

Carbon dioxide and methane evasion from a temperate peatland stream

Diane Hope,¹ Sheila M. Palmer,² Michael F. Billett, and Julian J. C. Dawson

Department of Plant and Soil Science, University of Aberdeen, Cruickshank Building, Aberdeen AB24 3UU, Scotland

Abstract

Peatland streams potentially represent important conduits for the exchange of gaseous carbon between the terrestrial ecosystem and the atmosphere. We investigated how gaseous evasion of carbon from the stream surface compared with downstream carbon transport at three locations on a Scottish headwater stream. Carbon dioxide was consistently above atmospheric saturation in the stream, with mean concentrations of 159.1, 81.8, and 29.5 $\mu\text{mol L}^{-1}$ at the lower, middle, and upper sites, respectively (i.e., 7.6, 3.9, and 1.2 times in excess of atmospheric equilibrium concentrations). Methane concentrations in stream water were much lower but showed a similar pattern. Rates of gaseous evasion from the stream surface to the atmosphere, determined experimentally using direct measurement of dissolved gas concentrations in conjunction with coinjection of conservative solute and volatile gas tracers, also declined downstream. Combined stream losses of all forms of carbon from the entire catchment (i.e., degassing from the stream surface and exports downstream) totaled 54,140 kg C yr^{-1} . Evasion of carbon dioxide from the stream surface accounted for 34% of this total, compared to 57% lost as dissolved organic carbon via export downstream. When expressed per unit area of watershed, the gaseous C evasion from the stream represents a loss of 14.1 g C $\text{m}^{-2} \text{yr}^{-1}$, which equals 28–70% of the estimated net carbon accumulation rate for such peatlands. This study shows that gaseous carbon loss from the surface of temperate headwater streams can be both spatially variable and significant in terms of rates of net annual land surface–atmosphere exchange at the catchment scale.

Although there is an extensive literature on dissolved organic carbon (DOC) in streams, much less attention has been given to gaseous forms of carbon (e.g., carbon dioxide and methane) in stream water (Hope et al. 1994). Typically, both carbon dioxide and methane are supersaturated in surface waters, with both streams and lakes frequently exhibiting gaseous partial pressures many times in excess of atmospheric equilibrium (Kling et al. 1991; Cole et al. 1994; Hamilton et al. 1994; Dawson et al. 1995; Jones and Mulholland 1998a,b). By evasion of this excess gaseous carbon, surface waters can act as conduits for a significant flux of carbon from terrestrial pools to the atmosphere (Kling et al. 1991; Cole et al. 1994; Hamilton et al. 1994). Most of the published evasion flux estimates are for lakes (e.g., Cole et al. 1994) and large rivers (e.g., DeAngelis and Scranton 1993; Raymond et al. 1997). However, small streams are where much groundwater initially enters surface drainage systems carrying a large load of dissolved gases, yet there are few published studies where gaseous carbon efflux rates have actually been measured for such streams (Jones and Mulholland 1998a,b).

Using measurements of carbon dioxide and methane content of stream water in conjunction with tracer experiments involving the coinjection of a conservative solute and a volatile gas tracer, we quantified the evasion flux of carbon dioxide and methane for a Scottish upland stream. We did

this for three separate study reaches, which represented the three distinct subcatchments in the watershed, as characterized by dominant soil types and topography. Carbon dioxide and methane content of soil pore waters were measured at sites representing three of the main soil types in the catchment. In addition, downstream carbon transport in the form of organic and inorganic carbon (including dissolved gases) were also measured. This approach allowed us to (1) estimate gaseous carbon evasion to the atmosphere from the whole stream surface, (2) investigate variations in gaseous carbon evasion along the stream in relation to differences in soil type and other catchment characteristics, and (3) compare gaseous losses of carbon via evasion to the atmosphere with losses of carbon by downstream transport.

Site description

The study site was a typical upland British first-order stream (130-ha catchment) located 56 km west of Aberdeen in northeast Scotland. The underlying bedrock is granite, overlain by glacial drift and organic-rich soils. The climate is cool temperate with a mean annual temperature of 8°C and a mean annual precipitation of 1,155 mm. The catchment (elevation 250 to 549 m) consists of a steep, narrow upper portion, a wide flatter central area with extensive peat accumulations, and a lower steep-sided section (Fig. 1). The stream is dominantly fed by shallow groundwater inputs along its entire length (Dawson et al. 2001). The stream channel is narrow (0.5 m wide) and turbulent in its upper reaches and flattens through a series of pools and gentle riffles in its midsection before becoming more turbulent again as the slope steepens in the lower reaches.

There are four main soil types in the catchment: histosols (Borohemists), spodosols (Haplothods), inceptisols (Haplumbrepts), and fluvents (Udifluvents), which cover 59, 22, 19, and <1% of the catchment area, respectively (for soil

¹ To whom correspondence should be addressed. Present address: Center for Environmental Studies, Arizona State University, Tempe, Arizona 85287-3211.

² Present address: Department of Civil and Environmental Engineering, Syracuse University, 220 Hinds Hall, Syracuse, New York 13244.

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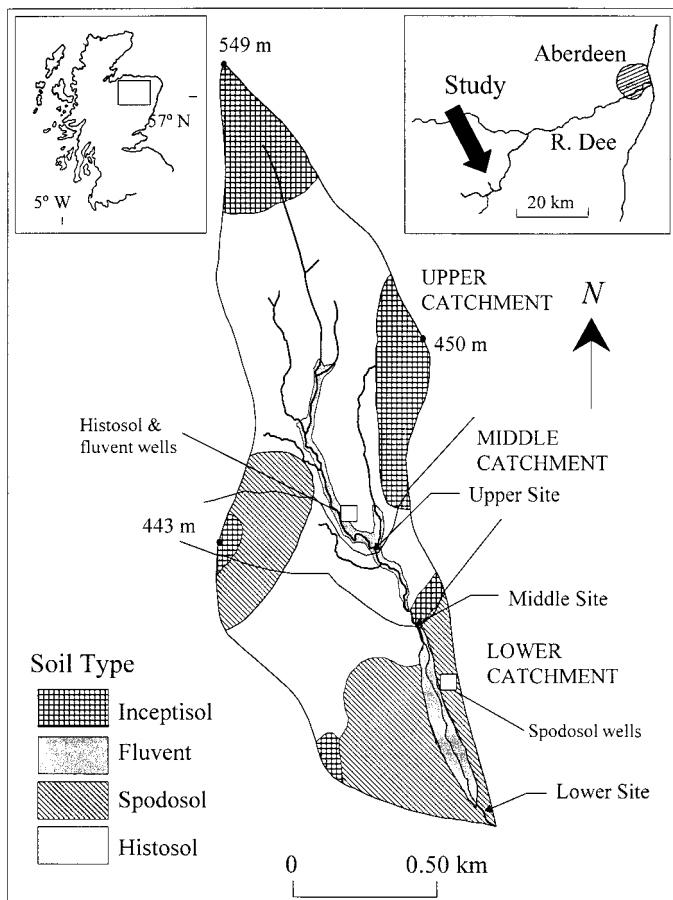


