Transfer of carbon dioxide and methane through the soil-water-atmosphere system at Mer Bleue peatland, Canada

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Abstract:
Surface waters associated with peatlands, supersaturated with CO₂ and CH₄ with respect to the atmosphere, act as important pathways linking a large and potentially unstable global repository of C to the atmosphere. Understanding the drivers and mechanisms which control C release from peatland systems to the atmosphere will contribute to better management and modelling of terrestrial C pools. We used non-dispersive infra-red (NDIR) CO₂ sensors to continuously measure gas concentrations in a beaver pond at Mer Bleue peatland (Canada); measurements were made between July and August 2007. Concentrations of CO₂ in the surface water (10 cm) reached 13 mg C l⁻¹ (epCO₂ 72), and 26 mg C l⁻¹ (epCO₂ 133) at depth (60 cm). The study also showed large diurnal fluctuations in dissolved CO₂ which ranged in amplitude from ~1.6 mg C l⁻¹ at 10 cm to ~0.2 mg C l⁻¹ at 60 cm depth. CH₄ concentration and supersaturation (epCH₄) measured using headspace analysis averaged 1.47 mg C l⁻¹ and 3252, respectively; diurnal cycling was also evident in CH₄ concentrations. Mean estimated evasion rates of CO₂ and CH₄ over the summer period were 44-92 ± 7.86 and 0.44 ± 0.25 µg C m⁻² s⁻¹, respectively. Open water at Mer Bleue is a significant summer hotspot for greenhouse gas emissions within the catchment. Our results suggest that CO₂ concentrations during the summer in beaver ponds at Mer Bleue are strongly influenced by biological processes with temperature increases, gas dissolution and hence evasion rates of CO₂ and CH₄ with respect to the atmosphere (Kling et al., 1991; Kling et al., 1997; Jones and Mulholland, 1998; Hope et al., 2001; Billett and Moore, 2008). This disequilibrium between water and atmospheric concentrations causes degassing (evaporation). Evasion rates depend on the concentration gradient across the degassing interface, and the gas transfer coefficient and solubility of the particular gas. The solubility of any gas in fresh water is negatively correlated with temperature. Therefore under most conditions, as temperature increases, gas dissolution and hence evasion also increases (MacIntyre et al., 1995). Both CO₂ and N₂O have a similar solubility in fresh water (0.039 and 0.029 mol l⁻¹ atm⁻¹ at 20 °C respectively) (Weiss, 1974; Weiss and Price, 1980), whereas CH₄ is a relatively

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Insoluble gas (0.0015 mol 1\(^{-1}\) atm\(^{-1}\) at 20 °C) and is often released to the atmosphere as bubbles (ebullition) (Wiesenburg and Guinasso, 1979). Methods which indirectly calculate CH\(_4\) evasion may underestimate actual fluxes by ignoring bubbles which would be accounted for in direct chamber measurements (Billett and Moore, 2008).

Studies aimed at quantifying fluxes to the atmosphere have previously had to rely on a relatively small number of isolated concentration or flux measurements to calculate long-term evasion rates (Kling et al., 1991; Frankignoulle et al., 1998; Jones and Mulholland, 1998; Hope et al., 2001; Billett and Moore, 2008). These are unable to capture diurnal, daily and in many cases weekly variability in concentrations due to the physical limitations of having to manually collect spot samples. In this study we use submerged non-dispersive infra-red (NDIR) CO\(_2\) sensors to make continuous summer concentration measurements giving much better temporal resolution.

This study aims to contribute to our understanding of CO\(_2\) and CH\(_4\) dynamics in peatlands based on the hypothesis that the aquatic system plays a major role in greenhouse gas (GHG) release. Specifically we aim to (a) study small-scale variability in dissolved CO\(_2\) and CH\(_4\) concentrations at a diurnal rather than seasonal timescale, (b) relate cycles in the water column to cycles elsewhere in the peatland ecosystem and in doing so understand what drives variability, and (c) estimate the importance of summer time evasion to both the C and the GHG budget of the catchment as a whole.

