharge is incapable of directly supporting the elevated pCO₂ documented in NHLD streams. However, passage of groundwater through biologically active, organic-rich sediments and soils leads to CO₂ enrichment that appears to be the source for this excess gas. These transition zones include CO₂-producing hyporheic sediments [Schindler and Krabbenhoft, 1998] as well as organic-
rich riparian and peat soils examined here.

A final line of evidence providing support for groundwater delivery of C gases was the temporally intensive measures of stream water O\textsubscript{2} and CO\textsubscript{2}. If aerobic metabolism and atmospheric exchange account for the majority of gas flux, then observations of these gases would fall on the 1:1 line, with a slope of -1 (Figure 7). In contrast, we observed data to the right of the 1:1 line, indicating an additional CO\textsubscript{2} source. Diurnal gas changes were superimposed upon a baseline amount of CO\textsubscript{2} at each site, represented by the CO\textsubscript{2} surplus concentration when O\textsubscript{2} was at equilibrium. We interpret this shift of the O\textsubscript{2}/CO\textsubscript{2} curve to the right as a measure of external inputs consistent with discharge of CO\textsubscript{2}-rich groundwater, with distinct differences in delivery of this enriched groundwater among sites.

### 5.2.3 In-stream Metabolism

While external sources clearly affect concentrations and therefore efflux of CO\textsubscript{2} in NHLD streams, metabolic processes also play a role in modifying and supplementing the baseline CO\textsubscript{2} level set by groundwater discharge. Using the single station metabolism method at Allequash Creek, NEP was estimated to be -479 mmol O\textsubscript{2} m\textsuperscript{-2} day\textsuperscript{-1} (CO\textsubscript{2} production of 647 mmol m\textsuperscript{-2} d\textsuperscript{-1}). While we clearly note the need for a more comprehensive metabolism technique that accounts for groundwater inputs [Hall and Tank, 2005], these values provide a view of the potential metabolic contribution to stream gas dynamics. The net heterotrophic status of this and other NHLD streams is not surprising as these systems are relatively enriched in colored DOC [Lottig et al., 2011], and indicates that ecosystem respiration contributes to CO\textsubscript{2} supersaturation. The slopes of O\textsubscript{2}/CO\textsubscript{2} curves did not overlap -1 (Figure 7, Table 3) which could be due to variable respiratory quotients, photosynthetic quotients, or differential diffusivity of O\textsubscript{2} vs. CO\textsubscript{2}. Unraveling the contribution of these drivers will require more investigation of coupled O\textsubscript{2} and CO\textsubscript{2} time series.
5.3 Regional Upscaling

Even in the lake-rich landscape of the NHLD where streams cover <1% of the total surface area, stream gas emissions, facilitated by high C gas partial pressures and high transfer velocities, are large enough to impact the regional C balance. NHLD streams emit 23.4 Gg C yr\(^{-1}\) to the atmosphere as CO\(_2\), which is nearly equivalent to the previous conservative estimate of total lake emissions from the NHLD (27 Gg C yr\(^{-1}\), [Buffam et al., 2011]). We suspect that our method underestimates CO\(_2\) fluxes because samples were always taken during the day when \(p\text{CO}_2\) is predicted to be lowest because of photosynthetic CO\(_2\) uptake (cf. [Crawford et al., 2013]). Recent work at similar spatial scales has demonstrated the substantial role of stream CO\(_2\) emissions in boreal landscapes of Sweden [Wallin et al., 2011], Canada [Teodoru et al., 2009] and northern Finland [Juutinen et al., 2013], but there is little data available to compare with other lake-rich landscapes. The boreal region studied by Teodoru et al. [2009] is also a lake-rich landscape (8.3% total lake area) and has very similar gas emissions between streams and lakes (23.9% and 34.8% of total fluxes, respectively).

Our findings, along with those of Teodoru et al., [2009] indicate the need for a shift away from a lake-centric view towards a more inclusive approach that incorporates all surface waters, groundwaters, and their interactions in lake-rich landscapes [Soranno et al., 2009].