Fig. 1. Map of Brocky Burn showing the location of the catchment, the main soil types, the position of the soil diffusion wells, the three subcatchments, and the location of the upper, middle, and lower sampling sites on the stream.

descriptions see Dawson et al. 2001). The histosols (deep peats from 0.5 to 5.25 m thick) dominate the central catchment area. Vegetation cover is dominantly heather (*Calluna vulgaris*) moorland used for grouse shooting and deer stalking. Mean annual stream water chemistry of Brocky Burn is characterized by low pH and high DOC (Table 1), along with low concentrations of base cations, major anions, and nitrate (see Dawson et al. 2001).

Methods

Field procedures—During the period of study (March 1997–August 1998) evasion of carbon dioxide and methane from the stream surface was measured on three separate, short (10–30 m) study reaches chosen to represent the main geomorphic and hydrologic features of the stream (Table 1). This was done by measuring carbon dioxide and methane concentrations in stream water, along with the coinjection of conservative solute (NaCl) and volatile gas (propane) tracers (Marzolf et al. 1994; Jones and Mulholland 1999a). Experiments were carried out on a total of nine separate occasions during the course of the study, consisting of three, four, and two experiments at the upper, middle, and lower study sites,

respectively, between July 1997 and November 1998 (Table 2).

Prior to each tracer experiment, stream water temperature and background-specific conductance were measured at both ends of the study reach (Hanna Instruments model 9500). Tracers were coinjected in a well-mixed section a few meters upstream of the study reach. NaCl solution was injected at a constant rate using a battery-powered peristaltic pump (Watson Marlow model 504s/RL) until the background conductance of the stream water had reached a steady reading between 70 and 100 $\mu\text{S cm}^{-1}$ above background at both ends of the study reach. Propane was injected into the stream from a 6-kg tank of Calor Propane gas through a weighted air curtain, which produced a wall of fine bubbles across the entire width of the stream channel. The first 0.5 kg of gas was outgassed prior to the experiment to avoid the initial disproportionate discharge of ethane from the cylinder (Genereux and Hemond 1992). The gas was injected into the stream at a constant rate using a regulator set to 100 kPa. A sheet of heavy-duty polyethylene was secured over the stream at the point of injection to increase gas–water contact time and to enhance the proportion of propane dissolved into the stream water. Samples for gas analysis were collected at each end of the study reach prior to the experiment and once steady state (as determined by specific conductance) had been reached. Concentrations of carbon dioxide and methane in stream water were measured directly using a headspace equilibration technique (Kling et al. 1991). A 40-ml sample of stream water was collected in a 60-ml plastic syringe from a depth of 10 cm below the stream surface and was equilibrated with a 20-ml headspace of ambient air (by vigorous shaking for 60 s). Samples of the initial and equilibrated headspace gas were collected in nylon syringes for subsequent analysis. Ambient atmospheric carbon dioxide (and methane) concentrations were determined on syringe samples of air collected at the same (Table 1). Duplicate samples of both stream water and atmosphere were collected and analyzed throughout the study.

In addition to the sampling done during the injection experiments, a number of additional sample collection activities were carried out. Stream water was sampled once every 2 weeks at all three study sites for the duration of the study period. Samples for carbon dioxide and methane were collected as described above. Separate stream water samples were collected in acid-washed glass bottles and filtered through pre-ashed Whatman GF/F (0.7 μm) glass fiber filters. Samples for pH determination were collected in 60-ml plastic syringes. Stage height and water temperature at the study sites were gauged continuously using thermistors, pressure transducers, and data loggers. Stream flow was measured by dilution gauging (see below) at the upper and middle sites and by installation of a flume at the lower site. Flow measurements made at different stage heights were used to calibrate the gauges to obtain continuous flow readings.

Concentrations of carbon dioxide and methane in the soil atmosphere were measured using soil gas diffusion wells located in the three main soil types (histosol, fluvent, and spodosol) in the central part of the catchment (Fig. 1). Wells consisted of 10-mm internal diameter brass tubing topped

Table 1. Physical characteristics and water chemistry for the upper, middle, and lower subcatchments and experimental reaches at Brocky Burn.

Physical characteristics	Study sites		
	Upper	Middle	Lower
Subcatchment characteristics			
Basin area (ha)	68	15	47
Altitudinal range (m)	405–549	390–405	270–390
Main stem length (m)	1,597	323	753
Stream surface area (m ²)	885*	489	809
% soil coverage			
Histosol	67	63	40
Spodosol	4	32	49
Inceptisol	27	5	11
Fluvent	2	<1	<1
Experimental reaches			
Length (m)	13.6	20.7	10.3
Width (m)	0.6	1.5	1.3
Stream surface area (m ²)	8.3	31.7	13.4
Channel slope (degrees)	3.2	11.3	7.1
Mean flow (L s ⁻¹)	18.7	22.8	35.6
Stream water chemistry			
pH	4.8	5.0	6.1
Dissolved free CO ₂ -C (μmol L ⁻¹)	155.2	79.5	24.0
(μatm)	2,674	1,361	424
Dissolved CH ₄ -C (μmol L ⁻¹)	1.8	0.3	b.d.
(μatm)	879	142	b.d.
HCO ₃ ⁻ (μmol L ⁻¹)	9	12	14
DOC (μmol C L ⁻¹)	1,433	1,300	1,150
POC (μmol C L ⁻¹)	67	58	33

* The stream surface area of the smaller tributaries in the upper catchment comprises an additional 644 m².

with a brass nut and gas-tight rubber septum. They were screened at depths of 0.15–0.20 m or 0.45–0.50 m with fine-gauge brass gauze covered with a thin layer of latex to form a waterproof gas-permeable membrane (Magnusson 1989). Clusters of 20 wells, 10 for each sampling depth, were lo-

cated in three of the main soil types (histosol, fluvisol, and spodosol) adjacent to the stream channel (Fig. 1). Wells were installed in December 1996 and allowed to settle in for a period of 12 weeks before sampling began. Gas samples from the wells (3–5 ml) were collected using a hypodermic

Table 2. Stream flow conditions, propane exchange coefficients, and gas evasion rates measured during the propane injection experiments at the upper, middle, and lower study reaches on Brocky Burn.

