



Transport and transformation of soil-derived CO₂, CH₄ and DOC sustain CO₂ supersaturation in small boreal streams



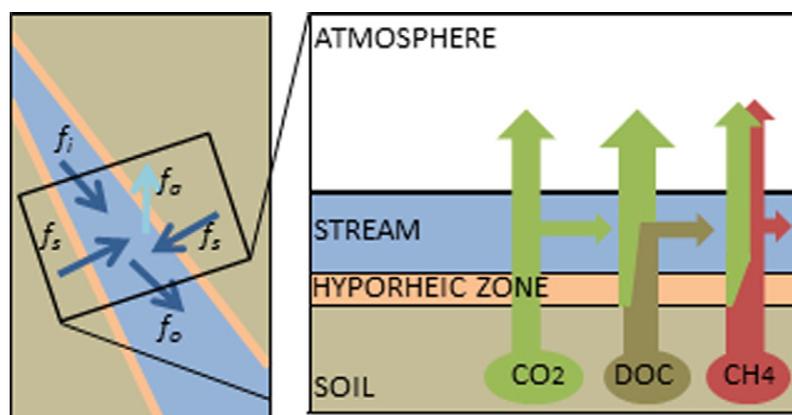
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HIGHLIGHTS

- We assessed the origin of CO₂ and CH₄ supersaturation in boreal streams
- The C mass balance integrated lateral inputs, transformations, and stream fluxes of CO₂, CH₄ and DOC
- Direct soil-derived CO₂ injections alone cannot explain the stream CO₂ fluxes
- Soil-derived DOC mineralization was the major source of stream CO₂ supersaturation
- Soil-derived CH₄ contributes significantly to both CH₄ and CO₂ fluxes in streams

GRAPHICAL ABSTRACT



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ABSTRACT

Streams are typically supersaturated in carbon dioxide (CO₂) and methane (CH₄), and are recognized as important components of regional carbon (C) emissions in northern landscapes. Whereas there is consensus that in most of the systems the CO₂ emitted by streams represents C fixed in the terrestrial ecosystem, the pathways delivering this C to streams are still not well understood. We assessed the contribution of direct soil CO₂ injection versus the oxidation of soil-derived dissolved organic C (DOC) and CH₄ in supporting CO₂ supersaturation in boreal streams in Québec. We measured the concentrations of CO₂, CH₄ and DOC in 43 streams and adjacent soil waters during summer base-flow period. A mass balance approach revealed that all three pathways are significant, and that the mineralization of soil-derived DOC and CH₄ accounted for most of the estimated stream CO₂ emissions (average 75% and 10%, respectively), and that these estimated contributions did not change significantly between the studied low order (≤ 3) streams. Whereas some of these transformations take place in the channel proper, our results suggest that they mainly occur in the hyporheic zones of the streams. Our results further show that stream CH₄ emissions can be fully explained by soil CH₄ inputs. This study confirms that these boreal streams, and in particular their hyporheic zones, are extremely active processors of soil derived DOC and CH₄, not just vents for soil produced CO₂.

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1. Introduction

Freshwaters form an important and active part of the continental carbon cycle and are closely connected to terrestrial ecosystems. It has been estimated that 10% to 30% of the carbon (C) fixed in terrestrial ecosystems is exported to freshwaters, which store, transform, and release it towards the ocean or into the atmosphere (Cole et al., 2007; Tranvik et al., 2009). Headwater streams are emerging as a key component of these aquatic networks and of regional aquatic C budgets, because although they cover a relatively small surface area, they are sites of extremely high biogeochemical activity and are often situated in areas with large soil C pools (Battin et al., 2008; Butman and Raymond, 2011; Humborg et al., 2010; Raymond et al., 2013; Wallin et al., 2013). We know that small streams are highly supersaturated in CO₂ (Butman and Raymond, 2011; Hope et al., 1994; Jones and Mulholland, 1998; Teodoru et al., 2009), and they potentially contribute as much or more than lakes within certain landscapes (Huotari et al., 2013; Lundin et al., 2013). More recently, it has been shown that streams are also highly supersaturated in CH₄, and therefore, are also an important component of the regional CH₄ budget (Campeau et al., 2014; Crawford et al., 2014; Stanley et al., 2015). There is consensus that CO₂ emissions from rivers represent carbon derived from the surrounding terrestrial ecosystem, although the sources of fluvial CH₄ are far less clear. Tracer and radioisotope studies have yielded valuable insight on the age of the terrestrial C pools that are being mobilized and exported, including terrestrially-derived CO₂ (Billett et al., 2012; Garnett et al., 2013; Schiff et al., 1998; Vihermaa et al., 2014), which have allowed to infer the sources of this C to rivers and its links to hydrology and soil properties. How the various pathways of delivery of terrestrial C to streams combine to eventually yield the fluvial C emissions, and the processes underlying these emissions, are still not well understood and are the focus of this paper.

Headwater streams are the first to collect surplus of soil water and transport it downstream along the river continuum. Because these headwater streams have such a tight hydrological connection to the surrounding soils, the general assumption has been that most of the stream CO₂ efflux is actually soil-derived CO₂ that has been injected to the stream via lateral soil water input. Although there are some empirical studies that have presented support to this assumption (Crawford et al., 2014; Hotchkiss et al., 2015), most studies to date are based on indirect evidence, and we have yet to fully quantify the importance of direct soil CO₂ injection on stream CO₂ dynamics. There are even fewer studies that have addressed the actual sources fuelling CH₄ supersaturation in these headwater streams. There is evidence of high CH₄ concentrations in surface soil water (Goody and Darling, 2005), but how much of this soil-derived CH₄ reaches the stream water remains uncertain. In addition, since CH₄ is readily oxidized at anoxic-oxic interfaces, it is possible that soil-derived CH₄ not only fuels stream CH₄ supersaturation, but also to the observed CO₂ supersaturation through oxidation. This possibility, however, has never been explicitly tested. In addition to CO₂ and CH₄, soils also deliver dissolved organic C (DOC) to streams. Indeed, soils are the major source of organic matter to freshwater ecosystems (Benner et al., 2004; Wilkinson et al., 2013). There is strong evidence that, far from being inert, a sizeable portion of the terrestrial DOC entering headwater streams is highly reactive, both to biological degradation and to photo-oxidation (Berggren et al., 2012; Lapierre and del Giorgio, 2014) and that small streams have the fastest organic C decay rates in the aquatic continuum (Catalán et al., 2016). This in turn implies that at least a portion of the observed CO₂ supersaturation (and perhaps some of the CH₄) must originate from the in-stream degradation of terrestrially-derived DOC, an issue that has been explored mostly indirectly and from a mass balance perspective without simultaneous measurements of soil water (Humborg et al., 2010; Mayorga et al., 2005; McCallister and del Giorgio, 2008).

There are several major challenges associated to determining the pathways of delivery of CO₂ to streams. For example, it is difficult to quantify the actual lateral inputs of water to streams, and the associated

actual loading of C, and therefore the existing studies have necessarily focused on a very small number of streams. Another major shortcoming of current studies is that they tend to focus on a single C species, and it is not clear how the movement and processing of the various soil-derived forms of C combine to shape the observed stream CO₂ and CH₄ dynamics. One key aspect that has seldom, if ever been considered is the fact that the major soil-derived C species are all delivered to streams by the same lateral soil water input, and therefore that the resulting patterns of stream CO₂, CH₄ and DOC concentration must be linked and quantitatively coherent, independent of the actual amount of lateral water input involved. It should therefore be possible to derive the contribution of each C species to the observed stream CO₂ fluxes using a mass balance approach, based on the parallel changes in the concentrations of CO₂, CH₄ and DOC between the soil waters that carry these C species and the receiving stream waters.

