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Key Points:

- $p\text{CO}_2$ and $p\text{CH}_4$ decrease, whereas the k_{600} increases with increasing stream order
- Small streams and spring thaw period play a large role in regional C balance
- Rivers are significant sources of CO_2 and unexpectedly large sources of CH_4

Supporting Information:

- Readme
- Auxiliary material

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Regional contribution of CO_2 and CH_4 fluxes from the fluvial network in a lowland boreal landscape of Québec

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Abstract Boreal rivers and streams are known as hot spots of CO_2 emissions, yet their contribution to CH_4 emissions has traditionally been assumed to be negligible, due to the spatially fragmented data and lack of regional studies addressing both gases simultaneously. Here we explore the regional patterns in river CO_2 and CH_4 concentrations ($p\text{CO}_2$ and $p\text{CH}_4$), gas exchange coefficient (k), and the resulting emissions in a lowland boreal region of Northern Québec. Rivers and streams were systematically supersaturated in both gases, with both $p\text{CO}_2$ and $p\text{CH}_4$ declining along the river continuum. The k was on average low and increased with stream order, consistent with the hydrology of this flat landscape. The smallest streams (order 1), which represent < 20% of the total river surface, contributed over 35% of the total fluvial greenhouse gas (GHG) emissions. The end of winter and the spring thaw periods, which are rarely included in annual emission budgets, contributed on average 21% of the annual GHG emissions. As a whole, the fluvial network acted as significant source of both CO_2 and CH_4 , releasing on average 1.5 tons of C (CO_2 eq) $\text{yr}^{-1} \text{ km}^{-2}$ of landscape, of which CH_4 emissions contributed approximately 34%. We estimate that fluvial CH_4 emissions represent 41% of the regional aquatic (lakes, reservoirs, and rivers) CH_4 emissions, despite the relatively small riverine surface (4.3% of the total aquatic surface). We conclude that these fluvial networks in boreal lowlands play a disproportionately large role as hot spots for CO_2 and more unexpectedly for CH_4 emissions.

1. Introduction

The boreal biome contains one of the world's highest densities of inland waters, which are now increasingly recognized as significant players in the overall carbon (C) and greenhouse gas (GHG) (CO_2 and CH_4) balance of this biome [Bastviken et al., 2011; Cole et al., 2007]. Over the past decade, it has become apparent that CO_2 emissions from boreal lakes and rivers are large, of the same magnitude as the C export to the sea [Aufdenkampe et al., 2011; Striegl et al., 2012; Wallin et al., 2013] and the landscape net ecosystem exchange [Billett and Harvey, 2012; Dinsmore et al., 2010; Jonsson et al., 2007].

Our understanding of the magnitude of CH_4 emissions from boreal aquatic ecosystems has lagged well behind that of CO_2 . A recent meta-analysis of existing data concluded that CH_4 emissions from boreal inland waters (lakes, rivers, and reservoirs but excluding wetlands) could be in the order of 8 Tg $\text{CH}_4 \text{ yr}^{-1}$ [Bastviken et al., 2011], in the same magnitude as the total CH_4 emissions from the northern wetlands (in the range of 30–40 Tg $\text{CH}_4 \text{ yr}^{-1}$) [Bartlett and Harriss, 1993], which are considered as one of the largest sources of CH_4 . These large-scale aquatic CH_4 emission estimates are based on few and spatially fragmented data but are also biased in terms of the types of systems covered. Up to the present, research on boreal CH_4 emissions has focused mainly on wetlands [Bartlett and Harriss, 1993; Macdonald et al., 1998; Roulet et al., 1992], and to a much lesser extent, on lakes [Bastviken et al., 2004, 2011; Juutinen et al., 2009] and reservoirs [Duchemin et al., 1995; Teodoru et al., 2012]. A major gap in these regional aquatic CH_4 budgets is the almost complete absence of information on the potential contribution of flowing waters [Bastviken et al., 2011].

Streams and rivers play a role as conduits for terrestrially produced CO_2 to the atmosphere [Cole et al., 2007; Oquist et al., 2009; Wallin et al., 2013] but are also increasingly recognized as reactors, processing large amounts of organic carbon leaching from terrestrial ecosystems and thus generators of CO_2 [Battin et al., 2008; Cole and Caraco, 2001; Humborg et al., 2010]. The combined result of these two functions (the conduit and the reactor) are extremely high CO_2 fluxes, contributing to up to 65% to the total aquatic CO_2 emissions,

while accounting for less than 5% of the total aquatic surface [Humborg *et al.*, 2010; Jonsson *et al.*, 2007; Teodoru *et al.*, 2009]. This in turn has motivated increased efforts to estimate CO₂ emissions from rivers and streams at regional and continental scales [Aufdenkampe *et al.*, 2011; Butman and Raymond, 2011; Humborg *et al.*, 2010].

Contrary to their role in CO₂ dynamics, streams and rivers have rarely been considered significant sites for CH₄ emissions, partly due to their relatively small surface coverage, and the perception that running waters do not provide suitable conditions for methane production. There is evidence, however, that these assumptions are unfounded: Streams have been shown to act as conduits for significant fluxes of terrestrially produced CH₄ to the atmosphere, as they are for CO₂ [Crawford *et al.*, 2013; Hope *et al.*, 2004; Jones and Mulholland, 1998a]. In addition, methane production has been documented in river systems [Richey *et al.*, 1988] and stream beds have also been identified as sources of atmospheric CH₄ through macrobubble release [Baulch *et al.*, 2011; Bergström *et al.*, 2007]. While this fragmented evidence suggests that streams and rivers may potentially be sites of significant CH₄ emissions, the paucity of published measurements on stream CH₄ emissions does not allow assessing the importance of CH₄ emissions at regional or even watershed scales. This is particularly problematic in northern landscapes, which are characterized by extensive and complex river networks.