Study reach	Date	Stream flow (L s ⁻¹)	Gas transfer coefficients		Instantaneous evasion rate (μg C m ⁻² s ⁻¹)	
			τ* (min)	K _{propane} (min ⁻¹)	CO ₂	CH ₄
Upper	12 May 98	4.3	4.47	0.014	76	1.4
	19 Jun 98	4.9	4.32	0.043	385	5.2
	24 Nov 98	22.4	2.10	0.098	531	4.1
Mean		10.4	3.63	0.051	331	3.6
Middle	8 Jul 97	6.6	7.88	0.158	111	0.3
	12 May 98	5.4	4.00	0.320	47	0.6
	16 Jun 98	12.6	3.12	0.285	239	0.9
	22 Sep 98	5.0	3.75	0.247	105	0.4
Mean		7.4	4.69	0.252	126	0.6
Lower	12 Aug 97	7.2	3.05	0.019	3	—
	16 Jun 98	24.1	2.07	0.127	39	—
Mean		15.6	2.56	0.073	21	—

* τ is reach length travel time.

needle and high-density nylon syringes. Sampling was carried out once every 2 weeks between March 1997 and August 1998 at the same time the routine stream water samples were collected.

Spatial variations in dissolved CO₂, CH₄, and total organic carbon (TOC) concentrations in stream water were investigated by carrying out three synoptic sampling campaigns on three additional dates during the study. Samples were taken at 36 sites along the entire length of Brocky Burn from just below where the stream rises to the lowest sampling site, as well as on five small tributaries. Samples were collected and analyzed as described above, except for TOC, which was measured on unfiltered samples.

Laboratory procedures—Analysis of carbon dioxide, methane, and propane in the headspace gas and ambient air samples was carried out within 24 hours of collection by flame ionization detection on a Chrompack 9001 gas chromatograph fitted with a methanizer. Samples were injected using a 250- μ L loop onto a Porpak Q column using a nitrogen carrier gas stream. Carbon dioxide and methane concentrations were determined by calibrating with standard gas mixtures. Henry's Law and the stream water temperature at the time of sampling were used to calculate K_h , which was then used with the gas concentrations in the equilibrated headspace samples, as well as the gas and water volumes equilibrated to compute the ambient partial pressures and concentrations of CO₂ and CH₄ in the water, as outlined by Kling et al. (1991). In the tracer experiments, the integrated area of propane was used for subsequent calculations, instead of actual concentration (Marzolf et al. 1994). DOC was determined on filtered samples by wet oxidation using a LABTOC carbon analyzer (Pollution and Process Monitoring Ltd.), whereas TOC was measured on unfiltered samples. Particulate organic carbon (POC) concentrations were determined from the filters by loss on ignition (Hope et al. 1997a). Gran alkalinity was measured by titration with 0.005 M H₂SO₄ using a GK2401C combined glass/reference electrode (Radiometer). pH was measured on the syringe samples using the same electrode in a closed chamber, which minimized gas exchange prior to measurement. Concentrations of HCO₃⁻ were then calculated from pH and Gran alkalinity, adjusting for the buffering effects of aluminum and organic acids typically found in acidic organic-rich stream waters and omitting a few outlying values obtained during high stream flows (Neal et al. 1998, 1999).

Calculations—The data from the injection experiments was used to determine the gas transfer coefficient (sensu Wannikhof 1992) for propane in the study reaches. This was then used to calculate the evasion flux of carbon dioxide and methane from the study reaches, following the procedure developed for small streams (Genereux and Hemond 1992; Marzolf et al. 1994; Jones and Mulholland 1998a). Water travel time through a study reach was measured using the time require to achieve 50% of the steady state specific conductance. Because the study reaches were short (10–30 m) and no decline in specific conductance was detected between the upper and lower sampling points, it was assumed that lateral inflow of water along these sections was minimal.

The gas transfer coefficient for propane K_{propane} (min⁻¹) along the study reach was calculated as

$$K_{\text{propane}} = \tau^{-1} \times \ln[(G_1 \times C_2)/(G_2 \times C_1)], \quad (1)$$

where τ is the reach travel time (min), C_1 and C_2 are the specific conductances (μ S cm⁻¹) at the upstream and downstream ends of the reach, respectively, and G_1 and G_2 are the integrated propane peak areas (i.e., relative concentrations) for the upstream and downstream points, respectively (Marzolf et al. 1994). The value obtained for K_{propane} was converted to K_{CO_2} using

$$K_{\text{CO}_2}/K_{\text{propane}} = (d_{\text{CO}_2}/d_{\text{propane}})^n, \quad (2)$$

where d_{CO_2} and d_{propane} are the respective gas diffusion coefficients (Genereux and Hemond 1992). The value for n in Eq. 2 can potentially vary from unity to -0.66 , the latter value being appropriate for calm conditions across lakes; we used a value of -0.5 , which is typically used for turbulent mountain streams and higher wind speeds (MacIntyre et al. 1995). d_{CO_2} and d_{propane} were calculated for the in situ stream water temperature x ($^{\circ}$ C) using the following equations developed from the data given in Unver and Himmelblau (1964) and Wise and Houghton (1966).

$$d_{\text{CO}_2} = 1.005 \times \exp^{(0.0231x)} \quad \text{and}$$

$$d_{\text{propane}} = 1.092 \times \exp^{(0.0235x)} \quad (3)$$

Stream water concentrations of carbon dioxide (CO_{2,streamwater}, μ mol L⁻¹) were determined from the concentrations of the equilibrated headspace and stream water temperature (Kling et al. 1991). Stream discharge (Q , L s⁻¹) during each experiment was assumed to be constant along a study reach and was calculated using the rate of NaCl injection (I), the concentration of the injected tracer (NaCl_{tracer}, mg L⁻¹), and the plateau concentration of stream water at the downstream end of the study reach (NaCl_{plateau}) (British Standards Institution 1995).

$$Q \text{ (L s}^{-1}\text{)} = I \frac{(\text{NaCl}_{\text{tracer}} - \text{NaCl}_{\text{plateau}})}{\text{NaCl}_{\text{plateau}}} \quad (4)$$