In this paper we apply this approach to explore the relative importance of direct soil CO₂ injection, soil-derived DOC degradation, and the oxidation of soil-derived CH₄ in sustaining stream CO₂ supersaturation and air-water CO₂ fluxes in 43 streams (Strahler order 0–3) located in the Côte-Nord boreal region of Québec, Canada, during summer base-flow conditions. We measured the concentrations of CO₂, CH₄ and DOC in each stream and in the immediately surrounding soil waters that feed these streams, and developed a mass balance for each stream that incorporates the change in all three C species between the two phases (Fig. 1). This approach seeks to find a solution that accounts for stream CO₂ fluxes by matching the observed difference in concentrations of the three C species between soil and stream waters, and explicitly allows for soil-derived DOC and CH₄ to fuel stream CO₂ fluxes through mineralization. Soil water must traverse the stream bed before reaching the open stream channel, and some of the transformations of the soil-derived C species likely occur at this interface, but we consider these hyporheic zones as an integral part of the stream system (Fig. 1), and for the purposes of establishing this C mass balance, we make no distinction between stream bed and stream channel. Our large-scale comparative approach is meant to incorporate some of the landscape heterogeneity in terms of hydrology, soil and stream properties that exists in this complex boreal landscape, in order to derive an average regional perspective on the drivers of stream CO₂ emissions. We therefore do not seek here to explain in detail the behaviour of individual streams, which would necessarily require an approach that intensively focused on one or a small set of streams, at the expense of a broader regional perspective.

2. Methods

2.1. Study sites, sampling, and laboratory analyses

We sampled 43 small rivers (from potentially temporary streams to Strahler order 3, Table A.1) in the boreal Côte-Nord region in Québec, Canada (50.0–50.9°N and 67.4–66.0°W). The region is situated on the Canadian Shield, dominated by Precambrian rocks with little carbonate formation (Schiff et al., 1990; Schindler et al., 1992; Soil Carbon Database, 1996), and thus the surface waters tend to have low DIC and alkalinity. The soil development type is Ferro-Humic Podzolic, it is well drained and dominated by fine sand. The mean annual temperature is 0.8 °C and the mean annual precipitation is 1156 mm (Sept-Îles meteorological station, mean 1971–2001, Environment of Canada). The sampled sites ranged from peat dominated soils to more mineral soils, with elevations ranging from 7 to 600 m.a.s.l. The rivers had mainly rocky bottoms and the waters had low turbidity but were generally colored with humic materials. There was in general little macrophyte development within the river channel itself, but the river banks were usually vegetated, mainly by *Alnus viridis* (Chaix.) D.C., *Salix* spp., *Poaceae* spp., and mosses. The most common tree species within the river catchment were black spruce (*Picea mariana* (Mill.) B.S.P.) and balsam fir (*Abies balsamea* (L.) Mill.) with some white birch (*Betula*

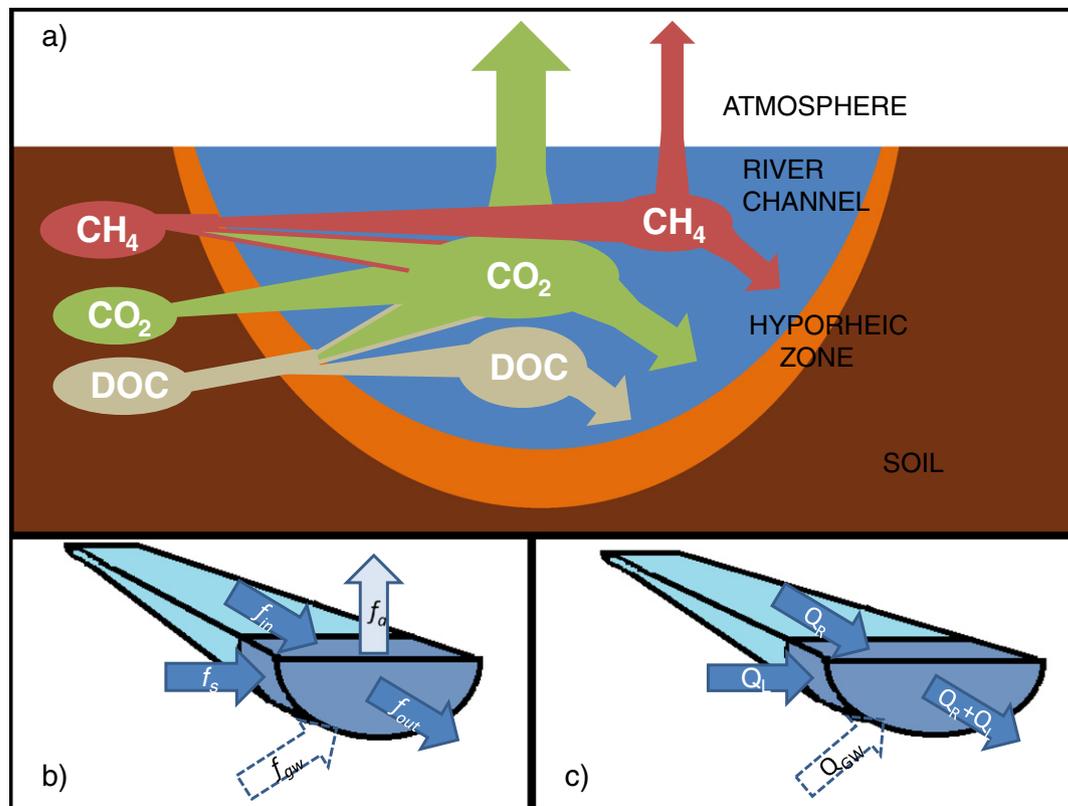


Fig. 1. Schematic representation of the soil/stream interactions within a stream section, showing (a) the lateral transport of soil derived CH_4 , CO_2 and DOC from soil water into streams and their respective fates, and (b) carbon, and (c) water fluxes. f_s is lateral flux from the soil into the river, f_{in} is discharge flux into the study section, f_{out} is discharge flux out from the study section, f_a is flux into the atmosphere, f_{gw} is the input from deep ground water source, Q_R is discharge into the study section, Q_L is lateral water input, and Q_{GW} is the possible input through deep ground water.

papyrifera Marsh.) and tamarack (*Larix laricina* (Du Roi) K. Koch). At each site we sampled the stream and the adjacent soil water and soils. Four to five soil samples per site were taken with a soil drill (diameter 5 cm) from 0 to 15 cm depth and combined for further analysis. Precipitation was minimal before and during the sampling period in July 2013, and the results thus represent true summer base-flow conditions.

Soil water was collected by installing two to three piezometers in the vicinity of the streams. The distance from the piezometers to the running water varied from 30 cm to 80 cm (average 40 cm). Piezometers were first emptied with a pump (Master-Flex 7518-12, Cole-Parmer Instrument Company, Vernon Hills, IL), and the fresh soil water accumulating in them after the first emptying was collected into acid washed 500-mL glass bottles. River water was collected directly in analysis vials, or by using a peristaltic pump if the stream was so shallow that the vials could not be fully submerged. Temperature, pH, conductivity, and dissolved oxygen were measured in situ using a multi-parameter probe (600XLV2-M, Yellow Springs Instruments, Yellow Springs, OH) for both stream and soil water (Table A.1). The measurements were conducted in a separate glass beaker for soil water, as well as for stream water if the probe could not be immersed directly in the water channel. The instrument detection limits were ± 0.15 °C, ± 0.2 , $\pm 0.5\%$ of reading 0.001 mS cm^{-1} and 2% of reading or 0.2 mg L^{-1} (which ever greater) for temperature, pH, conductivity and dissolved oxygen, respectively. The water samples (1 L of river water and minimum 0.5 L of soil water) were transported in a cooler to the laboratory for further analyses.