Here we present results from a large-scale survey of CO₂ and CH₄ concentration and emissions from the fluvial network in the Abitibi and James Bay regions of boreal Québec. These regions represent a type of boreal landscape that is widespread across North America and the Siberian Plateau characterized by a flat topography, clay-dominated deposits, and dominance of peat bogs and wetlands in the case of the James Bay region. In a companion paper, we explore the drivers of these fluxes and their connections to river properties [Campeau and del Giorgio, 2013]. The component that we present here focuses on upscaling the resulting fluxes across the fluvial network at the regional level.

Our approach in this paper is to quantify regional patterns in both surface water gas concentrations ($p\text{CO}_2$ and $p\text{CH}_4$) and gas transfer velocity (k_{600}), and to explore the geographical and hydrological factors that shape these regional patterns. We further combined the patterns in $p\text{CO}_2$, $p\text{CH}_4$, and k_{600} in relation to the Strahler stream order to develop estimates of CO₂ and CH₄ emissions from the entire fluvial network in a region covering over 44,000 km² for the complete ice-free season. In addition, we carried out measurements of $p\text{CO}_2$, $p\text{CH}_4$, and fluxes both under the ice and immediately after ice melt in a subset of rivers to incorporate late winter and early spring gas fluxes to our open water estimates of regional CO₂ and CH₄ emissions, in order to derive annual regional emissions that account for this critical period of the year. We have then combined the regional empirical models of ambient gas concentration and exchange with a detailed geographical analysis of the fluvial network to derive the actual CO₂ and CH₄ emissions from the ensemble of rivers in the two regions.

2. Material and Methods

2.1. Study Region and Sampling Design

We sampled rivers and streams located in the boreal mixed forest of Québec, Canada, within two distinct regions: Abitibi (47–48°N, 78–79°W) and James Bay (48–49°N, 78–79°W) (Figure 1). These two regions are marginal landforms created by the retreat of the Laurentian ice sheet that formed a large plain of glaciofluvial sediments rich in till, clay, and organic deposits. The regions differ from each other in terms of their forest and soil composition as well as their aquatic network configuration, with large lakes dominating the Abitibi region, and small lakes and wetlands more prevalent in the James Bay region (Table 1). The fluvial network in both regions is extensive and forms a trellis and dendritic drainage pattern, with systems ranging up to 6 Strahler stream orders. The low order streams (1 to 3) in the Abitibi region are intensively affected by beaver dams, which strongly influence the hydrological regime. However, beaver impoundments are almost non-existent in the James Bay region due to the sparse coverage of broadleaf forests.

We surveyed 46 different streams and rivers between May 2010 and May 2011, 31 located in the Abitibi region and 15 in the James Bay region (Figure 1). The streams and rivers were selected to include all different stream orders present in each region and to be part of independent catchments for a better representation of the regional landscape attributes. All 46 sites were visited once in midsummer (July and August 2010), and 32 sites were visited in early summer and in autumn (end of May and June 2010 and October 2010, respectively).

Figure 1. Map showing the delineation of the region for which we have estimated the annual fluvial CO_2 and CH_4 emissions ($44,182 \text{ km}^2$) and the distribution of sampled rivers and streams (stream order 1 to 6) across the two studied regions, Abitibi (below 49th parallel) and James Bay (above 49th parallel). The map also shows the low topography and the extent of the aquatic coverage, which comprises 9% of the territory.

2.2. Surface Water $p\text{CO}_2$ and $p\text{CH}_4$

Surface water $p\text{CO}_2$ and $p\text{CH}_4$ were measured using the headspace equilibrium method. Polypropylene syringes of 60 mL were used to collect 30 mL of stream water from approximately 10 cm below the surface and added to 30 mL of ambient air to create a 1:1 ratio of ambient air : stream water. For $p\text{CO}_2$, triplicate syringes were vigorously shaken for 1 min in order to equilibrate the gases in water and air. The resulting headspace was directly injected into an infrared gas analyzer (PP Systems, EGM-4). The original surface water $p\text{CO}_2$ was then calculated based on the headspace ratio and the in situ measured ambient air $p\text{CO}_2$ (equation S1 and details in the supporting information).

A similar procedure was used for collection of surface water $p\text{CH}_4$. The resulting 30 mL headspace, however, was rather injected into 30 mL glass vials equipped with rubber stoppers (20 mm of diameters red bromobutyl) filled with saturated saline solution (D. Bastviken, personal communication, 2010) and kept inverted until analysis. In the lab, the gas in the headspace of the vials was injected into a gas chromatograph with a flame ionization detector (Shimadzu GC-8A) to determine its CH_4 concentration. The original surface water $p\text{CH}_4$ was then calculated according to the headspace ratio (equation S1) and assuming a constant ambient air $p\text{CH}_4$ of $1.77 \mu\text{atm}$ [Denman et al., 2007].

Table 1. Landscape and Climatic Characteristics for the Abitibi and James Bay Regions^a

Region	Area (km^2)	Elevation (m)	Terrestrial Coverage (%)		Aquatic Coverage (%)		Dominant Soil Surface Deposit (%)		Dominant Tree Species
Abitibi	30,400	304 (± 28)	Coniferous	18%	Lakes	11%	Clay	53%	balsam fir (<i>Abies balsamea</i>)
			Broadleaf	9%	Wetlands	3%	Peat	18%	white spruce (<i>Picea glauca</i>)
			Mixedwood	41%	Fluvial	0.5%	Till	16%	white birch (<i>Betula papyrifera</i>)
			Shrubland	10%	Network		Bedrock	10%	american aspen (<i>Populus tremuloides</i>)
			Other ^b	8%			Sand	4%	
James Bay	13,782	296 (± 33)	Coniferous	43%	Lakes	3%	Clay	68%	black spruce (<i>Picea mariana</i>)
			Broadleaf	2%	Wetlands:	18%	Peat	30%	
			Mixedwood	20%	Fluvial	0.4%	Till	2%	Undergrowth
			Shrubland	11%	Network				mosses (<i>Hypnaceae</i>)
			Other ^b	3%					shrubs (<i>Ericaceae</i>)

^aThe land cover data were provided by the National Topographic Data Base (NTDB).

^bOther types of terrestrial coverage include agricultural land, grassland, or bare ground.