The gas evasion flux from the stream surface was then calculated for a study reach using the following reaeration flux equation (Young and Huryn 1998).

$$\begin{aligned} \text{CO}_{2,\text{evasion}} \text{ (}\mu\text{mol L}^{-1}\text{ s}^{-1}\text{)} \\ = \text{CO}_{2,\text{streamwater-atm}} \times K_{\text{CO}_2} \times \tau \times Q \end{aligned} \quad (5)$$

CO_{2,streamwater-atm} is the difference between the reach stream water CO₂ concentration and the atmospheric equilibrium CO₂ concentration (μ mol L⁻¹) and Q is the stream flow (L s⁻¹) from the study reach. Equation 5 was chosen in preference to that used by Jones and Mulholland (1998a) because the latter tends to underestimate the flux in streams with relatively high gas exchange coefficients (Marzolf et al. 1998). The same equation was used for CH₄, substituting K_{methane} , which was taken to be $K_{\text{propane}}/0.93$ (Jones and Mulholland 1998a). Because the concentration of CH₄ in ambient air samples was regularly below detection limits, an ambient concentration in air of 1.7 μ atm was used (Jones and Mulholland 1998a). The resulting evasion rates were then ex-

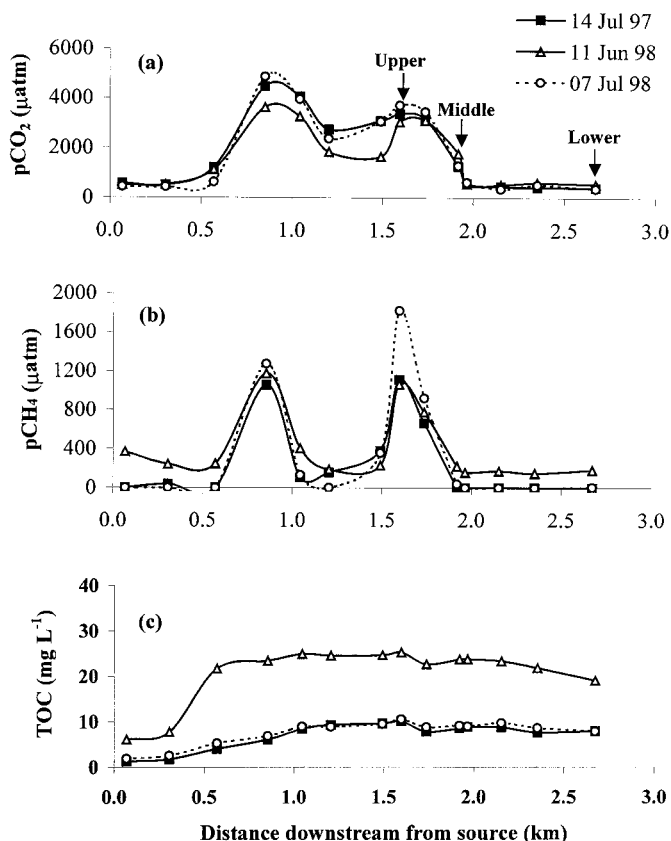


Fig. 2. Downstream changes in (a) the partial pressure of dissolved CO₂ (pCO₂), (b) the partial pressure of dissolved CH₄ (pCH₄), and (c) the concentration of TOC in stream water on three separate synoptic sampling campaigns carried out during the study. Sampling dates were 14 Jul 1997, 11 Jun 1998, and 7 Jul 1998. Location of the three main study reaches are indicated by the arrows.

pressed in terms of the study reach stream surface area (mg C m⁻² s⁻¹).

Flux estimation—The mean instantaneous gas evasion flux rates determined from the injection experiments carried out on three, four, and two occasions for the upper, middle, and lower study reaches, respectively, were then assumed to be representative of the entire main stem upstream to the next sampling point. In each case, evasion (mg C m⁻²) was multiplied by the entire stream surface area in the respective subcatchments (Table 1) and converted to an annual flux. For the upper subcatchment, the procedure was modified in two ways. First, for the initial 0.5 km of stream below the source, the stream surface area was omitted from the calculations because stream water CO₂ concentrations here were not significantly elevated with respect to the atmosphere (Fig. 2a); hence, CO₂ evasion rates were likely to be low. Second, gas evasion from small tributaries, which all drained areas of deep peat upstream of the upper site, was assumed to occur at the same rate (per unit stream surface area) as at the upper site (Table 1) because the synoptic sampling data showed that high stream water CO₂ and CH₄ concentrations (and by inference, high evasion rates) oc-

curred wherever the stream channel was adjacent to deep peat.

Evasion fluxes for the three main stem sections and tributaries were then summed to give an annual flux for the whole catchment. These estimates are likely to be conservative because they were calculated using only the flow conditions at the time of the injection experiments, which by necessity were carried out at times of lower than average flow. Although there may be a positive relationship between instantaneous evasion flux and stream flow, there were insufficient data to develop evasion–flow relationships. Losses of carbon downstream in the form of DOC, POC, HCO₃⁻, dissolved CO₂, and dissolved CH₄ were also estimated for each site using the mean instantaneous flux data to calculate an annual export for each constituent (Littlewood 1992).

Statistical analysis—Flow-concentration relationships for the various forms of carbon were investigated using correlations and simple linear regression. Differences K_{CO_2} and CO₂ evasion between sites were examined using one-way analysis of variance; significant differences ($P < 0.05$) were further evaluated using Tukey's multiple comparison test. The variation in carbon dioxide and methane concentration in soil diffusion wells between soil types was assessed using the same method.

Results

Stream flow at the upper, middle, and lower sites averaged 18.7, 22.8, and 35.6 L s⁻¹, respectively, during the entire study. However because of the difficulty of keeping equipment in place in the stream channel during higher flow conditions, injection experiments were largely conducted during lower than average flow conditions, although at least one experiment at each site was conducted at slightly higher than average flow conditions (Table 2). Stream water and soil diffusion well samples were collected once every 2 weeks on a total of 36 occasions, encompassing a representative range of stream flow conditions.