Water samples from both streams and soil waters were taken for DOC, dissolved CO_2 and CH_4 concentrations. DOC concentrations were measured with a TOC analyzer (OI 1010, OI Analytical, College Station, TX, precision 0.05 mg L^{-1}) after filtering ($0.45 \mu\text{m}$ PES cartridge, Sarstedt AG & co, Nümbrecht, Germany) and sodium persulfate digestion. Gas concentrations were measured using the headspace technique: A 60-mL syringe was partly filled with water (30 mL for stream

waters and 10 mL for soil waters), and developed a headspace using ambient air; the syringes were vigorously shaken for 2 min to equilibrate the air inside the syringe with the water. CO_2 concentrations in the headspace were then immediately measured with a portable infrared gas analyzer (EGM-4, PP-systems, Amesbury, MA, precision of 0.1–1% depending on measured concentration), and air samples for CH_4 analysis were injected into vials containing a hypersaline solution, and stored upside down until the analysis with a gas chromatographer (GC-8A/GC-2014, Shimadzu, Kyoto, Japan) equipped with a FID (flame ionization detector, with a precisions of 5% of concentrations 0–1000 ppm and 20% of concentrations of 1000–15,000 ppm). Concentrations in the water were then back-calculated using in situ temperatures, gas solubility, and Henry's law. We further measured the river width, depth and water velocity, the latter by timing the movement of a small floating ball. River discharge (Q_R , $\text{m}^3 \text{ s}^{-1}$) was then calculated as velocity \times (width \times maximum depth)/2, assuming a triangular cross-section.

Soil samples were stored at 4 °C, and back in the laboratory were mixed well and dried in the oven (60 °C, 48 h). Dry soil was sequentially sieved through 2 mm, 500 μm and 45 μm sieves to analyze the texture of the soil, and the proportion of each granular size class was calculated. A subsample of soil passing through 2 mm sieve was placed in the oven at 500 °C for 4 h to remove organic matter, and then reweighed, and to calculate the organic matter content (as % of the dry weight). The study region is situated on bedrock where no carbonates are present (Schindler et al., 1992), and inorganic C was a negligible fraction of the total soil C content.

2.2. Mass balance approach and calculations

We developed a framework that allowed us to explore the contribution of the main pathways (direct soil-derived CO_2 injection,

mineralization of soil-derived DOC mineralization and oxidation of soil-derived CH₄) to stream CO₂ dynamics, based on finding the mass balance solutions that satisfied the premise that the same lateral water input, Q_L, is delivering simultaneously all C species to streams. The mass balance for CO₂, CH₄ or DOC for a given river section in general is composed of the upstream C inputs (f_{in}), the lateral C inputs from the soil (f_s), the downstream output (f_{out}) and the C gas (CO₂ and CH₄) exchange with the atmosphere (f_a) (Fig. 1b). The approach assumes that over the very short water retention time of the hypothetical river stretch these processes are at steady state, such that the concentrations of CO₂ in the river remain constant, so that the inputs and outputs are equal (Eq. (1)):

$$f_{in} + f_s = f_a + f_{out} \quad (1)$$

f_{in} can be estimated by multiplying the river discharge at the top of the section (Q_R, Fig. 1c) by concentration of the C species in the river water (CO_{2R}, CH_{4R}, DOC_R, or the sum of the three C species, C_R); f_s can be estimated by multiplying the lateral soil water input (Q_L) by the soil water concentrations of the C species (CO_{2S}, CH_{4S}, DOC_S, or the sum of the three species, C_S); f_{out} can be estimated by multiplying the discharge at the bottom of the section (Q_R + Q_L) by C_R; the flux to the atmosphere (f_a) can be estimated based on the difference in measured partial pressures in the river water from atmospheric equilibrium (Δgas), the temperature dependent Henry's constant (kH), the gas transfer velocity (k), and the surface area of the section (A). Eq. ((1)) can thus be written as (Eq. ((2))):

$$C_R \times Q_R + C_S \times Q_L = C_R \times (Q_R + Q_L) + k \times kH \times \Delta gas \times A \quad (2)$$

Q_L is the only variable involved in this mass balance that was not measured, yet it can be estimated from Eq. ((2)) for each of the C species considered here. Eq. ((2)) can be applied to total C, as well as to the individual mass balances for CO₂ and CH₄, and further developed to take into account the main transformation processes. Since the three C species are delivered to streams by the same water, the individual mass balances should yield the same Q_L.

In the case of the stream CO₂ balance, in addition to direct terrestrial CO₂ injection, we must consider mineralization of soil-derived DOC, and the oxidation of soil-derived CH₄, both of which can take place in the hyporheic zone or in the stream water column and contribute to the observed stream CO₂ concentration; under this scenario, solving for Q_L in Eq. ((2)) yields (Eq. ((3))):

$$Q_L = \frac{k_{CO_2} \times kH_{CO_2} \times \Delta p_{CO_2} \times A}{(CO_{2S} - CO_{2R}) + (DOC_S - DOC_R) + (CH_{4S} - CH_{4R}) \times OX} \quad (3)$$

where (CO_{2S} - CO_{2R}) represents the difference between soil and river water CO₂ concentration, and therefore the direct contribution of soils to river CO₂ outgassing, (DOC_S - DOC_R) represents the mineralization of soil-derived DOC (assuming that the entire loss of DOC is turned into CO₂), and (CH_{4S} - CH_{4R}) × OX represents the portion of soil-derived CH₄ that is oxidized to CO₂, all contributing to river CO₂ concentration. Likewise, we can solve Q_L to balance the observed stream CH₄ concentrations allowing for the oxidation of soil derived CH₄ (Eq. ((4))):

$$Q_L = \frac{k_{CH_4} \times kH_{CH_4} \times \Delta p_{CH_4} \times A}{(CH_{4S} - CH_{4R}) \times (1 - OX)} \quad (4)$$

where (CH_{4S} - CH_{4R}) × (1 - OX) is the portion of soil-derived CH₄ that is not oxidized, which has to equal the observed CH₄ outgassing + outflow from the stream. OX was not measured, but can be derived from the mass balance itself. Since the three C species are delivered to streams by the same water (Q_L), we can make Eq. ((3)) = Eq. ((4)),

thus removing Q_L, and then derive the value of OX that satisfies this equality.

$$OX = \frac{f_{a,CH_4} \times ((CO_{2S} - CO_{2R}) + (DOC_S - DOC_R)) + f_{a,CO_2} \times (CH_{4S} - CH_{4R})}{(CH_{4S} - CH_{4R}) \times (f_{a,CO_2} + f_{a,CH_4})} \quad (5)$$

where f_{a,CO₂} and f_{a,CH₄} are the fluxes of CO₂ and CH₄ into the atmosphere, respectively. Once we have OX, we can then solve Eq. ((3)) for Q_L, which in turn allows us to determine the actual lateral flux of soil-derived CO₂ ((CO_{2S} - CO_{2R}) × Q_L), the flux of DOC-derived CO₂ ((DOC_S - DOC_R) × Q_L), and the flux of CH₄-derived CO₂ ((CH_{4S} - CH_{4R}) × OX) × Q_L. We can then calculate the contribution of each of these pathways to the observed CO₂ efflux to the atmosphere in each stream.