**SITE CHARACTERISTICS**

Mer Bleue peatland (45°40′N, 75°50′E) is located approximately 10 km east of Ottawa, Ontario, and is the site of the Eastern Peatland flux station for Fluxnet Canada (http://www.fluxnet-canada.ca, 2008). Mer Bleue contains an ombrotrophic raised bog with an average elevation of 69 m a.s.l. The bog, which formed c. 6000 years BP succeeding a fen formed c. 8500 years BP, covers approximately 2800 ha. Peat depth ranges from 1 m to 2 m near the edges to 5–6 m near the centre, underlain by continuous marine clay deposits (Billett and Moore, 2008). The bog surface has a typical hummock-hollow microtopography covered in vascular ericaceous (Chamaedaphne calyculata, Ledum groenlandicum, Kalmia angustifolia) and deciduous shrubs (Vaccinium myrtilloides) and sedges (Eriophorum vaginatum), with an understorey of Sphagnum mosses. Trees such as Picea mariana, Larix laricina and Betula populifolia occur in patches across the peatland. The margin of the peatland, where it abuts gravel and sand ridges, comprises open-water beaver ponds, with inundated transition zones of Typha latifolia and floating mats of mosses and sedges leading into the bog.

A series of raised peat domes has lead to the formation of three distinct drainage ‘fingers’ which drain the peatland from east to west into the Ottawa river valley with a gradient of approximately 0.0008 (Billett and Moore, 2008). Unlike the spring and autumn periods, during the summer months ground and surface water flow is slow through the centre of the bog moving into a low-energy continuous network of beaver dams at the perimeter.

The climate of the region is defined as mid-continental cool. Mean annual temperature and precipitation are 5.8 °C and 910 mm respectively and the growing season lasts from May to September. During the period of this study (July and August 2007), mean temperature was 19.8 °C, compared to a 29 year (July/August) average 20.2 °C; total precipitation over the 2 months was 256 mm compared to a 29 year average of 178 mm (http://www.climate.weatheroffice.ec.gc.ca, 2008). The precipitation:runoff ratio is 0.4 with more than 55% of annual runoff occurring during spring snowmelt (Roulet et al., 2007).

**MATERIALS AND METHODS**

A combination of continuous and single point measurements were made throughout July and August 2007 in open water and at three locations at the bog-pool interface (Figure 2). Data collected from a flux tower site located approximately 250 m from the pond was also used to aid interpretation of the beaver pond data (Humphreys, unpublished data).

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Figure 1. Carbon budgets of two ombrotrophic peatlands: (a) Auchencorth Moss, Scotland and (b) Mer Bleue, Canada (Billett et al., 2004; Roulet et al., 2007; Billett and Moore, 2008).
Field measurements

At the open water site (site 1, Figure 2) continuous measurements of dissolved CO₂ were made using two Vaisala CARBOCAP® (transmitter series, GMT220), non-dispersive infra-red absorption (NDIR) CO₂ sensors. The sensors were enclosed within water-tight, gas permeable membranes and connected to a Campbell Scientific CR1000 datalogger (Johnson et al., 2006). The sensors were installed at the site at the beginning of July 2007 and ran until the end of August 2007. Sensors were placed at depths of 10 cm and 60 cm below the water surface. For two weeks during August 2007, CO₂ concentrations were measured using a third sensor, held approximately 10 cm above the water surface. Additional sensors were used to measure water depth (PDCR 1830 series pressure transducer), temperature at 60 cm depth (CS 108) and conductivity, temperature (CS547A) and pH (CSIM11) at 10 cm depth. Measurements were made once per minute with 10 minute averages recorded.

In addition to the continuous measurements at the open water site, single spot measurements of CO₂, CH₄ and N₂O concentrations at 10 cm and 60 cm depths were made using the headspace technique (Kling et al., 1991; Hope et al., 2001; Billett et al., 2004; Billett and Moore, 2008). A 20 ml sample of pond water was equilibrated with 20 ml of gas standard (CO₂ 380 ppm, CH₄ 0 ppm, N₂O 0 ppm) by shaking under water for 1 min; the headspace was then transferred to gas-tight syringes and transported back to the laboratory for analysis. To investigate gas concentration gradients within the water column, headspace measurements were made on four separate occasions at incremental 10 cm intervals throughout the water profile. Water samples were collected at the same time as the headspace measurements for analysis of DOC. Spot measurements were made weekly during July–August and every other day between 26 July and 6 August. In addition, hourly samples were collected between 13:00 30 July and 12:00 31 July to investigate diurnal variation.