Stream water C concentrations—Concentrations of the various forms of carbon in Brocky Burn showed distinct spatial and temporal variation—with marked differences between the three sites, as well as temporal differences largely related to variations in stream flow. The mean free CO₂ concentration decreased from 155.2 µmol L⁻¹ at the upper site to 79.5 µmol L⁻¹ and 24.0 µmol L⁻¹ at the middle and lower sites, respectively. The equivalent values expressed in units of partial pressure were 2,674, 1,361 and 424 µatm, respectively. This compared with an average atmospheric CO₂ partial pressure of 350 µatm in the catchment. Hence, stream CO₂ was 7.6, 3.9, and 1.2 times in excess of atmospheric equilibrium. The mean dissolved CH₄ concentration in stream water was much lower and also decreased downstream from 1.9 µmol L⁻¹ (908 µatm) at the upper site and 0.3 µmol L⁻¹ (143 µatm) at the middle site to below the detection limit (<0.05 µmol L⁻¹) at the lower site. This compared with average atmospheric CH₄ partial pressures of 4.9 µatm at the upper site, 5.3 µatm at the middle site, and below detection limits at the lower site, meaning that stream

CH₄ was on average between 185 and 27 times in excess of atmospheric equilibrium at these two sites. Stream water temperatures averaged 6.5, 6.7, and 7.5°C at the upper, middle, and lower sites, respectively.

Mean DOC concentrations at the three main study sites also decreased downstream from 1,433 $\mu\text{mol L}^{-1}$ at the upper site to 1,300 and 1,150 $\mu\text{mol L}^{-1}$ at the middle and lower sites, respectively (Table 1). Average POC concentrations were markedly lower than for DOC at all three sites but increased slightly downstream, whereas the bicarbonate portion of the dissolved inorganic carbon showed little variation between sites (Table 1).

Data from the three synoptic sampling events carried out along the entire stream revealed a striking downstream pattern in dissolved CO₂, CH₄, and TOC (Fig. 2). The downstream variations in dissolved gas concentrations were closely related to changes in the soil types adjacent to the stream channel. Gas concentrations were relatively low in the uppermost section of the stream, where it drained steep slopes and shallow inceptisols. CO₂ and CH₄ concentrations then increased rapidly, peaking at two points in the middle reaches (Fig. 2a,b) corresponding to where the stream drains the deepest peat accumulations in the central part of the catchment. Dissolved gases then declined rapidly in the lower third of the stream, where both the stream channel and surrounding catchment slopes become steeper and the proportion of spodosolic mineral soils increases (Table 1). Although the overall pattern along the stream was similar for both CO₂ and CH₄, the latter tended to show a more rapid decline downstream of the peak concentrations (Fig. 2b). TOC concentrations in the stream were also low immediately downstream from the source of the stream at a small spring but then began to increase around the same point as the dissolved gases, where the catchment slopes became less steep and the stream began to drain areas of deep peat. However unlike the gases, TOC concentrations then remained elevated along the remainder of the stream channel and did not decline in the lower reaches (Fig. 2c).

There were some significant flow-related variations in concentrations of the various forms of carbon in Brocky Burn. At the upper site, both carbon dioxide ($r^2 = 0.58$; $P < 0.0001$) and methane ($r^2 = 0.68$; $P < 0.0001$) concentrations were negatively correlated with stream flow rate (Fig. 3). There was no correlation between stream flow rate and dissolved gases at the middle and lower sites ($P > 0.05$). Neither DOC or POC were correlated with flow at the upper site ($P > 0.05$). However, DOC did show a weak positive correlation with flow rate at the middle ($r^2 = 0.11$; $P = 0.046$) and lower ($r^2 = 0.13$; $P = 0.034$) sites, and POC was positively correlated with flow ($r^2 = 0.35$; $P = 0.0001$) at the lower site. The concentration of HCO₃⁻ showed an increasingly negative correlation with flow at all three sites ($r^2 = 0.52, 0.69, \text{ and } 0.86$ at the upper, middle, and lower sites, respectively; $P < 0.0001$ in all cases).

Soil carbon dioxide and methane concentrations—The partial pressure of carbon dioxide in the soil atmosphere varied from an average of 6,260 μatm in the spodosols to 29,125 and 32,361 μatm in the fluvents and histosols, respectively (i.e., typically between 18 and 92 times greater

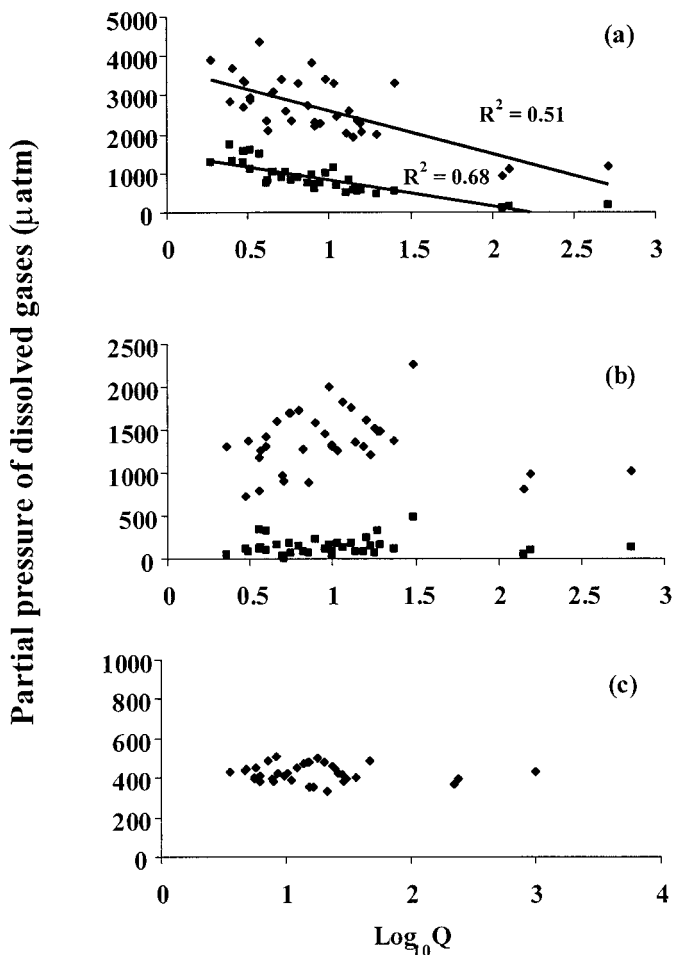


Fig. 3. The relationship between stream flow Q (L s^{-1} and log-transformed) and the partial pressure of dissolved CO₂ (diamonds) and CH₄ (squares) in stream water at the three sample sites on Brocky Burn.

than atmospheric values). Carbon dioxide partial pressures in the histosols and fluvents were significantly higher than in the spodosols (Tukey test $P < 0.0001$) but not significantly different from each other (Table 3). Carbon dioxide partial pressures decreased significantly with depth in the histosols, showed the reverse trend in the fluvents, and did not vary with depth in the fluvents. Methane partial pressures were significantly higher (Tukey test $P < 0.0001$) in the fluvent wells (4,569 μatm) than in the histosol wells (2,951 μatm) and increased significantly (Tukey test $P = 0.011$) with depth in both soil types (Table 3). Methane was consistently below detection limit in the spodosol wells.