We applied this conceptual framework to develop a mass balance on a hypothetical 100-meter section of each of our streams, since our previous work has shown that over this spatial scale there are usually no discernible changes in the concentrations of CO₂ in these small order streams (P. del Giorgio Pers. Com.), which is one of the pre-requisites of our approach. Although we had measurements of soil water CO₂, CH₄ and DOC concentrations for each of our stream sites, it is well known that these can be very heterogeneous and vary largely even within a given site (Schindler and Krabbenhoft, 1998; Stoyan et al., 2000), and therefore we applied a regional average soil water concentration (mean value of all soil water samples) to all the individual stream mass balances, in order to smooth out some of this spatial heterogeneity. However, the mass balances calculated using the individual C concentrations of soil water at each site yielded very similar results (see Discussion). For the river portion of the mass balance, we used the actual measured water concentrations for each stream. For stream water-air gas fluxes (f_a, mg C m⁻² d⁻¹), we used a constant atmospheric partial pressure (390 μatm for pCO₂ and 1.8 μatm for pCH₄) and a fixed gas transfer coefficient (k, m d⁻¹) for any given river order (Table A.1), derived from our own measurements. Gas transfer coefficients were measured using floating chambers (Campeau et al., 2014) in a separate set of 50 rivers of different order within the same region, and here we used the average k-values for the river orders relevant to this study (Table A.1). These vary from 0.67 to 1.66 for CO₂ and from 0.67 to 1.64 for CH₄.

2.3. Verifying lateral inputs

It has to be emphasized that the purpose of this exercise was not to estimate Q_L per se, but rather to use Q_L as the common denominator to derive a unique mass balance solution accounting for the observed stream CO₂ outgassing that combines the observed soil concentrations of all three C species simultaneously. It is nevertheless important to ascertain whether the estimated values of Q_L derived from this mass balance are reasonable for this type of stream. Because we did not have actual measurements of lateral water flow (Q_L), we derived an alternative estimate of Q_L that is based on measured flow accumulation and discharge, which we could use to verify our mass balance results. Stream discharge was calculated from measured water velocity (m s⁻¹) and stream morphometry across 48 additional river sites in the same region (not shown here) using a 2-D Acoustic Doppler Velocimeter (Sontek, FlowTracker), and these discharge values were combined with the discharge measurements made on 29 out of the 43 sites included in this study. We obtained high resolution digital elevation models (DEMs) (23 m × 23 m) from GeoBase and extracted flow accumulation values for the sites where discharge was measured for each of the 77 rivers, from the flow accumulation raster generated using the hydrology toolbox in ArcGIS 10. We then used the extracted flow accumulations and the measured discharges to build a regional model (Fig. A.1) relating both variables, that we could then use to

predict the discharge at the beginning and end of each of our hypothetical 100-m stream sections based on their respective flow accumulations, which we extracted from ArcGIS. The difference between the modelled discharge at the start and end of each section represents the theoretical lateral water input for each stream (Q_{L_mod} , $m^3 d^{-1} m^{-1}$), which were further compared to the Q_L derived from the mass balance (Eq. (3)). In order to compare the estimated Q_L between different rivers, we further calculated the lateral input rate (k_L , m^{-1}) by dividing the estimated Q_L by the measured Q_R .

2.4. Statistical analysis

The differences between CO_2 , CH_4 and DOC concentrations in soils and rivers as well as between river orders were compared with the Mann-Whitney U test at the significance level of $p < 0.05$. In the results we present mean \pm standard error values unless otherwise stated. We used the Kruskal-Wallis test to compare the averages of several groups. All statistical analyses were made using R 3.0.0 software (R Core Team, 2013).

3. Results

3.1. River and catchment characteristics

The soils at the sampling sites were mostly sandy and sandy loam textures. The measured discharge (Q_R) in the studied rivers varied from 0.003 to 1172 $L s^{-1}$ although most of the rivers had discharge lower than 5 $L s^{-1}$ (Table A.1). Regional runoff and river discharge were extremely low during the sampling period, which coincided with one of the driest summers in the past decades. The studied streams transported from 0.2 to 1157 $g C m^{-2} d^{-1}$ downstream as CO_2 , CH_4 and DOC. DOC was always the largest contributor (89(± 0.01)%) to this combined river C downstream flux. The contribution of CO_2 was on average 11(± 1.1)%, whereas CH_4 contributed <1(± 0.08)% of the total C transport downstream. Based on the measured concentrations and the estimated k -values (Table A.1), the studied rivers emitted into the atmosphere on average 796 ± 90 $mg C m^{-2} d^{-1}$ as CO_2 , and 24 ± 6 $mg C m^{-2} d^{-1}$ as CH_4 during this low flow period, and the total atmospheric C flux ($CO_2 + CH_4$) ranged from 0.07 to 2.4 $g C m^{-2} d^{-1}$. On average, 98(± 0.3)% of this total atmospheric C flux was CO_2 and 2(± 0.3)% CH_4 , but the CH_4 contribution increased up to 15(± 1.7)% if we consider the emissions as CO_2 equivalents.

3.2. CO_2 , CH_4 , and DOC in soil and stream waters

All the studied rivers were supersaturated in both pCO_2 and pCH_4 compared to the atmosphere (1718 ± 138 and 1111 ± 271 μatm , respectively, Fig. 2, Table A.1). Methane was more variable than pCO_2 across both soil waters (CV = 1.17 and 0.70, CH_4 and CO_2 respectively) and streams (CV = 1.54 and 0.50, CH_4 and CO_2 respectively), whereas DOC was the least variable across samples (CV = 0.66 and 0.52 in soils and streams, respectively). CO_2 , CH_4 and DOC concentrations were higher in soil water than in the adjacent stream water in all but a few cases, and overall the concentrations of the three C species differed significantly between the two ecosystems (Fig. 2). In streams, CO_2 concentrations were higher than CH_4 concentrations ($p < 0.0001$), whereas the reverse was true for the soil waters, where CH_4 concentrations were significantly higher than CO_2 concentrations ($p < 0.0001$). Consequently, the average molar CH_4/CO_2 ratios were significantly different between the two ecosystem (0.02 \pm 0.002 in streams and 0.41 \pm 0.07 in soils, $p < 0.0001$). DOC contributed the largest amount to total C mass both in soils and in rivers, but the molar ratio ($CO_2 + CH_4$)/DOC was significantly higher in soils than in rivers (0.30 \pm 0.07 and 0.15 \pm 0.03, respectively, $p = 0.028$). It is interesting to note that in all cases, our soil water samples were oxalic (>40% saturation), suggesting that extremely high DOC, CH_4 and CO_2 concentrations may

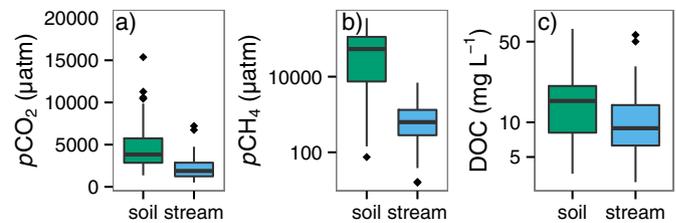


Fig. 2. The partial pressure of (a) CO_2 (pCO_2 , μatm), and (b) methane (pCH_4 , μatm), and (c) DOC concentration ($mg L^{-1}$) in the 43 studied streams (blue) and adjacent soil waters (green) in the Côte-Nord region, Québec, Canada. Concentrations in soil waters were significantly higher than in river waters in the three cases (Mann-Whitney U $p < 0.001$, $p < 0.001$ and $p = 0.004$ for CO_2 , CH_4 and DOC, respectively). Boxplots show the median, 25th and 75th percentiles, and the whiskers extend to the furthest data point that is within 1.5 times the interquartile range; dots are outliers.

coexist in oxygenated soil water, further facilitating the potential mineralization of both CH_4 and DOC.