2.3. Determination of $k\text{CO}_2$ and CO_2 Fluxes

Instantaneous CO_2 fluxes ($f\text{CO}_2$) ($\text{mmol m}^{-2} \text{ d}^{-1}$) across the water-air interface were measured in situ using floating chambers, following Vachon *et al.* [2010]; see details in the supporting information. All $f\text{CO}_2$ measurements were made at the same location and time as surface water $p\text{CO}_2$ measurements. In brief, the chamber was placed on the water surface, pressure was released, and the $p\text{CO}_2$ in the chamber was subsequently recorded every minute for 10 min. The rate of change in $p\text{CO}_2$ in the chamber was used to estimate the CO_2 flux, $f\text{CO}_2$ ($\text{mol m}^{-2} \text{ d}^{-1}$) (equation S2 and details in the supporting information). We further used $f\text{CO}_2$ to estimate $k\text{CO}_2$ by inverting the equation describing Fick's law, (see equation S3 and details in the supporting information). To simplify the exploration of regional patterns of gas exchange across the fluvial network, we standardized $k\text{CO}_2$ to a Schmidt number of 600 to derive a k_{600} , following the equation from Jähne *et al.* [1987] (equation S4 and details in the supporting information).

2.4. Quantifying Diffusive and Nondiffusive CH_4 Fluxes

The CH_4 fluxes ($f\text{CH}_4$) were measured with the floating chamber; at the same time, the CO_2 flux was determined, except that the change in $p\text{CH}_4$ in the floating chamber was determined at 0, 5, and 10 min, by withdrawing 30 mL from the chamber's headspace through an enclosed system of syringes. These air samples were stored in airtight vials and analyzed in the laboratory as described above. The rate of change of $p\text{CH}_4$ in the floating chamber was used to calculate the $f\text{CH}_4$ with the equation S2 (see supporting information) and replacing CO_2 by CH_4 . We estimated the potential contribution of nondiffusive $f\text{CH}_4$ to the overall $f\text{CH}_4$ [Prairie and del Giorgio, 2013] by first calculating the theoretical diffusive $k\text{CH}_4$ on the basis of our empirically determined k_{600} (equation S5 and details in the supporting information) and then calculating the theoretical diffusive CH_4 flux ($\text{mmol m}^{-2} \text{ d}^{-1}$; equation S6 and details in the supporting information). We then used the difference between fD_{CH_4} and the $f\text{CH}_4$ measured from the floating chambers as an estimate of the potential nondiffusive $f\text{CH}_4$ [Prairie and del Giorgio, 2013].

2.5. Quantifying CO_2 and CH_4 Emissions During the Spring Thaw

We carried out measurements of $p\text{CO}_2$ and $p\text{CH}_4$ under ice and gas fluxes immediately after ice melt in a subset of the rivers; we have used the resulting patterns in gas buildup to incorporate late winter and early spring gas fluxes to our open water estimates of regional CO_2 and CH_4 emissions in order to derive more robust annual emissions. We quantified the CO_2 and CH_4 emissions during the spring thaw using the average CO_2 and CH_4 fluxes to the atmosphere measured with floating chambers in mid-April, approximately 7 days after the start of the ice break, and in early-May, approximately 21 days after the start of the ice break. We assumed a linear decrease in the average CO_2 and CH_4 fluxes between mid-April to early-May and used this relationship to estimate the average daily CO_2 and CH_4 fluxes for the entire spring thaw period (approximately 30 days).

2.6. River Characterization

Stream properties were determined, either directly on site or from digitized maps with a resolution of 1:50,000 scale made available at Natural Resources Canada (National Topographic Data Base (NTDB)). All geographical analyses were performed on ArcMap geographic information system version 9.3 with hydrological extensions. For each sampled site, we delineated the catchment area and calculated the cumulative length of digitized stream and river segments within this area. This corresponds to the total length of streams and rivers upstream of the sampled site (total stream length, TSL), which was used as an index of the position of each river within the fluvial network hierarchy. This index is analogous to the Strahler stream order but allowed to better explore gas dynamics along continuous gradients. We also manually determined the Strahler stream order from the digitized streams and rivers (NTDB) for each of the 46 sampled sites in order to facilitate comparison with previous studies and also upscaling, as described below. Sites that were too narrow to appear on digitized maps were considered as a separate category (stream order 0). We measured the channel width and depth in situ with a measuring tape or a sonar depth meter at the cross section of the stream or river. The available material did not allow measuring these properties directly on site for the largest rivers (stream order 6), and for these we used satellite images to estimate the average width. We also measured water velocity (m s^{-1}) at discrete points across the channel (from 1 to 5, depending on stream width) using a 2-D Acoustic Doppler Velocimeter (Sontek, FlowTracker) and used this combined with stream morphometry to derive water discharge.

2.7. Determining Total River and Stream Areal Coverage

Streams and rivers are represented on digitized maps as fragmented segments, which do not facilitate estimates of the regional abundance and surface occupied by streams and rivers on the basis of their sizes or lengths. Consequently, we chose to base our regional-scale estimate of total fluvial area on the tributary classification system of Strahler stream orders, which is derived from the total stream length, and on that basis calculate the total area covered by each of the six different stream orders present in the fluvial network of both regions. We performed a digital elevation model (DEM) interpolation to calculate the length (m) of each stream order in the two regions and combined it to the average channel width (m) corresponding to each stream order from the data collected on the field for our 46 sampled sites (Table S1 and details in the supporting information).

2.8. Upscaling Fluvial CO₂ and CH₄ Emissions

We combined the patterns in $p\text{CO}_2$, $p\text{CH}_4$, and gas exchange (k_{600}) to estimate the average diffusive CO₂ and CH₄ fluxes for each Strahler stream order and used these to upscale fluxes to the entire fluvial network in a region covering 44,182 km². The total CO₂ and CH₄ diffusive emissions were calculated by combining our estimates of areal extent of each stream order (Table S1) to their respective mean surface water $p\text{CO}_2$ and $p\text{CH}_4$ (μatm) and k_{600} (m d⁻¹). The average nondiffusive CH₄ emissions per stream order were combined to the diffusive fluxes to yield an estimate of total CH₄ emissions.