Along the bog–pool interface (sites 2–4, Figure 2) soil atmosphere wells were installed and spot samples collected at the same frequency as samples in the open water site. The soil-atmosphere wells consisted of watertight, gas permeable tubing (ACCUREL® PP V8/2 HF) inserted into the soil at two different depths (10–50 cm and 50–90 cm) and in replicates of two.

Data utilized from the Flux tower site (site 5, Figure 2) included NEE, meteorological data, soil temperature and soil CO₂ concentration. Soil CO₂ was measured in situ, using a total of five NDIR CO₂ sensors, three installed above the water table at depths of 5, 10 and 20 cm below a hummock and two at depths of 5 and 10 cm in a hollow (Roulet, unpublished data). Soil temperature was measured adjacent to each CO₂ sensor. For the purpose of this study, an average CO₂ concentration and average soil temperature is calculated from all five sensors. Measurements were made once per minute and a half-hourly average recorded.

Short-wave radiation was recorded at the flux tower as part of the meteorological dataset. Radiation entering the water column was estimated as total short-wave radiation minus surface reflectance, calculated using the Fresnel equations (Kirk, 1983).

Analytical methods

CO₂ concentrations from the headspace samples and soil atmosphere wells were determined using a Shimadzu Mini-2 gas chromatograph (GC) with a flame ionization detector (FID) and methanizer (99% reduction efficiency). A separate Shimadzu GC with FID was used to measure CH₄; column and detector temperatures for the two GCs were 45°C and 100°C, respectively. N₂O concentrations were determined on a Shimadzu 14-A GC using an electron capture detector (ECD). Ultrahigh purity N₂ was used as the carrier gas for the 14-A
GC with column and detector temperatures of 50 °C and 315 °C, respectively. Coefficients of variation and detection limits for the GCs were: CO₂ 1–3% and 15 ppm, CH₄ 1–3% and 0.3 ppm, and N₂O 1–5% and 0.2 ppm. Gas concentrations are expressed in units of partial pressure (pCO₂, pCH₄ and pN₂O), mg l⁻¹ or excess partial pressure (εpCO₂, εpCH₄ and εpN₂O), defined as the partial pressure of gas in solution divided by the partial pressure of the gas in equilibrium with the atmosphere. Continuous concentrations of atmospheric CO₂ were modelled by fitting a sine wave function to the data collected using the third NDIR sensor located 10 cm above the pond surface. Parameter values for the amplitude, height and offset of the sine function were determined by minimizing the sum of squared differences using the Excel Solver program. Samples of ambient air were collected and analysed alongside headspace samples, and these values used in the subsequent calculation of gas concentrations using Henry’s Law for the spot samples.

Water samples were analysed for DOC on a Shimadzu TOC-VCSn analyser using high-temperature (720 °C) catalytic oxidation and measurement with a NDIR detector. Ultra-Zero Air was used as both carrier and reference gas. The coefficient of variation in detection accuracy was ~3–5%.

Calculation of evasion

To avoid systematic error in the sensor reading, the volume fraction output of the NDIR sensors was corrected for variations in temperature and pressure. The reference temperature and pressure for the sensors were 22.5 °C ± 1% and 100-7 kPa ± 1%, respectively. Concentrations were corrected using the method described in Tang et al. (2003).