There was an overall significant positive relationship between pCO_2 and pCH_4 across streams and soil waters, but the large offset in CH_4 relative to CO_2 in soil waters resulted in two distinct relationships that differed in slope but in particular, in their respective intercepts (Fig. 3a). pCO_2 and pCH_4 were also correlated to DOC concentration, but these relationships were weak and only significant in streams (Fig. 3b, c). Although the concentration of each C species tended to be positively correlated between stream and the adjacent soil water, none of these relationships were significant ($p > 0.05$, not shown). These relationships suggest that although CO_2 , CH_4 and DOC concentrations are broadly linked to each other, and between soil and stream waters, the stoichiometry of C in streams is not the result of transport only, but transformation processes must change this C stoichiometry during transit from soils to streams.

3.3. Balancing water and C fluxes

We used the framework described in Section 2.2 to further explore the connections between stream and soil water C dynamics, and to reconstruct the observed CO_2 dynamics in the streams. Our scenario involved matching the combined CO_2 , CH_4 and DOC soil water inputs to the observed stream CO_2 dynamics, further allowing for the degradation of both soil-derived DOC and CH_4 to generate stream CO_2 to close the mass balance (Eq. (3)). The estimated lateral water inputs that satisfied this combined mass balance ($Q_{L_combined}$) averaged 0.11 $m^3 d^{-1} m^{-1}$ (median 0.06, range 0.01 to 0.88 $m^3 d^{-1} m^{-1}$) (Fig. 4), and corresponds to an average lateral water input rate (k_L) of 0.001 (± 0.0003) m^{-1} . These Q_L values derived from the combined mass balance are in excellent agreement with the Q_L values predicted for the same streams from the extracted flow accumulation (Q_{L_mod} in Fig. 4), suggesting that this combined mass balance realistically captures the movement of water and materials from soils to streams. In contrast, excluding DOC mineralization and CH_4 oxidation from the CO_2 mass balance in Eq. (3), and therefore assuming that river CO_2 fluxes are exclusively driven by the injection of soil-derived CO_2 , yields unrealistically high Q_L needed to close the CO_2 mass balance ($Q_{L_CO_2}$ in Fig. 4), one order of magnitude higher than those derived from both the combined mass balance and flow accumulation. Likewise, assumption that there is no oxidation of soil-derived CH_4 , and that therefore all of the soil-derived CH_4 contributes to the stream CH_4 fluxes yields unrealistically low estimates of Q_L ($Q_{L_CH_4}$ in Fig. 4), one order of magnitude lower than $Q_{L_combined}$ and Q_{L_mod} (Fig. 4). These results together suggest that mineralization of soil-derived DOC and CH_4 is absolutely required in order to realistically reconstruct not only the CO_2 budget, but also the CH_4 budget of these small boreal streams.

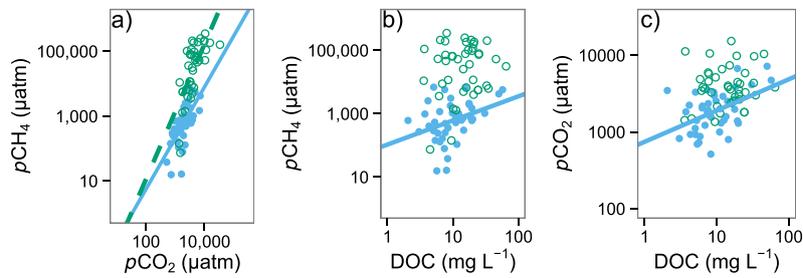


Fig. 3. Relationship between (a) $p\text{CO}_2$ and $p\text{CH}_4$, (b) $p\text{CH}_4$ and DOC, and (c) $p\text{CO}_2$ and DOC in stream (blue filled circles) and soil (green open circles) waters. The linear regression equations for streams (blue solid line) are: $\log_{10}(p\text{CH}_4) = 1.58 \times \log_{10}(p\text{CO}_2) - 2.41$, $r^2 = 0.47$ $p < 0.001$; $\log_{10}(p\text{CO}_2) = 0.01 \times \text{DOC} + 3.11$, $r^2 = 0.27$ $p < 0.001$; $\log_{10}(p\text{CH}_4) = 0.02 \times \text{DOC} + 2.48$, $r^2 = 0.17$ $p = 0.006$. The only significant equation for soils (green dashed line) is: $\log_{10}(p\text{CH}_4) = 2.08 \times \log_{10}(p\text{CO}_2) - 3.12$, $r^2 = 0.51$ $p < 0.001$.

3.4. Contribution of the different pathways to stream CO_2 emissions

The composition of soil water C averaged $14(\pm 2)\%$, $7(\pm 1)\%$, and $79(\pm 3)\%$ for CO_2 , CH_4 , and DOC, respectively, but as the result of the processing described in the Section 3.3, the final distribution of these C species in the stream water was very different ($11(\pm 1)\%$, $0.2(\pm 0.1)\%$, and $89(\pm 1)\%$ for CO_2 , CH_4 , and DOC, respectively). Based on Eq. (3), the contribution of the three sources (direct soil-derived CO_2 injection, soil-derived CH_4 oxidation and soil-derived DOC degradation) to stream CO_2 outgassing averaged $15(\pm 2)\%$, $10(\pm 2)\%$, and $76(\pm 3)\%$, respectively (Fig. 5). Although a few streams clearly diverged in terms of the average contribution of the three processes, the vast majority of streams closely followed the average pattern (Fig. 5), and the relative contribution of these three processes to CO_2 outgassing did not change significantly along the river continuum from order 0 to 3 streams (Fig. 5, right panels). We did not find any significant correlations between the contribution of different CO_2 sources and catchment landcover, vegetation type or soil characteristics, even though they varied largely among catchments (Table A.1). These results suggest that in

this range of stream orders, the degradation of soil-derived DOC, in the water column or most likely in the hyporheic zone (as we discuss in sections below), is overwhelmingly the main source of CO_2 outgassing and further demonstrate that the oxidation of soil-derived CH_4 is also a significant source of CO_2 in these boreal streams.