The total annual emissions were determined by combining the estimated CO₂ and CH₄ emissions for the spring thaw period (30 days) to the estimate for the ice-free season (184 days), representing a combined 214 days. This choice of periods was based on the data we obtained with continuous water level and temperature records from level loggers (Trutrack, WT-HR Mark 3 data loggers, Intech instruments LTD) that we deployed on a subset of 13 streams (Figure S1 and details in the supporting information). The resulting data allowed us to reconstruct the annual temperature and discharge cycle for streams of different orders. The ice-covered period (151 days from November to April) was considered neutral in terms of gas fluxes. This assumption is unrealistic and needs to be further investigated; likely resulting in an overall underestimation of the annual fluxes.

2.9. Statistical Analyses

Statistical analyses were executed on JMP®9.3 (SAS institute). Data were log transformed in order to meet conditions of homoscedasticity and normality when needed. We performed simple linear regressions (SLR) and covariance analyses (ANCOVA) to test significant differences in the patterns observed with the SLR models between either the two regions (Abitibi and James Bay) or between the different sampling periods of the ice-free season. In several cases, data points were removed from the analysis in order to meet the statistical assumptions, in which cases we analyzed the Cook's distances to validate the removal of those data points. Those outliers are presented and identified on the figures and were nonetheless integrated in the upscaling exercises to derive regional fluvial emissions.

3. Results

3.1. Regional Patterns of Surface Water $p\text{CO}_2$ and $p\text{CH}_4$ and Gas Exchange (k_{600})

Despite contrasting landscape properties between the Abitibi and James Bay regions (Table 1), the average $p\text{CO}_2$, $p\text{CH}_4$, k_{600} , $f\text{CO}_2$, and $f\text{CH}_4$ were not significantly different between the two regions (Table 2). The surface water $p\text{CO}_2$ and $p\text{CH}_4$ were systematically supersaturated relative to the atmosphere across the fluvial network in both regions, ranging 2 orders of magnitude for $p\text{CO}_2$ and over 4 orders of magnitude for $p\text{CH}_4$ (Table 2). We observed a power law decrease of both mean open water surface water $p\text{CO}_2$ and $p\text{CH}_4$ (μatm) with increasing total stream length (TSL, in kilometers) (Figures 2a and 2b)

$$\log p\text{CO}_2 = 3.61 - (0.18 \log \text{TSL}) \quad r^2 = 0.68, n = 41, p < 0.0001 \quad (1)$$

$$\log p\text{CH}_4 = 3.45 - (0.34 \log \text{TSL}) \quad r^2 = 0.69, n = 39, p < 0.0001 \quad (2)$$

There was no statistically significant difference in the large-scale patterns for either $p\text{CO}_2$ or $p\text{CH}_4$ between the Abitibi and James Bay regions (ANCOVA (Figure 2a) intercept ($p > 0.43$) and slope ($p > 0.61$); ANCOVA (Figure 2b) intercept ($p > 0.60$) and slope ($p > 0.75$)).

Table 2. Summary of Average, Minimum, and Maximum Surface Water $p\text{CO}_2$, $p\text{CH}_4$, $f\text{CO}_2$, and $f\text{CH}_4$ Obtained Directly From Chamber Measurements and Gas Exchange Velocity ($k\text{CO}_2$) Derived From the Chamber CO_2 Evasion Measurements^a

	All Sites				Abitibi		James Bay		t Test p-Value
	n	Average	Min	Max	n	Average	n	Average	
$p\text{CO}_2$ (μatm)	134	2,959	509	10,537	104	3,125	30	2,384	0.07
$p\text{CH}_4$ (μatm)	129	1,781	24	28,684	100	2,030	29	923	0.16
$k\text{CO}_2$ (m d^{-1})	110	0.86	0.07	4.33	80	0.87	30	0.83	0.86
$f\text{CO}_2$ ($\text{mg C m}^{-2} \text{d}^{-1}$)	110	888	19.70	5,879	80	905	30	847	0.79
$f\text{CH}_4$ ($\text{mg C m}^{-2} \text{d}^{-1}$)	97	97.8	0.33	2,576	69	122	29	37.0	0.27

^aAverages for the two regions, Abitibi and James Bay are also presented with the respective p value for statistical differences between the two regions. The table includes the data collected during the ice-free season (May to October) and excludes all the measurements made during the ice-covered periods (November to March) and spring thaw (April and May).

Figure 2. (a) Surface water $p\text{CO}_2$ (upper), (b) $p\text{CH}_4$ (lower) (both in μatm), and (c) gas exchange coefficient (k_{600} , in m d^{-1}) as a function of the total stream length (TSL) (km). Data are log transformed and each dot represents the average $p\text{CO}_2$, $p\text{CH}_4$, or k_{600} for each of the 46 different streams and rivers sampled over the ice-free season (from May to October). Error bars represent the standard error for each site between the sampling periods. The light gray and dark gray dots represent the sites in the Abitibi and James Bay region, respectively, while the white dots represent the sites that were removed from the analysis (equations (1)–(3)). In the fluvial network of Abitibi and James Bay, the $p\text{CH}_4$ was especially variable among the smallest headwater streams (stream order 0), where it ranged from 59 to 9611 μatm . We excluded three small headwater streams of the regional pattern of $p\text{CO}_2$ and $p\text{CH}_4$ for which the $p\text{CH}_4$ was distinctively below the regional trend throughout the ice-free season likely driven by catchment CH_4 inputs. Only two outliers appear on Figure 2c because the two smallest headwater streams were too narrow to install the floating chamber and measure gas fluxes. We also removed two streams sampled in steep hillslopes, where the stream flow was much faster than in any of the other streams, and which had a $p\text{CO}_2$ and $p\text{CH}_4$ well below the regional trend, possibly due to turbulence-enhanced atmospheric evasion.