Our estimate of stream CO\(_2\) emissions is much higher than the 1.4 Gg C yr\(^{-1}\) calculated by Buffam et al. [2011] for the NHLD. Our larger estimate is primarily due to the larger mean \(K_{CO2}\) documented in this study, but our randomized up-scaling procedure also contributes to a higher estimate because we did not group streams and fluxes by stream size as in Buffam et al., [2011] because no relationship between stream size (as measured by catchment area, width, or Q) was detected. Mean \(K_{CO2}\) in 2012 was 3.8 m d\(^{-1}\) (range = 0.34 to 13.5 m day\(^{-1}\)) compared to the value of 2 m d\(^{-1}\) chosen by Buffam et al., [2011] based on
published values for streams across the globe. Clearly, selecting lower values of $K_{CO2}$ would decrease our total flux estimate, but the magnitude would not change. Our chamber design has shown comparable $K_{CO2}$ values to volatile gas tracer experiments and published values for boreal landscapes [Crawford et al., 2013]. At present, there are very few $K_{CO2}$ values for direct comparison with NHLD streams, but in general, our values were greater than those documented in some low-gradient Québec streams using a similar chamber technique (typically $< 1 \text{ m day}^{-1}$) [Campeau et al., 2014]. We acknowledge that chambers likely add bias to flux estimates by disturbing the water surface and level of turbulence [cf., Campeau et al., 2014], but we cannot yet quantify the magnitude of this uncertainty. Work by Gålfalk et al. [2013] indicates that careful application of the chamber technique does not lead to an overestimate of $K_{CO2}$. However, a more thorough comparison of chamber techniques in small streams is needed, and comparisons need to be made with established models like those developed for channelized Swedish streams [Wallin et al., 2011], and for larger North American streams [Raymond et al., 2012]. Higher mean $K_{CO2}$ measured in this study could also be due to chemical enhancement of CO$_2$ exchange [Stumm and Morgan, 1996; Wanninkhof and Knox, 1996] when pH$>$7 and water temperature is $\sim$20° [Bade and Cole, 2006]. The range of temperatures and pH from our weekly and survey dataset indicate that chemical enhancement of gas transfer is likely for some streams.

In addition to CO$_2$, streams emit 189 Mg C yr$^{-1}$ as CH$_4$ to the atmosphere (6.30 Gg CO$_2$-eq), which is 26% of the total estimated CO$_2$ flux with respect to warming potential. Stream CH$_4$ dynamics have been documented by few authors [Baulch et al., 2011; Crawford et al., 2013; Jones and Mulholland, 1998; Hope et al., 2001; Billett and Moore, 2008]. Yet, work by Bastviken et al. [2011] suggests that lakes and streams are important components of global methane and greenhouse gas budgets. The realization that anaerobic processes are important stream processes in this region and perhaps many others [Jones and Holmes, 1996]
requires that future research incorporate processes such as methane production and emission.

Normalized to the area of the NHLD, streams emit 3.74 g C m\(^{-2}\) yr\(^{-1}\), compared to approximately 5 g C m\(^{-2}\) yr\(^{-1}\) (DOC+DIC) exported annually by streams in the NHLD [Buffam et al., 2011]. The stream evasion/export ratio therefore is approximately 0.75:1 (1.48:1 including lake emissions) which is higher than the ratio for Sweden (0.2:1, [Humborg et al., 2010]), but less than the ratio for the rest of the Mississippi River basin (0.9:1, [DuBois et al., 2010]), the Yukon River basin (1:1, [Striegl et al., 2012]) or the Amazon (6.6:1, [Richey et al., 2002]). The NHLD riverine evasion/export ratio is comparable to broad estimates for the globe (0.83:1 to 1.2:1, [Cole et al., 2007; Battin et al., 2009]) which suggests that the NHLD does not have anomalous C gas emissions relative to total C cycling and that our results may apply to other lake-rich landscapes around the globe.

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Figure 1. Distributions of stream $pCO_2$ (a) and stream $pCH_4$ (b) from the weekly sampling program in 2012.
Figure 2. Distributions of weekly stream CO$_2$ flux (a), CH$_4$ flux (b), and gas transfer velocity [$K_{CO2}$, (c)] from the weekly sampling program in 2012.
Figure 3. Longitudinal transect $pCO_2$ from streams without upstream lakes (left column; a,c,e) and streams draining lakes (right column; b,d,f); points are the mean (n=5), error bars equal one standard deviation; blue lines are predictions of $pCO_2$ derived from the first sampling location (0 m) with losses by emission at constant rates, assuming no new inputs and no in-stream consumption of CO$_2$; streams are Stella (a), Lost (b), Mud (c), White Sand (d), North (e), Aurora (f).
Figure 4. Longitudinal transect $p\text{CH}_4$ from streams without upstream lakes (left column; a,c,e) and streams draining lakes (right column; b,d,f); points are the mean (n=5), error bars equal one standard deviation; blue lines are predictions of $p\text{CH}_4$ derived from the first sampling location (0 m) assuming constant emission rates, no new inputs and no in-stream consumption of CH$_4$; sites are as indicated in Figure 3
Figure 5. Boxplots of the δ¹⁸O signature of stream water from streams with no upstream lake (left) and streams draining lakes (right) (n=60)
Figure 6. Mean (+1 standard error) $pCO_2$ concentrations among different groundwater categories in the Allequash Creek catchment.
Figure 7. Plot of CO$_2$ and O$_2$ dynamics in streams and lakes in the NHLD; regression parameters in Table 3; excess saturation calculated from Henry’s Law corrected for temperature.