4. Discussion

Our understanding of the magnitude of riverine fluxes has greatly improved in recent years, and it is now firmly established that rivers, particularly smaller streams, are major sources of CO_2 and CH_4 especially on an areal basis but also on a whole inland water system level (Campeau and del Giorgio, 2014; Crawford et al., 2014, 2013; Stanley et al., 2015). Our results further support this pattern, as we found that all the sampled boreal streams were highly supersaturated in both CO_2 and CH_4 (Fig. 2). In boreal streams, which are generally shallow and rapidly mixed, and therefore tend to quickly equilibrate with the atmosphere, sustaining this supersaturation necessarily requires constant replenishment of CO_2 and CH_4 . In the case of CH_4 , this supersaturation could potentially be generated by methanogenesis in the stream bed, or also by inputs of CH_4 from soils. The sources explaining CO_2 supersaturation are more diverse, but it is generally believed that it must derive from C inputs from the surrounding soils because autotrophic processes in streams cannot generate CO_2 supersaturation. However, studies addressing this issue show contrasting results, and whereas some suggest

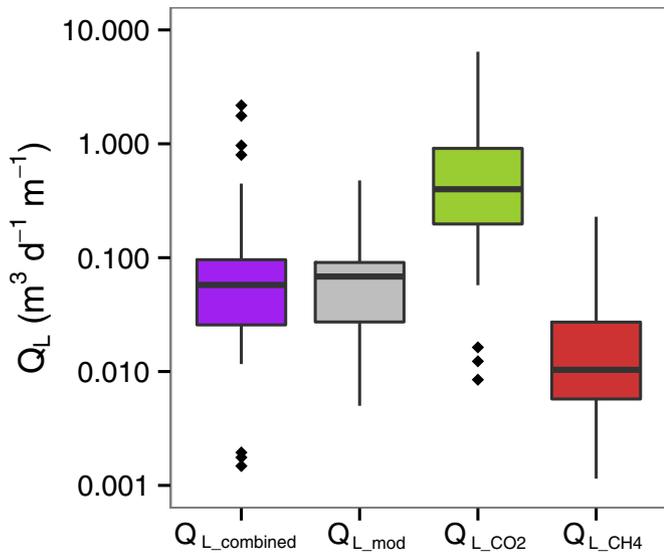


Fig. 4. Lateral water input (Q_L , $\text{m}^3 \text{d}^{-1} \text{m}^{-1}$, calculated with Eq. (3) required to sustain the observed stream CO_2 and CH_4 fluxes, assuming that 1) stream CO_2 concentrations are driven by the combined contribution of soil-derived CO_2 , mineralization of soil-derived DOC, and oxidation of soil-derived CH_4 ($Q_{L_combined}$), 2) stream CO_2 concentrations are driven exclusively by soil derived CO_2 (Q_{L_CO2}), 3) the soil-derived CH_4 contributes exclusively to sustain the stream CH_4 concentrations (Q_{L_CH4}), and for comparative purposes, the modelled Q_L for all of these streams based on GIS-derived flow accumulation and measured discharge is shown (Q_{L_mod} , see Section 2.2). Note the logarithmic scale in the Y axis. Boxplots show the median, 25th and 75th percentiles, and the whiskers extend to the furthest data point that is within 1.5 times the interquartile range; dots are outliers.

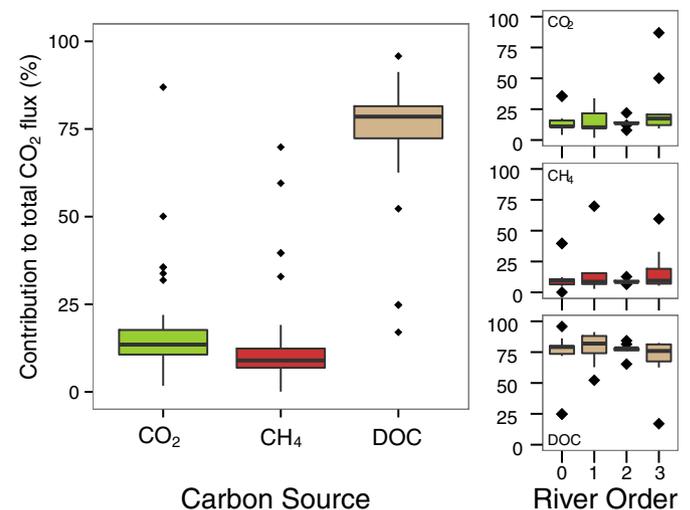


Fig. 5. Contribution of soil-derived CO_2 , oxidation of soil-derived CH_4 , and degradation of soil-derived DOC to CO_2 efflux from small rivers in Côte-Nord, Canada. Left panel shows the overall median and distribution, right panel shows the median and distribution by stream order. Boxplots show the median, 25th and 75th percentiles, and the whiskers extend to the furthest data point that is within 1.5 times the interquartile range; dots are outliers.

that river CO₂ emissions mostly represent the reallocation and degassing of soil respiration (Abril et al., 2014; Burrows et al., 2014; Crawford et al., 2014; Hotchkiss et al., 2015; Sand-Jensen and Staehr, 2011; Striegl et al., 2012), other studies conclude that in-stream metabolism of terrestrial organic C accounts for the majority of river CO₂ emissions (Battin et al., 2008; Cole and Caraco, 2001; Humborg et al., 2010; Lynch et al., 2010). Clearly our understanding of the relative importance of these various pathways underlying riverine emissions is still lagging behind our understanding of the magnitude of these fluxes.

It is important to emphasize that although the application of the mass balance involves estimating the groundwater discharge, Q_L , which delivers all the C species, the latter is not the focus of the study, but rather our aim was to determine the potential contribution of terrestrial CO₂, CH₄ oxidation, and DOC degradation to stream CO₂ fluxes using Q_L as the common denominator for the loading of soil-derived C. The fact that the modelled Q_L values based on flow accumulation and regional runoff (see Section 2.3) were very similar to the ones calculated from the mass balance approach (Fig. 4) suggests that the basic premises of our approach are sound and that our estimates of Q_L required to close the mass balance are realistic.

Our observation of major differences in the concentrations of CO₂, CH₄ and DOC between soil waters and streams, which in addition varied widely among the three C species (Fig. 3) inevitably implies selective processing of some of these C species somewhere between soil and stream water. Our mass balance calculations suggest that, even though soil CO₂ concentrations were on average 2.4 fold higher than those in stream waters, the injection of soil-derived CO₂ could not by itself account for the observed stream CO₂ outgassing (Fig. 4), and therefore that soil-derived DOC mineralization and soil-derived CH₄ oxidation must contribute to the observed stream CO₂ outgassing (Fig. 5). Moreover, if no DOC or CH₄ were converted to CO₂, their resulting concentration in the stream would be unrealistically high. The fact that this combined mass balance is the only one yielding realistic Q_L estimates (Fig. 4) further reinforces the conclusion that a significant portion of the soil-derived DOC and CH₄ must be oxidized before reaching stream waters, therefore contributing to the measured CO₂ concentrations and emissions from streams.

In this regard, the mineralization of soil-derived DOC appeared to be by far the largest contributor to stream CO₂ fluxes (on average 75%). This result may seem somewhat counterintuitive, since our study rivers are all low order and with tight connections with surrounding soils, and it would thus be expected that direct soil CO₂ injection would play a major role, yet it agrees with an increasing volume of literature demonstrating that soil-derived DOC is in fact extremely reactive. Indeed, freshly-loaded soil-derived DOC has been shown to be highly reactive and rapidly used by bacteria (Berggren et al., 2007; Fasching et al., 2014; Guillemette et al., 2013), and preliminary data on the DOC composition of these same streams and rivers indicates that soil waters are enriched in highly biologically reactive pools that quickly disappear within the upper reaches of headwater streams (R. Hutchins, Pers. Com.). This soil-derived DOC that is loaded to headwater streams in these boreal landscapes has also been shown to be extremely photo-reactive (Lapierre and del Giorgio, 2014).