Evasion from the water surface was calculated indirectly using wind speed to predict gas transfer velocity, combined with the partial pressure difference across the air–water interface. The method is based on established relationships between wind speed and gas transfer velocity (Wanninkhof, 1992; MacIntyre et al. (1995). The equation used to calculate gas fluxes (FCO₂) is described below for CO₂ (Equation (1)) (Billett and Moore, 2008; Borges et al., 2004), where k is the gas transfer velocity (cm h⁻¹), α is the solubility coefficient and ΔpCO₂ is the difference in partial pressure between the surface water and the atmosphere. The solubility coefficient α is temperature and salinity dependent. Values of α for CO₂, CH₄ and N₂O were derived from Weiss (1974), Wiesenberg and Guinasso (1979), and Weiss and Price (1980), respectively.

The transfer velocity k is a function of turbulence, the kinematic viscosity of the water and the molecular diffusion coefficient of the gas. In Equation (2) (MacIntyre et al., 1995) wind speed (m s⁻¹) at 10 m above the water surface υ₁₀ is used to describe turbulence, and the Schmidt number Sc is a function of the latter two terms. The equation is derived from a least-squares power law fit through the results of lake experiments using SF₆ as a deliberate tracer. k(600) refers to the transfer velocity normalized to Sc = 600, the Schmidt number of CO₂ at 20 °C in freshwater. Values of Sc used in Equation (2) for CO₂, CH₄ and N₂O are taken from MacIntyre et al. (1995).

Wind speed at 10 m (υ₁₀) is calculated using the semi-empirical log wind profile relationship shown in Equation (3) with the assumption of atmospheric stability (Montheith and Unsworth, 1990). Friction velocity υₜ was measured at the flux tower site (site 5, Figure 2). k describes von Karman’s constant (0.41), d is the zero plane displacement calculated as 0.65 times the height of the roughness elements (0.2 m) and z₀ is the surface roughness calculated as 0.077 for Mer Bleue (Lafleur et al., 2005). It is assumed that the wind speed at 10 m above the flux tower is representative of wind speed above the open water site. Laboratory measurements of CO₂ flux suggest that k becomes independent of υ₁₀ at low wind speeds (Ocampo-Torres et al., 1994). MacIntyre et al. (1995) therefore suggest using a υ₁₀ value of 1.5 m s⁻¹ for all values of equal to or less than 1.5 m s⁻¹.

\[
FCO₂ = k\alpha \Delta pCO₂ \quad (1)
\]

\[
k(600) = 0.45\upsilon₁₀^{1.6}(Sc/600)^{-0.5} \quad (2)
\]

\[
υₜ = \frac{υₜ}{k} \ln \left( \frac{z}{d} \right) \quad (3)
\]

Statistical analysis

Datasets with measurement frequencies of less than 1 hour were treated as time series and suitable statistical methods applied (see below). No significant autocorrelation was found in datasets with measurement frequencies of 1 hour or more.

As part of the exploratory analysis into the CO₂ cycles, time series datasets were adjusted, where necessary, for autocorrelation and seasonality (in this case diurnal fluctuations) using autoregression (up to order 2) and a cosine wave function. The adjusted datasets were then compared using cross-correlation analysis to establish maximum correlation lag times. The direction of the lag was used to eliminate variables that followed CO₂ concentrations, so that only variables presumed to have a causal correlation to CO₂ were included in subsequent models.

Relationships between water column and soil CO₂ concentrations, and water column CO₂ and CH₄ concentrations with various independent variables, were modelled using stepwise regression with the inclusion of an autocorrelation term (<=order 2) where appropriate. Both forward and backward selection stepwise regressions were performed and compared to aid selection of the most appropriate explanatory model.

Where average values are quoted the ± refers to 95% confidence intervals unless stated otherwise. In datasets which display significant autocorrelation and hence the assumption of independence is not met, standard errors
and t-statistics are calculated using the effective rather than the real sample size.

**RESULTS**

**Comparison of pCO$_2$ headspace and NDIR values**

The pCO$_2$ values calculated from the headspace measurements were compared to the corresponding 10 min mean pCO$_2$ values calculated using the NDIR sensor. The results were then compared using a paired t-test with a 95% confidence limit. Mean pCO$_2$ at 10 cm was 11 786 ± 4838 μatm and 17 323 ± 1450 μatm measured using the headspace and NDIR methods, respectively. Despite headspace measurements averaging ~30% less than NDIR measurements, due to the high variability in the headspace samples the difference was not statistically significant (t = 1.89, p = 0.09, n = 13). Concentrations at 70 cm were significantly different with mean headspace and NDIR pCO$_2$ values of 17 371 ± 1681 and 50 137 ± 211 μatm, respectively (t = 40.2, p < 0.01, n = 11). A more detailed comparison between measurement methods is discussed in Johnson et al. (manuscript in preparation for Limnology and Oceanography; Methods).