Tracer experiments—Stream flow during the tracer injections averaged 10.4, 7.4, and 15.6 L s^{-1} at the upper, middle, and lower sites, respectively (i.e., considerably lower than the average flow conditions over the entire study period). Reach travel times were typically between 2 and 4 min (Table 2). Carbon dioxide concentrations in Brocky Burn at the time of the injection experiments averaged 149.4, 39.0, and 6.9 $\mu\text{mol L}^{-1}$ at the upper, middle, and lower sites, respectively. Methane concentrations ranged from 1.1 to 7.1 μg

Table 3. Partial pressures (in μatm) of CO₂ (pCO₂) and CH₄ (pCH₄) in the soil atmosphere measured in the histosols, fluvents, and podosols in the Brocky Burn catchment. Average values and coefficients of variation (C.V.) for the period of study ($n = 36$ sampling occasions) are shown for all soil diffusion wells in each soil type and for the two depth intervals (10 wells at each depth in each soil type). Different superscripts denote means that are significantly different ($P < 0.05$) as determined by Tukey's multiple comparison test.

Soil type	Shallow (25–30 cm)		Deep (45–50 cm)		Combined	
	Mean	C.V.	Mean	C.V.	Mean	C.V.
pCO₂						
Histosol (deep peat)	35,980 ^a	0.27	28,740 ^c	0.25	32,360 ^e	0.29
Fluvent (riparian)	25,890 ^{bd}	0.34	32,270 ^{bcd}	0.29	29,130 ^e	0.33
Spodosol (podzol)	9,730 ^c	0.56	2,500 ^f	0.48	6,260 ^h	0.89
pCH₄						
Histosol (deep peat)	381 ^a	1.89	5,430 ^b	0.37	2,950 ^d	1.02
Fluvent (riparian)	381 ^a	1.50	8,760 ^c	0.52	4,570 ^c	1.15
Spodosol* (podzol)	—	—	—	—	—	—

* CH₄ concentrations below detection limits in spodosol wells.

L⁻¹ at the upper site, <1 $\mu\text{g L}^{-1}$ at the middle site, and below the detection limit at the lower site.

The values obtained for K_{propane} averaged 0.054, 0.252, and 0.073 min⁻¹ at the upper, middle, and lower sites, respectively. The K_{CO_2} and K_{CH_4} values calculated from K_{propane} were slightly higher, ranging from 0.015 to 0.344 min⁻¹ overall, with the highest values at the middle site. Within-site variations in gas transfer coefficients seemed largely linked to stream flow, with the highest exchange coefficients measured during the highest flows, but this trend was less clear at the middle site, where stream flow (and exchange coefficients) during the experiments varied only by a factor of two. The mean values of both K_{CO_2} and K_{CH_4} were significantly higher (Tukey test $P = 0.011$) at the middle site (0.264 and 0.271 min⁻¹) compared to the upper site (0.054 and 0.055 min⁻¹). The lower values of K_{CO_2} at the upper and lower sites (0.080 min⁻¹) did not differ significantly from each other (Tukey test $P < 0.05$); hence, gas exchange between stream and atmosphere appeared to be greatest around the middle section of the stream, where channel slope and turbulence was greatest.

Despite this, evasion rates per unit stream surface area were highest at the upper site, where the concentration differential between stream water and atmosphere was greatest, and declined successively at the middle and lower sites. The average instantaneous flux for CO₂ at the upper site was 331 $\mu\text{g C m}^{-2} \text{s}^{-1}$ compared to 126 and 21 $\mu\text{g C m}^{-2} \text{s}^{-1}$ at the middle and lower sites, respectively (Table 2). Methane eva-

sion, although considerably lower than carbon dioxide, showed a similar pattern with average efflux rates of 3.6 and 0.6 $\mu\text{g C m}^{-2} \text{s}^{-1}$ at the upper and middle sites, respectively (Table 2).

Carbon dioxide and methane evasion fluxes—Based on the evasion rates measured at the three study reaches, it was estimated that 18,483 kg C yr⁻¹ were lost via combined CO₂ and CH₄ evasion from the entire stream surface, with declining losses from the upper, middle, and lower subcatchments, respectively (Table 4). Carbon losses from the catchment downstream in the form of DOC, POC, HCO₃⁻, dissolved CO₂, and CH₄ totaled 35,657 kg C yr⁻¹, of which 86% was in the form of DOC (Table 4).

Discussion

Gaseous flux estimates—Gaseous evasion, dominantly in the form of carbon dioxide, was estimated to represent at least 34% of the total stream-mediated exports of carbon (i.e., the sum of losses via both gaseous evasion and hydrologic transport downstream) from the entire Brocky Burn watershed. Gaseous efflux was most important in the upper main stem and tributaries, accounting for 43% of total stream-mediated exports from the upper catchment, compared to 49% lost downstream as DOC (Fig. 4). Evasion also accounted for 32% of stream-mediated exports for the middle subcatchment compared to 48% lost as DOC. How-

Table 4. Annual carbon losses via gaseous evasion and downstream export from each subcatchment, the whole stream, and the entire Brocky Burn catchment (i.e., total stream losses expressed per square meter of the entire watershed surface area).

	Gaseous evasion loss			Downstream export				Total C
	CO ₂ -C	CH ₄ -C	DOC	POC	HCO ₃ ⁻ -C	CO ₂ -C	CH ₄ -C	
Stream reach (kg C yr ⁻¹)								
Upper (and tributaries)	15,929*	29*	18,228	1,677	13	997	7	
Middle	1,936	55	3,000	213	13	899	3	
Lower	534	0	9,635	2,355	5	516	0	
Whole stream (kg C yr ⁻¹)	18,399	84	30,863	4,245	31	516	0	54,140
Catchment (g C m ⁻² yr ⁻¹)	14.1	0.1	23.7	3.3	<0.1	0.4	0	41.4

* Tributaries account for 36% of the CO₂ and 14% of the CH₄ gaseous evasion losses from the stream surface in the upper subcatchment.