Although our approach does not allow resolving where exactly this degradation takes place, it strongly suggests that much of the DOC and CH₄ oxidation occurs in the hyporheic zone of these streams. Measurements in other rivers of the same order from the Côte-Nord region suggest an average total water column respiration of ca. 85 µg C L⁻¹ d⁻¹ (P. del Giorgio, unpublished data), which would translate into a potential water column CO₂ production rate of 11 mg C m⁻² d⁻¹ (assuming a mean depth of 0.13 m). This would represent <2% of the observed CO₂ flux, whereas our mass balance suggests that DOC mineralization contributes on average 75% of river CO₂ flux. In addition, previous studies in similar rivers have shown that the combined biological and photochemical degradation of DOC within the stream channel is insufficient to account for the observed CO₂ fluxes (Lapierre and del Giorgio,

2014). It is thus clear that most of the degradation of terrestrial DOC must occur before it reaches the river channel, likely in the hyporheic zone, which is known to be a hotspot of biogeochemical activity (Fiebig et al., 1990; Krause et al., 2011; Rinehart et al., 2015; Schindler and Krabbenhoft, 1998; Stegen et al., 2016). In this regard, the DOC removal that we observe here is commensurate with what has been reported for artificial stream bed reactors (Sleighter et al., 2014). We acknowledge, however, that other processes such as DOC flocculation (Droppo et al., 1998) or sorption to mineral soil (Kaiser and Kalbitz, 2012) may remove DOC without producing CO₂ and therefore that we could be overestimating the role of DOC although these processes are likely minor in small boreal streams considered here. Overall our results reinforce the shift in paradigm concerning the reactivity of soil-derived DOC, but emphasize the fact that most of the transformations and mineralization of the highly reactive pools occurs at the soil/water interface in headwater streams, and it is thus not surprising that studies that have focused on the reactivity of terrestrially-derived DOC further downstream in the network have concluded that this organic C is mostly recalcitrant.

The above likely applies to the oxidation of methane as well. The stream bed has been assumed to be a source of CH₄ to the river water (Hlaváčová et al., 2006; Krause et al., 2011), but our results would suggest that, regardless of whether methane production occurs here or not, the hyporheic zone is in fact a net sink of soil-derived CH₄, since the estimated fraction of soil-derived CH₄ that was oxidized in transit averaged 0.82 (± 0.03), and was relatively constant across streams. This is in accordance to laboratory experiments showing that CH₄ produced or injected to hyporheic sediments can be almost entirely removed by oxidation, especially at the sediment-water interface (Rulík et al., 2013), so that relatively little CH₄ escapes into the stream waters, where oxidation tends to be low (Anthony et al., 2012). To our knowledge, CH₄ oxidation has never been included in attempts to understand stream CO₂ supersaturation, and our results show, that in addition to fuelling CO₂, soil CH₄ can explain the actual river CH₄ dynamics, which is a much less studied component of river C dynamics than CO₂.

Interestingly, the estimated contribution of the three C species to stream CO₂ was remarkably consistent across our 43 study rivers, with only a handful of sites deviating significantly from this average, and we found no clear pattern in these contributions along a gradient of increasing river order (Fig. 5). This was somehow unexpected, and there are several studies that have suggested that the relative contribution of these pathways to riverine C concentrations and emissions should change along the river continuum (Hotchkiss et al., 2015; Vannote et al., 1980), since the degree of coupling with the surrounding soils, the availability of DOC and the relative importance of autochthonous processes should gradually shift as we depart from the terrestrial ecosystem. However, our target streams were all relatively small (Strahler order ≤ 3), and it is very likely that the role of the different pathways may change towards higher order rivers (Hotchkiss et al., 2015).

Our study necessarily involved assumptions and oversimplifications, which undoubtedly add uncertainty to our calculations. Our mass balance approach assumes steady state within the hypothetical stream reach, i.e. that the inputs and outputs are in steady state, and therefore that there is no net change in pCO₂ along the reach. Although this assumption is likely not met, because there are surely small scale spatial variations in C species within these rivers, the variability of C species along the hypothetical reach is likely minimal relative to the differences in concentrations between soil and stream waters, which are the main drivers of the mass balance. These differences are much greater than what we could ever detect along a 100 m stretch of any of these rivers. Further, we did not include DIC other than CO₂ in our mass balance, because at the average alkalinity and pH measured in the studied sites, both soil and stream waters (Table A.1), our calculations based on the carbonate equilibrium suggest that very little (<5%) of this soil-derived carbonate and bicarbonate will turn into CO₂ once in the streams, and vice versa regarding soil-derived CO₂ entering streams (Vachon et al.,

2016). In fact, basing the estimates of CO₂ on the DIC speciation equilibrium using DIC, alkalinity and pH may actually result in major biases in the CO₂ mass balance in these systems (Abril et al., 2015). It is clear, however, that these results cannot be directly extrapolated to fluvial networks where re-equilibration of the carbonate system may play a larger role in shaping CO₂ concentrations due to the regional geology and chemistry. We further acknowledge that streams also receive inputs of POC, which are unaccounted for in our mass balance, but given the fact that POC is generally <10% of DOC (Dinsmore et al., 2010) and less immediately available than DOC, we have not included it in our calculations. The contribution of POC might be comparable to the contribution of CH₄ in systems prone to erosion, but our studied rivers had mainly forested catchment and thus the POC fluxes are most likely minor.

Another source of uncertainty in our mass balance calculations is the large heterogeneity that exists in the concentrations of DOC and especially of gases across soil waters, which has also been reported before (Sey et al., 2008; Stoyan et al., 2000). The local soil texture and structure and local topography affect both the movement of water in the soil, and the amount and nature of the C that is transported by this water (Fasching et al., 2015; Schiff et al., 1998). However, we did not find any relationship between any of the soil or catchment characteristics that we measured and the observed concentrations of C species in soil water, which we could use to model this variability, and clearly more detailed soil and hydrologic analysis are needed to understand this large spatial variability in soil water C concentrations. In order to smooth out some of this heterogeneity, we pooled all our soil water data into a regional average, and we applied that whole-catchment average to all subsequent mass balance calculations. When we calculated the mass balance using the soil water concentrations measured at each individual site, however, we obtained very similar results compared to those using the average regional soil water concentrations (details not shown), suggesting that this potential spatial heterogeneity in soil water concentrations would not significantly alter the general trends presented here. Our regional estimate, however, allowed us to account for at least some of the variability in the pathways of water delivery from soil to streams, and therefore the fact that the soil water we measured may not always be that entering the stream at the point of sampling.

It is important to emphasize that our results represent a summer snapshot and do not incorporate the potential temporal variability in the export and composition of soil derived carbon (Fasching et al., 2015; Lambert et al., 2013). Since the sampling was performed during an extremely dry summer, the observed patterns correspond to a scenario of base flow, which would tend to decrease the importance of

direct CO₂ injection (Öquist et al., 2009) and maximize the contribution of in-stream/hyporheic zone processing. This might explain the large contribution of terrestrial DOC degradation to stream CO₂ efflux observed here (Fig. 5), and it is thus likely that these relative contributions will change throughout the hydrological cycle. Previous studies have shown that the age and composition of organic C exported from catchments vary greatly as a function of precipitation, runoff and groundwater discharge (Billett et al., 2012; Garnett et al., 2013; Vihermaa et al., 2014), even seasonally within a given catchment (Schiff et al., 1998). Our results should thus not be extrapolated to landscapes with very different hydrology, geology and soil patterns, to larger order rivers even within the same region, and to other hydrological periods within the same catchments. We nevertheless contend that this exercise yields robust insight into the functioning of these small streams and on their connection to the surrounding catchment, as well as into the different pathways underlying the observed spatial changes in stream CO₂ and CH₄ concentrations and emissions.