Figure 3. (a) Total CH₄ flux measured with the floating chamber, as a function of the strictly diffusive CH₄ flux (both in $\text{mg C m}^{-2} \text{d}^{-1}$) derived from the k_{600} . Nondiffusive $f\text{CH}_4$ corresponds to points that fall above the 1:1 line. (b) Nondiffusive $f\text{CH}_4$ ($\text{mg C m}^{-2} \text{d}^{-1}$) as a function of surface water $p\text{CH}_4$ (μatm). Data are log transformed and fitted to a power model (equation (4)).

The k_{600} , derived from floating chamber measurements, varied significantly throughout the seasons ($p < 0.0001$), following changes in discharge and water velocity. Autumn (October) and spring (late-April and early-May) high-flow periods had the highest average k_{600} (1.65 and 2.71 m d^{-1} , respectively), whereas the lowest average k_{600} (0.68 m d^{-1}) occurred during summer base flow (June to August). There was a significant positive relationship between the k_{600} (m d^{-1}) and the TSL (km) (Figure 2c)

$$\log k_{600} = -0.42 + (0.18 \log \text{TSL}) \quad r^2 = 0.27, n = 41, p = 0.0003 \quad (3)$$

As opposed to gas concentration ($p\text{CO}_2$ and $p\text{CH}_4$) and k_{600} , there was no significant pattern of either $f\text{CO}_2$ or $f\text{CH}_4$ with TSL, resulting in a rather constant average flux rate (Table 2) across the fluvial network.

3.2. Diffusive and Nondiffusive CH₄ Fluxes

To quantify the nondiffusive component of the total $f\text{CH}_4$, we compared the $f\text{CH}_4$ measured in the floating chambers with the diffusive $f\text{CH}_4$ ($fD\text{-CH}_4$) calculated based on the measured k_{600} . The comparison between $f\text{CH}_4$ and $fD\text{-CH}_4$ (Figure 3a), with most of the values falling above the 1:1 line, indicates the presence of nondiffusive CH₄ fluxes, averaging 70.3 $\text{mg C m}^{-2} \text{d}^{-1}$ and ranging from 0 to 2421 $\text{mg C m}^{-2} \text{d}^{-1}$. There was a positive relationship between the estimated nondiffusive $f\text{CH}_4$ ($\text{mg C m}^{-2} \text{d}^{-1}$) and the $p\text{CH}_4$ (μatm) (Figure 3b)

$$\log N - Df\text{CH}_4 = -2.22 + (1.10 \log p\text{CH}_4) \quad r^2 = 0.48, n = 59, p < 0.0001 \quad (4)$$

3.3. CO₂ and CH₄ Dynamics During Spring Thaw

There was a significant under-ice gas accumulation during winter, with $p\text{CO}_2$ and $p\text{CH}_4$ peaking at the end of the winter, averaging 4793 μatm $p\text{CO}_2$ $n = 13$ (range 1018 to 17,599 μatm) and 14,863 μatm $p\text{CH}_4$ $n = 13$ (range 103 to 162,933 μatm) (Figures 4a and 4b). Following ice break, both $p\text{CO}_2$ and $p\text{CH}_4$ decreased rapidly,

Figure 4. Box-and-whisker plots showing the surface water (a) $p\text{CO}_2$, (b) $p\text{CH}_4$, (c) $f\text{CO}_2$, and (d) $f\text{CH}_4$ for the different sampling periods. The gray boxes represent median values (middle lines), first and third quartiles (outer lines). Whiskers represent the complete range from maximum to minimum values, while the white squares represent mean values and open circles represent the maximum values. The different sampling periods on the box plots correspond to the end of the ice-covered period (March), approximately 1 week after the ice break (mid-April), approximately 3 weeks after the ice break (early-May), and the overall ice-free season from late May to the end of October.

returning to ice-free season averages (Figures 4a and 4b). During spring thaw, $f\text{CO}_2$ was twofold higher than the average fluxes measured during the ice-free season, averaging $2766 \text{ mg C m}^{-2} \text{ d}^{-1}$ in April and $1529 \text{ mg C m}^{-2} \text{ d}^{-1}$ in May (Figure 4c). In contrast, $f\text{CH}_4$ was lower in April and May than during the ice-free season, averaging $16.9 \text{ mg C m}^{-2} \text{ d}^{-1}$ and $5.8 \text{ mg C m}^{-2} \text{ d}^{-1}$, respectively (Figure 4d). These fluxes, integrated over a period of 30 days, resulted in C evasion from the entire fluvial network of 13,075 tons of $\text{CO}_2\text{-C}$ and 75 tons of $\text{CH}_4\text{-C}$ to the atmosphere.

3.4. Regional Estimates of Fluvial CO_2 and CH_4 Emissions

The regional-scale estimates (Table 3) demonstrated that the contribution to total fluvial C emissions decreased with increasing stream order, from the highest contribution from the order 1 streams (8057 tons of $\text{CO}_2\text{-C}$ and 1195 tons of $\text{CH}_4\text{-C}$) to the smallest from order 6 rivers (2394 tons of $\text{CO}_2\text{-C}$ and 29 tons of $\text{CH}_4\text{-C}$). The emissions from the stream order 1 also include the emissions from the small headwater streams (stream order 0), which represented 842 tons of $\text{CO}_2\text{-C}$ and 60 tons of $\text{CH}_4\text{-C}$. The fluvial network released a total of

Table 3. Summary Table Presenting the Results From the Upscaling Exercise Estimating Fluvial CO_2 , CH_4 , and Total GHG Emissions for the Abitibi and James Bay Regions^a