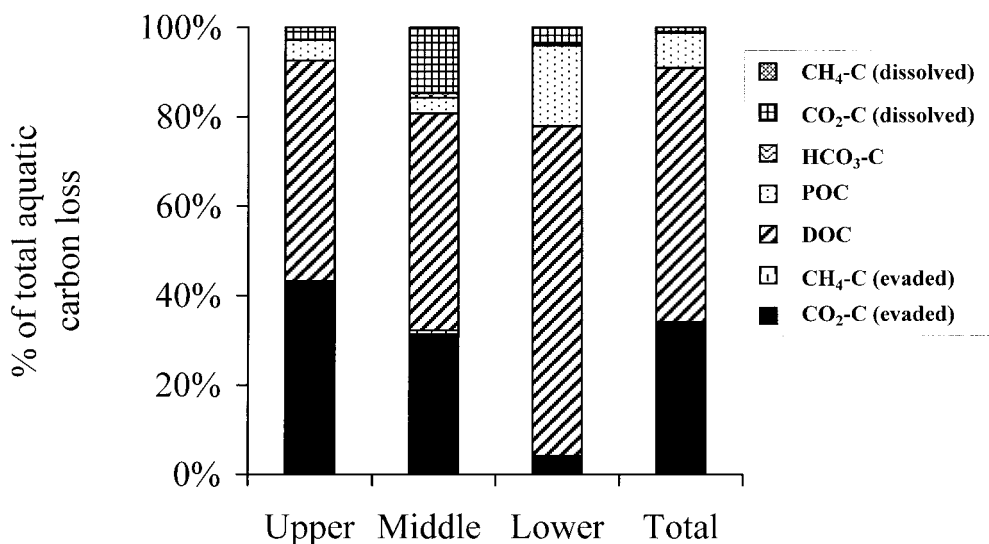


Fig. 4. Contribution of gaseous carbon evasion (CO_2 and CH_4) and downstream exports (dissolved CO_2 , dissolved CH_4 , DOC, POC, and HCO_3^-) to total annual carbon losses via the stream from the three main subcatchments and the entire Brocky Burn catchment. Exports of carbon downstream from middle and lower subcatchments are not cumulative, having been adjusted to account for the exports entering from upper and middle subcatchments, respectively.

ever degassing was much less important in the lower part of the stream, accounting for only 4% of stream-mediated exports from the lower subcatchment compared to 72% lost downstream as DOC and 18% as POC.

Although the contribution of gaseous evasion to overall carbon exports was large (34% of all stream exports), the estimates presented here are likely to be conservative. Direct measurement of evasion at higher stream flows was not possible due to practical difficulties; hence, the injection experiments were carried out under below-average flow conditions for all three sites. Typically, DOC and POC exports increase markedly with stream flow in this type of catchment (Hope et al. 1994). In contrast, stream water CO_2 and CH_4 concentrations were negatively correlated to flow at the upper site in this study (presumably because of the dilution and exhaustion of soil sources brought about by prolonged rainfall and rapid runoff), whereas they showed no change with flow at the middle and lower sites (Fig. 3). However, increasing turbulence will also enhance rates of gas evasion at higher stream flows.

Comparisons with other studies—The carbon dioxide evasion rates measured from the stream surface at Brocky Burn covered a wide range of variation from 259 to 45,878 $\text{mg C m}^{-2} \text{d}^{-1}$. Although the lower end of this range is consistent with previous work, the upper limits are considerably larger (Table 5). Stream surface methane evasion rates for Brocky Burn ranged from 0 to 345 $\text{mg C m}^{-2} \text{d}^{-1}$ and were comparable to existing literature values (Table 5). In comparison to previously published estimates for a temperate first-order stream (Jones and Mulholland 1998b), mean evasion rates for both gases measured at Brocky Burn were significantly higher, despite the fact that propane transfer coefficients were not markedly larger (Genereux and Hemond 1992). Overall, the higher evasion rates from Brocky Burn are

largely due to very high concentrations of dissolved gases produced by respiration within the organic-rich soils upstream of the upper and middle stream sampling sites. Transport of gas-laden water to the stream channel results in the marked concentration differential between the stream water and the atmosphere and, hence, the high rates of degassing seen.

The much higher gas concentrations in Brocky Burn compared to Walker Branch (Jones and Mulholland 1998a,b) are likely to result primarily from differences in the routing of gaseous transport between the two catchments. The soils in Walker Branch are mostly thin, freely draining acrisols (Ultisols) with relatively high rates of soil respiration and CO_2 evasion from the soil surface, averaging 2,148 $\text{mg m}^{-2} \text{d}^{-1}$ (Jones and Mulholland 1998b). In such catchments, the stream is likely to constitute only a minor pathway for gaseous carbon transport and loss. In contrast, the peats in the Brocky Burn catchment are typically waterlogged to within 0.5 m (or less) of the surface for much of the year. Because vertical diffusive transport of CO_2 and CH_4 through waterlogged peat is considerably slower than horizontal transport via mass flow (Clymo and Pearce 1995), gaseous carbon evasion from the soil surface is impeded. This results in relatively low evasion rates from peatland surfaces—around 100 to 634 $\text{mg m}^{-2} \text{d}^{-1}$ for carbon dioxide and 11 to 79 $\text{mg C m}^{-2} \text{d}^{-1}$ for methane (Clymo and Pearce 1995; Fowler et al. 1995). Hence, much of the gaseous soil carbon in Brocky Burn is transported laterally to the stream, which consequently represents a much more important pathway for carbon loss from the catchment than in Walker Branch.

Spatial variations of gaseous carbon in soils and stream water—The downstream patterns in evasion rates and concentrations of dissolved gases seen in Brocky Burn appear to be closely related to the distribution of the organic-rich

Table 5. A summary of carbon dioxide and methane flux data from published studies of gaseous evasion from streams, rivers, ponds, and lakes in temperate and boreal regions. The fluxes are all expressed as a loss of carbon per square meter of water surface area per day. The selection includes only those references from which such a daily flux estimate is available or can be readily calculated and emphasizes studies carried out in peatland systems.