Overall, our results suggest that in order to understand C emissions from streams, we must consider all the C species potentially involved, because their individual dynamics and fates are inseparably linked not only through their common transport via groundwater, but also through processing, which converts one C species into another. It is thus possible that a partial assessment of the processes underlying stream C emissions will lead to a biased understanding of the mechanisms underlying them, and may partly explain the disparity of results found across the literature. For example, most studies to date have inferred the relative contribution of soil-derived CO₂ from local or regional balances of either inorganic or organic C (Crawford et al., 2014; Hotchkiss et al., 2015), but few have attempted to incorporate the actual amounts of these C species delivered by soil waters to rivers (Peter et al., 2014), and none, to our knowledge, has simultaneously considered CO₂, DOC and CH₄. These linked soil-stream C pathways must necessarily add up to the ecosystem fluxes that we observe, and it is through establishing this integrative C balance that we gain a novel perspective on stream CO₂ dynamics, which not surprisingly differs from that which emerges from addressing each process individually.

Acknowledgements

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Appendix A. Supplementary data

Table A.1

Background information on the studied rivers, the adjacent sampled soils, and their catchments divided by river order, mean values (\pm standard errors).

	Unit	River order				
		0	1	2	3	ALL
RIVERS						
N		15	8	11	9	43
Width	m	0.4(\pm 0.1)	0.9(\pm 0.2)	3.8(\pm 1.8)	3.4(\pm 0.9)	2.0(\pm 0.5)
Depth	m	0.07(\pm 0.01)	0.2(\pm 0.04)	0.2(\pm 0.14)	0.4(\pm 0.07)	0.2(\pm 0.04)
Velocity	m s ⁻¹	6.7(\pm 2.4)	11.7(\pm 2.9)	12.7(\pm 5.7)	12.2(\pm 2.4)	10.4(\pm 1.9)
Q _R	L s ⁻¹	0.88(\pm 0.31)	11.4(\pm 7.7)	138.5(\pm 129.2)	140.2(\pm 51.5)	68.3(\pm 34.7)
k CO ₂	m d ⁻¹	1.102	0.672	0.919	1.659	1.088(\pm 0.2)
k CH ₄	m d ⁻¹	1.110	0.667	0.908	1.639	1.081(\pm 0.2)
pCO ₂	µatm	1821(\pm 223)	2141(\pm 345)	1318(\pm 244)	1564(\pm 309)	1717(\pm 139)
pCH ₄	µatm	1526(\pm 582)	1420(\pm 638)	577(\pm 328)	863(\pm 185)	1111(\pm 271)
CO ₂ flux	mg m ⁻² d ⁻¹	920(\pm 153)	656(\pm 146)	471(\pm 132)	1087(\pm 224)	796(\pm 90)
CH ₄ flux	mg m ⁻² d ⁻¹	35(\pm 13)	19(\pm 9)	11(\pm 7)	21(\pm 6)	24(\pm 6)
DOC	mg L ⁻¹	10.7(\pm 1.5)	7.7(\pm 1.5)	7.6(\pm 0.7)	10.0(\pm 1.6)	9.2(\pm 0.7)
Temperature	°C	14.8(\pm 1.2)	16.1(\pm 1.5)	15.8(\pm 1.4)	14.7(\pm 1.7)	15.3(\pm 0.7)

(continued on next page)

Table A.1 (continued)

	Unit	River order				
		0	1	2	3	ALL
pH		6.0(±0.2)	6.4(±0.2)	7.0(±0.2)	6.3(±0.2)	6.4(±0.1)
Conductivity	$\mu\text{s cm}^{-1}$	41(±10)	31(±5)	29(±6)	27(±6)	33(±4)
Oxygen	%	84(±4)	91(±7)	91(±7)	94(±4)	89(±3)
CATCHMENTS						
Area	km^2	0.2	0.9	9.7	12.9	
Wetlands	%	0.0(±0.0)	1.3(±1.3)	0.3(±0.2)	0.5(±0.2)	0.4(±0.3)
Broad + mixed forest	%	11(±7)	14(±6)	20(±10)	14(±6)	15(±4)
Conifer forest	%	82(±9)	73(±12)	71(±11)	75(±7)	76(±6)
Slope		8.0(±1.8)	6.0(±1.6)	9.0(±0.9)	7.7(±1.0)	7.8(±0.8)
Altitude	m	336(±50)	216(±62)	283(±50)	206(±50)	276(±27)
OrgM in soil ^a		15(±6)	17(±11)	33(±10)	9(±3)	18(±4)
2000–500 nm ^b	%	37(±3)	30(±6)	38(±7)	26(±4)	33(±3)
500–45 nm ^b	%	55(±3)	65(±6)	57(±7)	65(±4)	60(±3)
pCO ₂	μatm	4640(±909)	3684(±625)	3686(±817)	6340(±1470)	4615(±523)
pCH ₄	μatm	38,566(±16,396)	39,402(±9952)	59,838(±26,023)	97,154(±27,702)	58,216(±11,062)
DOC	mg L^{-1}	20(±4)	14(±4)	20(±2)	21(±6)	19(±2)
Temperature	°	15.0(±0.7)	14.3(±0.9)	17.3(±1.0)	15.1(±0.8)	15.4(±0.4)
pH		5.8(±0.1)	6.0(±0.2)	6.2(±0.2)	6.1(±0.1)	6.0(±0.1)
Conductivity	$\mu\text{s cm}^{-1}$	485(±409)	372(±172)	137(±92)	171(±55)	303(±132)
Oxygen	%	64(±2)	52(±4)	70(±7)	61(±5)	62(±2)

^a Organic matter in soil.

^b Mineral soil granular size class, % of total dry weight < 2 mm.

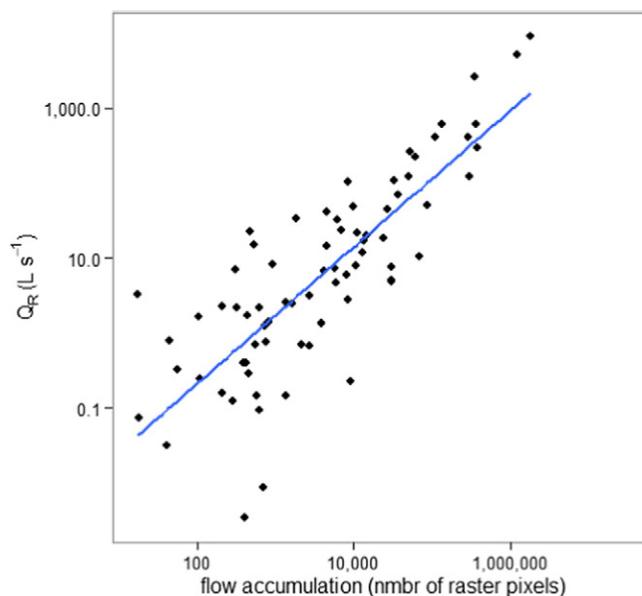


Fig. A.1. Log-linear model predicting discharge (Q_R , L s^{-1}) from flow accumulation (facc, number of raster pixels, created using the hydrology toolbox in ArcGIS 10). $\log_{10}(Q_R) = 0.909 \times \log_{10}(\text{facc}) - 2.48$, $R^2 = 0.66$, $p < 0.0001$.

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