Strahler Stream Order	Regional Area (km ²)	$p\text{CO}_2$ (µatm)	$p\text{CH}_4$ (µatm)	k_{600} (m d ⁻¹)	$f\text{CO}_2$ (mg C m ⁻² d ⁻¹)	Diffusive $f\text{CH}_4$ (mg C m ⁻² d ⁻¹)	Non-diffusive $f\text{CH}_4$ (mg C m ⁻² d ⁻¹)	CO_2 Emissions Tons of C (yr ⁻¹)	CH_4 Emissions Tons of C (yr ⁻¹)	GHG Emissions Tons of C (eq CO_2)
1	38.45 (±28.5)	3,981	2,746	0.56	1,139	42.43	126.49	8,057	1,195	18,098
2	27.07 (±17.1)	3,184	1,736	0.58	998	23.02	43.42	4,964	331	7,742
3	30.96 (±29.1)	2,209	1,005	0.49	462	10.48	12.84	2,630	133	3,746
4	30.26 (±28.0)	1,569	647	1.38	992	22.48	19.78	5,521	235	7,498
5	34.41 (±14.5)	1,443	585	2.28	1,079	31.84	63.16	6,834	601	11,886
6	28.99 (±7.2)	937	146	1.24	449	4.35	1.07	2,394	29	2,637
Emissions during the ice-free season (184 days)								30,402	2,524	51,607
Emissions during the spring thaw (30 days)								13,075	75	13,411
Annual fluvial emissions (214 days)								43,477	2,600	65,018

^aThe table presents average $p\text{CO}_2$, $p\text{CH}_4$, k_{600} , CO_2 , CH_4 fluxes (diffusive and non-diffusive), and the specific regional coverage (km²) (see Table S1 and details in the supporting information) for each Strahler stream order present in the region. Rivers and streams cover a total of 190 km^2 (±124) in the region (total area of $44,182 \text{ km}^2$). The first estimate represents the C emissions for the ice-free season, corresponding to 184 days (from May to October inclusively). This estimate is further combined with the estimated spring thaw CO_2 and CH_4 emissions to yield a final value for total annual emissions (214 days). The estimates of fluvial greenhouse gas (GHG) emissions assume a CH_4 warming potential 23 times stronger than CO_2 , over a 100 year time horizon. When standardized per unit of C, this potential represents 8.4 times increase in radiative forcing.

30,402 tons of CO₂-C and 2524 tons of CH₄-C to the atmosphere over the ice-free period (184 days). The addition of spring-thaw fluxes increases the total annual fluxes to 43,477 tons of CO₂-C and 2600 tons of CH₄-C during the 214 days open water period (Table 3), which scaled to the whole landscape yield emissions of approximately 1.04 t C km⁻² yr⁻¹; for which spring thaw GHG emissions contributed 30% of the annual CO₂ emissions and 3% of the annual CH₄ emissions. Expressed in terms of total warming potential, these emissions represent 65,018 tons of GHG (as CO₂ eq), or approximately 1.5 t C (CO₂-eq) km⁻² (landscape) yr⁻¹.

4. Discussion

4.1. Regional Patterns of pCO₂ and pCH₄

The surface water pCO₂ in the fluvial network of Abitibi and James Bay was in the upper range of published values from other boreal regions [Humborg *et al.*, 2010; Koprivnjak *et al.*, 2010; Striegl *et al.*, 2012; Teodoru *et al.*, 2009; Wallin *et al.*, 2010]. The surface water pCH₄ was also in the upper range of values reported in rivers and streams from boreal regions [Crawford *et al.*, 2013] and arctic or temperate regions [Billett and Moore, 2008; Hope *et al.*, 2004; Jones and Mulholland, 1998a]. The pCH₄ ranged 4 orders of magnitude and was much more variable than pCO₂, especially among the smallest headwater streams (stream order 0), where it ranged from 59 to 9611 μatm.

The surface water pCO₂ and pCH₄ decreased as a function of the total stream length (TSL) in both Abitibi and James Bay (Figures 2a and 2b). This pattern of declining pCO₂ with increasing stream order has been reported for other regions [Butman and Raymond, 2011; Crawford *et al.*, 2013; Humborg *et al.*, 2010; Striegl *et al.*, 2012; Teodoru *et al.*, 2009; Wallin *et al.*, 2010] and has been explained by a combination of factors, including dilution of the lateral soil-water inputs [Crawford *et al.*, 2013; Wallin *et al.*, 2010], gas evasion to the atmosphere [Dawson *et al.*, 1995; Oquist *et al.*, 2009], and decreasing organic C degradation with increasing stream order [Battin *et al.*, 2008; Dawson *et al.*, 2001]. In contrast to pCO₂, there have been few descriptions of patterns in pCH₄ within river networks. Striegl *et al.* [2012] and Crawford *et al.* [2013] reported a similar pattern in the Yukon river system, but Jones and Mulholland [1998b] observed the opposite pattern in a highland river continuum where pCH₄ actually increased slightly downstream, suggesting that topography plays a major role in determining these patterns in gas dynamics [Jones and Mulholland, 1998b].

Our results thus suggest that regional patterns of pCH₄ and pCO₂ are similar, both in direction and magnitude, and likely respond similarly to major landscape and hydrological features of these lowland boreal networks. The flat topography and the consistently slow stream flow that it generates possibly plays a role in controlling these patterns and maintaining the high levels of surface water pCO₂ and pCH₄ over the whole region. These patterns emerge even when combining systems from distinct catchments and suggest that the decline of pCO₂ and pCH₄ with increasing stream size may be independent of specific catchment properties. Although these patterns offer little insight on the underlying processes driving the persistent decrease of pCO₂ and pCH₄ with increasing stream size, they highlight that C-gas concentration can be predicted on the basis of simple geographical indexes. Since TSL correlates well with catchment area and stream discharge, it offers a tool for a broad extrapolation of C-gas patterns and quantification of gas fluxes.