Study site	Flux (mg C m ⁻² d ⁻¹)*		Reference
	C-CO ₂	C-CH ₄	
Rivers			
Brocky Burn, Scotland	259–45,878	0–345	This study
Walker Branch, Tennessee	1,884–4,476	0.3–10	Jones and Mulholland (1998a,b)
Pacific Northwest rivers	—	0–238	Lilley et al. (1996)
Hudson River	192–444	6.1	Raymond et al. (1997), DeAngelis & Scranton (1993)
Arctic rivers (1st–6th order), Alaska	137–1,370	—	Kling (pers. comm.)
Ponds and lakes			
Boreal reservoir (postflood) NW Ontario	982–1,009	66	Kelly et al. (1997)
Boreal reservoir, Quebec	500–1,100	5–10	Duchemin et al. (1995)
Oligotrophic lakes	0.3–2.5	–51–102	Rudd et al. (1993)
Reservoirs	3.0–5.7	391–411	Rudd et al. (1993)
Arctic lakes	–66–718	—	Kling et al. (1991, 1992)
Boreal beaver pond	1,525	70	Roulet et al. (1997)
Wetland ponds, Hudson Bay	1,009–3,000	83–135	Hamilton et al. (1994)
Esthwaite Water, England	9–92	—	Maberley (1996)
Mirror Lake, New Hampshire	71–137	—	Cole & Caraco (1998)

* A negative sign indicates an ingress of carbon to the water from the atmosphere.

soil types with high in situ gas concentrations. Low dissolved gas concentrations in the initial section of the stream, where shallow mineral soils dominate, increase markedly as the stream passes through the histosols and fluvents in the central portion of the catchment (Fig. 2). The two peaks in dissolved gas concentrations ~0.8 and 1.7 km from the stream source coincide with where the stream passes through the deepest (>3 m thick) peat horizons (Deacon pers. comm.). These organic-rich soils constitute a significant input of shallow groundwater supersaturated in CO₂ and CH₄ to the stream, as evidenced by δ^{12/13}C isotopic data, which showed that stream water CO₂-C had an almost identical isotope signature to the soil atmosphere at the upper site (Palmer et al. 2001). Evasion rates of both gases from the stream surface were highest in the upper reach of the study, where the differential in CO₂ and CH₄ concentrations between the stream surface and atmosphere was greatest. Presumably gaseous evasion loss from the stream surface in the middle reach exceeds new inputs, as dissolved concentrations of both gases declined along this section. The sustained decline in dissolved gas concentrations downstream from the middle study site (Fig. 2) coincides with an increase in the extent of spodosols, which have relatively low gas concentrations in the soil pores (Table 3). Moreover, a decline in the delivery of dissolved gases via mass flow in the lower part of the catchment, along with the conversion of more inorganic carbon to bicarbonate as CO₂ degasses and the pH of the stream rises (Dawson et al. 2001), are both likely to contribute to the observed decline in carbon dioxide evasion downstream.

Although the overall pattern for methane is broadly similar to that of carbon dioxide, overall evasion rates are two orders of magnitude lower. Methane inputs appear to be

more localized than for carbon dioxide, with the highest soil pore water concentrations found in the deeper (45–50 cm) organic soil horizons (Table 3), particularly along the central section of the main stem. The decline in CH₄ concentrations is more pronounced than that shown by CO₂, presumably because CH₄ is lost via both evasion and oxidation once in the stream channel (Jones and Mulholland 1998a).

TOC concentrations also increased in the stream on passage through the deep organic soils in the central portion of the catchment. However, the processes that would cause TOC concentrations to decline in the stream's lower reaches are in-stream respiration and dilution by groundwater inputs low in TOC, both of which are relatively low in this lower section (Dawson 2001). Hence, in contrast to the pattern shown by the gases, TOC concentrations remain elevated along the middle and lower sections of the stream.

Role of gaseous evasion in terrestrial carbon dynamics—Peatlands constitute the main terrestrial carbon pool in temperate and boreal systems (Gorham 1991). For example in Britain, the total soil organic carbon content is estimated to be 22 × 10¹² kg C, 75% of which is in Scottish peatlands (Howard et al. 1995). The soil organic carbon storage in the Brocky Burn catchment is estimated to be 80 kg C m⁻² (Deacon pers. comm.), and the current best estimate of the net rate of carbon accumulation in British peatlands is 20–50 g C m⁻² yr⁻¹ (Clymo et al. 1998; Cannell et al. 1999). When the annual estimates of total gaseous evasion losses from Brocky Burn are expressed per unit area of the entire catchment, then degassing represents a loss of at least 14.1 g C m⁻² yr⁻¹, which represents 28–70% of the estimated net accumulation rate. Downstream transport of carbon (as DOC, POC, HCO₃⁻, dissolved CO₂, and CH₄) constitutes an addi-

tional loss of 27.6 g C m⁻² yr⁻¹ on a per-unit catchment area basis from Brocky Burn (Table 4). Such downstream losses are typical for peatland streams in upland Britain, particularly where there are large accumulations of soil organic carbon (Hope et al. 1997a,b).

Few studies have incorporated gaseous carbon losses from surface waters into carbon budgets. However, Kling et al. (1991, 1992) estimated that gaseous evasion from arctic lakes and streams average 24 g C m⁻² yr⁻¹ for the landscape as a whole (i.e., between 25 and 50% of the net annual carbon accumulation rate for tundra). Our data show that gaseous evasion from peat-dominated headwater streams are of a similar order of magnitude and are likely to constitute a localized but significant source of gaseous carbon evasion from temperate upland landscapes. If terrestrial carbon accumulation is assessed by core sampling, the removal of gaseous and dissolved soil carbon via shallow groundwater flow to surface waters will have already been accounted for. However direct measurement of land-atmosphere gaseous carbon exchange, which ignores carbon losses from (and via) surface waters, may significantly overestimate terrestrial carbon accumulation rates (Kling et al. 1991; Waddington and Roulet 1996; Kelly et al. 1997). Also, lakes and ponds with active degradation of peat at the bottom of the water column (e.g., Hamilton et al. 1994; Roulet et al. 1994) will offset carbon accumulation rates for the peatland as a whole.

Aquatic carbon transport, including degassing from streams and rivers, should be included explicitly in land-atmosphere exchange for peat-dominated temperate ecosystems. The downstream variation in gaseous carbon evasion seen in Brocky Burn highlights the importance of accounting for spatial variation in streams and their surrounding catchments. Our data show that dissolved gas concentrations and evasion rates can vary significantly along a headwater stream where catchment characteristics such as topography, soil type, organic horizon thickness, and hydrology show marked variation. Had only the measurements from the lowest study site been used, the resulting whole-catchment evasion flux estimate would have been an order of magnitude lower than that obtained using data from all three sites.

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