To quantify the bias introduced by collecting headspace samples only during daylight hours, and to assess the importance of sampling frequency, a series of manipulations were carried out on the NDIR dataset. One epCO$_2$ value was randomly selected from the continuous NDIR dataset for each day between 09:00 h and 17:00 h, and a mean July and August epCO$_2$ value calculated. This process was repeated to simulate measurement frequencies of twice weekly, weekly and fortnightly. The results were then compared to the mean July and August epCO$_2$ value calculated. During July and August 2007, epCO$_2$ values were calculated for each measurement frequency. The results were then compared to the mean July and August epCO$_2$ calculated from the full continuous dataset. Across all measurement frequencies, the mean overestimation in epCO$_2$ caused by daytime sampling was approximately 3.5%. Although the magnitude of the mean did not change with sampling frequency, the width of the confidence intervals increased significantly as sampling frequency decreased.

**July and August concentrations**

During July and August 2007, pCO$_2$ concentrations at 10 cm, measured continuously using the NDIR sensors, ranged from 10 472 μatm ([C] = 5.01 mg l$^{-1}$) to 26 616 μatm ([C] = 14.2 mg l$^{-1}$) with a mean of 16 268 ± 1700 μatm ([C] = 7.64 ± 0.80 mg l$^{-1}$). This corresponds to epCO$_2$ values of between 28.2 and 71.5, with a mean of 43.6 ± 4.60. From the headspace spot samples over the same period, mean pCO$_2$ concentration was 11 786 ± 4838 μatm ([C] = 5.38 ± 2.21 mg l$^{-1}$) (n = 13) corresponding to an epCO$_2$ of 31.5 ± 12.9. Deep water CO$_2$ concentrations were around three times greater than surface water concentrations. pCO$_2$ concentrations ranged from 49 286 μatm to 51 420 μatm ([C] = 23.3 to 25.1 mg l$^{-1}$) with a mean of 49 946 ± 165 μatm ([C] = 23.9 ± 0.22 mg l$^{-1}$). The mean epCO$_2$ value at 60 cm was 128 ± 0.31.

pCH$_4$ over the summer period (n = 13) ranged from 249 μatm ([C] = 0.1 mg l$^{-1}$) to 7795 μatm ([C] = 3.7 mg l$^{-1}$) with a mean of 3210 ± 1002 μatm ([C] = 1.5 ± 0.5 mg l$^{-1}$), epCH$_4$ reached a maximum of 7795, with a mean of 3252 ± 1589. Similar to CO$_2$, deep water CH$_4$ concentrations were approximately three times greater than surface water concentrations with a mean pCH$_4$ at 60 cm of 10 669 ± 6252 μatm ([C] = 5.21 ± 3.30 mg l$^{-1}$) and epCH$_4$ 8937 ± 3900. N$_2$O concentrations in the water column were very low and no significant difference was observed between the two measured depths. Mean pN$_2$O (n = 9) for the summer was 0.66 ± 0.43 μatm. The mean epN$_2$O was 1.68 ± 1.63; on two of the nine sampling occasions water column N$_2$O concentrations were below atmospheric concentrations. The mean DOC concentration in the open water over July and August was 113 ± 4.80 mg l$^{-1}$. Individual values ranged from 67.1 to 125 mg l$^{-1}$.

The results from the depth profile measurements in the open water for CO$_2$, CH$_4$ and N$_2$O (Figure 3), showed that on three out of four sampling occasions CO$_2$ concentrations increased with depth, with a pronounced increase at a depth of 40 cm. On both 6 and 9 August, a peak was also observed at 30 cm. Similar to the CO$_2$ profiles, on three out of four sampling occasions, CH$_4$ concentrations showed a dramatic increase at approximately 40 cm depth. No clear pattern was evident in the N$_2$O profiles.