4.2. Patterns of k₆₀₀ and the Influence of Hydrology

The pattern in gas exchange coefficient across rivers is likely one of the key physical factors influencing gas concentrations. In flowing waters, k₆₀₀ is mainly governed by the internal turbulent energy [MacIntyre *et al.*, 1995], such that gas exchange rates tend to be linked to hydrology, itself related to stream morphology and slope [Raymond *et al.*, 2012; Wallin *et al.*, 2011]. The flat regional topography strongly influences the patterns of river velocity and discharge and therefore of turbulence-driven gas exchange. In this regard, our results show that k₆₀₀ increased as a function of TSL (Figure 2c), which in this region may be linked in part to the increased water discharge and velocity along the same gradient, leading to higher turbulence [Raymond *et al.*, 2012; Wallin *et al.*, 2011], or the increased influence of wind shear in larger rivers [Alin *et al.*, 2011; Raymond and Cole, 2001]. The second major observation is that our measured k₆₀₀ tend to be on average very low, generally below 1 m d⁻¹. Previous studies that have focused on large rivers or on upland watersheds have reported a systematic decrease of the k₆₀₀ along the river continuum, with values ranging from 3 to 14 m d⁻¹ in headwater streams [Crawford *et al.*, 2013; Wallin *et al.*, 2011] declining to 1–4 m d⁻¹ in large rivers [Cole and Caraco, 2001; Raymond and Cole, 2001; Striegl *et al.*, 2012], although a handful of others focusing on

lowlands [i.e., *Sand-Jensen and Staehr*, 2011] have also found consistently low values of k_{600} . It is clear that topography plays a major role in shaping these regional patterns in river gas exchange.

It is possible that our use of the floating chambers systematically underestimated river gas exchange, in comparison to previous studies, which have used gas tracers to quantify reaeration rates. We acknowledge that the floating chamber approach can be problematic, particularly in fast flowing waters, because these point measurements may not capture the complex turbulence regime that characterizes many of these rivers [*Vachon et al.*, 2010]. In order to assess these potential biases, we recalculated the k_{600} for all our sites using four of the seven models proposed by *Raymond et al.* [2012], which are based on simple morphometric and hydrologic variables such as river slope, width, and velocity. These predicted values of k agreed well with our own measurements, both in average magnitude (average between 0.74 and 0.87 m d^{-1}) and in pattern (with r^2 ranging from 0.12 to 0.20 for the different models), suggesting that these lowland boreal river networks are indeed characterized by low average gas exchange coefficients that increase with stream size.

4.3. Regional-Scale Estimates of Fluvial CO_2 and CH_4 Emissions

The combined patterns of declining $p\text{CO}_2$ and $p\text{CH}_4$ with increasing TSL (Figures 2a and 2b), and increasing k_{600} along the same gradient (Figure 2c), resulted in a relatively narrow range in CO_2 and CH_4 fluxes to the atmosphere among rivers, although there was a slight declining trend with increasing stream order (Table 3). Our regional estimates of CO_2 and CH_4 emissions suggest a large contribution of small order streams (Table 3), a pattern that has been observed before [*Crawford et al.*, 2013; *Koprivnjak et al.*, 2010; *Teodoru et al.*, 2009]. The contribution to total fluvial CO_2 and CH_4 emissions decreased with stream order following the pattern of $p\text{CO}_2$ and $p\text{CH}_4$ (Table 3), suggesting that in lowland regions, where the k_{600} does not vary greatly and remains overall low (Table 2 and Figure 2c), the local variability in fluxes is mainly driven by either the delivery of terrestrially produced CO_2 and CH_4 or in-stream production rather than by turbulence and gas exchange.

Expressed per unit landscape area, the fluvial network in the Abitibi and James Bay regions released a total of 1.5 tons of C (CO_2 equivalent) $\text{km}^{-2} \text{yr}^{-1}$ to the atmosphere, which is within the range reported for other boreal regions, for example, 2.1 tons of $\text{CO}_2\text{-C km}^{-2} \text{yr}^{-1}$ in the Eastmain region of northern Québec [*Teodoru et al.*, 2009] and 1.84 tons of $\text{CO}_2\text{-C km}^{-2} \text{yr}^{-1}$ [*Humborg et al.*, 2010] and 1.56 tons of $\text{CO}_2\text{-C km}^{-2} \text{yr}^{-1}$ [*Jonsson et al.*, 2007] in Sweden. Other studies, however, have reported higher fluxes, for example, in the Yukon river basin, 9.5 tons of C (CO_2 eq) $\text{km}^{-2} \text{yr}^{-1}$ [*Striegl et al.*, 2012] and 12 tons of C $\text{km}^{-2} \text{yr}^{-1}$ for the contiguous U.S. [*Butman and Raymond*, 2011]. Our results, nonetheless, confirm the major role played by fluvial networks in boreal landscapes C emissions and the need to include them in regional aquatic carbon budgets. Expressed as CO_2 equivalents, CH_4 accounted for a significant proportion (34%) of the annual fluvial GHG warming potential, especially in the smaller streams where it accounted for up to 55% (Table 3). This surprisingly large contribution of CH_4 implies that current budgets, based solely on CO_2 , greatly underestimate GHG emissions from northern fluvial networks.

4.3.1. Contribution of Fluvial CH_4 Emissions and the Nondiffusive $f\text{CH}_4$

Our results indicate that nondiffusive $f\text{CH}_4$ is a significant pathway of CH_4 emissions in these fluvial networks, as it was systematically observed and sometimes reached 1 order of magnitude above the strictly diffusive $f\text{CH}_4$ (Figure 3a). Discrepancies between total $f\text{CH}_4$ (measured in floating chamber) and strictly diffusive $f\text{CH}_4$ (estimated on the basis of $k\text{CO}_2$, the latter measured in parallel in the same chambers) have been explicitly reported previously in lakes, reservoirs [*Prairie and del Giorgio*, 2013], and rivers [*Beaulieu et al.*, 2012] and is implicit in data reported in other studies [*Billett and Harvey*, 2012; *Striegl et al.*, 2012]. It has been hypothesized that this process is due to the low solubility of CH_4 and its tendency to form microscopic bubbles, especially under very high CH_4 saturation. In this regard, we observed that the apparent nondiffusive $f\text{CH}_4$ also increased as a power function of the surface water $p\text{CH}_4$ (Figure 3b), as previously reported by *Prairie and del Giorgio* [2013]. These microbubbles may then escape to the atmosphere at a relatively constant rate and contribute to the total CH_4 flux measured in the chambers. Since this component of the CH_4 flux is not a function of the gas exchange coefficient, it will not be captured in flux estimates based on an empirical or assumed k_{600} . The nondiffusive $f\text{CH}_4$ contributed to 56% of the total CH_4 emissions during the ice-free season (Table 3), underscoring the importance of incorporating this pathway in estimates of total CH_4 emissions.

Our estimates of fluvial CH₄ emissions do not include macrobubble mediated (ebullition) fluxes, which involves the localized release of large CH₄-rich bubbles originating from the sediments [Bastviken *et al.*, 2004], which were generally not captured by short-term floating chamber experiments (10 min). Previous studies of rivers in a neighboring boreal region of Canada concluded that this ebullitive fCH₄ contributed between 20 and 67% to the measured total stream CH₄ fluxes [Baulch *et al.*, 2011]. In addition, the role of littoral and riparian vegetation has not been assessed in these calculations but could nonetheless contribute to the regional-scale CH₄ emissions [Bergström *et al.*, 2007]. Our estimates of total river CH₄ emissions, which are already surprisingly large, nevertheless likely underestimate the true total CH₄ fluxes from these boreal fluvial networks.

4.3.2. Importance of CO₂ and CH₄ Emissions During Spring Thaw

Under-ice accumulation of biogenic gases during winter in boreal lakes has been reported to generate significant gas fluxes during the brief period of the spring thaw [Demarty *et al.*, 2011; Kortelainen *et al.*, 2006], but this process has rarely been documented in flowing waters [Dyson *et al.*, 2011]. We observed that the average end of winter *p*CO₂ and *p*CH₄ were both significantly higher than the ice-free season concentrations (Figures 4a and 4b). There was a progressive decline in *p*CO₂ and *p*CH₄ during the 1 month spring thaw (Figures 4a and 4b), which coincided with high-measured *f*CO₂ (although low *f*CH₄) during the same period (Figures 4c and 4d). The regional fluvial CO₂ and CH₄ emissions during this 30 day period contributed to 30% of the annual fluvial CO₂ emissions (13,075 tons of C) and 3% to CH₄ emissions (75 tons of C).

These disproportionately large CO₂ emissions during the spring thaw suggest a constant replenishment of surface water *p*CO₂ throughout the period by terrestrial inputs of organic and inorganic material [Ågren *et al.*, 2008; Mann *et al.*, 2012]. In contrast, CH₄ emissions barely peaked in the spring, suggesting modest replenishment during the spring thaw, as CH₄ production in stream appears strongly modulated by water temperature [Billett and Moore, 2008; Campeau and del Giorgio, 2013; Macdonald *et al.*, 1998]. Together, spring thaw CO₂ and CH₄ emissions contributed approximately 21% of the estimated annual GHG emissions from these rivers. This result emphasizes the need to include the brief period of spring thaw in annual emission budgets for boreal rivers and streams. We assumed that no fluvial C evasion occurred during the winter season. It is important to note that although streams and rivers were generally covered with a thick layer of ice and snow, there were nevertheless small patches of open water along the fluvial network, which could allow significant CO₂ and CH₄ evasion. In addition, the permeability of ice cover to gas fluxes still remains poorly documented. Together, this suggests that the winter contribution to annual aquatic C fluxes may be even larger than what we report here.

4.4. Contribution of Rivers to Total Aquatic CO₂ and CH₄ Emissions

Boreal rivers and streams have been reported to contribute disproportionately to total aquatic CO₂ emissions (up to 65%) relative to the surface they occupy [Aufdenkampe *et al.*, 2011; Humborg *et al.*, 2010; Jonsson *et al.*, 2007; Teodoru *et al.*, 2009]. In contrast, it has often been assumed that fluvial networks contribute modestly to total aquatic CH₄ emissions in comparison to lakes [Bastviken *et al.*, 2011]. The potential contribution of CO₂ and CH₄ emissions from the Abitibi and James Bay fluvial network in the regional aquatic GHG budget can be further assessed by comparing these values to measured ranges of CO₂ and CH₄ fluxes from boreal lakes in this region [Lapierre and del Giorgio, 2012; Lapierre *et al.*, 2013]. We applied the median lake CO₂ (311.6 mg C m⁻² d⁻¹, *n* = 88) and CH₄ fluxes (4.5 mg C m⁻² d⁻¹, *n* = 83) observed for the lakes sampled in the Abitibi and James Bay region to the total number and areal coverage of lakes in the region (3,825 km²), and estimate that the total aquatic emissions in the region, including both lakes and rivers, range from 0.3 Tg of C as CO₂ to 6.3 Gg of C as CH₄, annually (over a 214 days open water period). The fluvial network would thus contribute to 14% of the total aquatic CO₂ emissions, but up to 41% of the total aquatic CH₄ emissions, while covering only 4% of the total aquatic surface. This type of exercise has rarely been performed for boreal aquatic CH₄ emissions and in this case challenges our current perception of flowing waters as minor sources of atmospheric CH₄.

Our study thus reinforces the notion that rivers play a disproportionate role in regional landscape CO₂ budgets [Aufdenkampe *et al.*, 2011; Butman and Raymond, 2011], but more importantly, point to riverine CH₄ emissions as an emerging component of the boreal carbon and greenhouse gas budgets. Using our own regional estimates in combination with total boreal river surface data, provided by Bastviken *et al.* [2011], yields a first-order estimate of CO₂ emissions from rivers and streams for the entire boreal biome of 0.02 Pg of CO₂-C annually, which agrees well with current estimates from Aufdenkampe *et al.* [2011] for the boreal biome. Surprisingly, the same calculation for CH₄ yields total emissions by boreal rivers and streams of

1.09 Tg CH₄-C yr⁻¹ to the atmosphere, which is almost 1 order of magnitude above the current estimates for boreal fluvial CH₄ emissions of 0.15 Tg CH₄-C yr⁻¹ [Bastviken et al., 2011]. This suggests that CH₄ emissions from fluvial networks in boreal landscapes may have been systematically underestimated. Although we acknowledge that the estimates from these lowland boreal regions do not necessarily represent the landscape heterogeneity of the boreal biome, our results undoubtedly show an unexpectedly high contribution of CH₄ to total fluvial GHG dynamics.

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