Soil CO$_2$ concentrations measured using NDIR sensors installed at the flux tower site (site 5, Figure 2), ranged from 161 to 2032 ppmv with a mean of 885 ± 103 ppmv. Measurements made by manually sampling the soil atmosphere wells at the bog-pool interface showed significantly higher concentrations. The mean soil atmosphere CO$_2$ concentration ranged from approximately 8418 ppmv in the site 4 shallow well to >90 000 ppmv in the site 3 deep well (Figure 4). In general, CO$_2$ concentrations in the soil atmosphere wells appeared to be higher in the deep (50–90 cm) wells than in the shallow wells (10–50 cm) (Figure 4a). Mean summer CH$_4$ concentrations ranged from 2279 ± 667 ppmv in the site 4 shallow well to 7052 ± 909 ppmv in the deep well at site 3 (Figure 4b). The mean N$_2$O concentration across all wells was 1.33 ± 0.32 ppmv (Figure 4c). For both CH$_4$ and N$_2$O, mean concentration at sites 1 and 3 were highest in the deep wells, with the opposite true of site 2. To test the significance of these observed patterns, a two-way ANOVA was carried out on log-transformed concentrations of each gas using depth and site as independent variables. For both CO$_2$ and CH$_4$ concentrations, site was the only significant variable at the 95% confidence limit (CO$_2$: F = 5.22, p = 0.01; CH$_4$: F = 4.50, p = 0.02). Neither site nor depth had a significant effect on N$_2$O concentration.
Diurnal cycles

From the continuous CO₂ measurements in the open water (site 1, Figure 2), clear diurnal cycles were evident in both the surface and deep water concentrations (Figure 5a and 5b). Concentrations of CO₂ in the surface water had a diurnal range of approximately 3136 ppmv. Deep water CO₂ cycles were much steadier and more consistent, with a diurnal range \( \frac{1}{10} \) order of magnitude lower than the surface (320 ppmv). Peak CO₂ concentration in deep water was at 16:00 h with a minimum concentration at approximately 06:00 h. Near-surface water concentrations often showed two distinct daytime peaks at approximately 10:00 h and 19:00 h with the minimum occurring during darkness at approximately 02:00 h. The soil CO₂ concentrations also showed a diurnal pattern, but unlike water concentrations, the peak occurred at around midnight with the minimum at approximately 13:00 h (Figure 5c).

From the 24 hour spot sampling regime, a diurnal pattern was found in the surface water CH₄ concentrations (Figure 6) with minimum values between 00:00 and 04:00. The pattern of near surface CO₂ concentrations was consistent with that observed from the NDIR sensors: minimum CO₂ concentrations were between approximately 00:00 h and 03:00 h. A weak diurnal pattern was also found in the DOC concentrations with the peak concentration occurring at approximately 05:00 h (Figure 6). No diurnal pattern was visible in either deep water CH₄ concentrations or water column N₂O concentrations.

Drivers of cycles

To gain a better understanding of what drives aquatic cycles of CO₂, concentrations were compared to other cycles within the peatland ecosystem. Figure 7 shows the
were similar, particularly between the soil and surface water where the double peaks described earlier can be seen, there was a lag in the system. After correcting for autocorrelation and seasonality, cross-correlation analyses were carried out between surface water, deep water and soil CO$_2$ concentrations and against other explanatory variables. Explanatory variables included air and soil temperature, air pressure, surface and deep water temperature, short-wave radiation, short-wave radiation adjusted for surface reflectance, wind speed, 24-, 48- and 72-hour antecedent rainfall, water depth, pH and conductivity.

Significant correlation peaks for surface water CO$_2$ concentration (site 1, Figure 2) with soil concentration (site 5, Figure 2) occurred at lags of $-4.5$, $-32.0$ and $-40.5$ hours. The negative sign indicates that soil concentrations lag behind water concentrations. No significant correlation peaks were identified between deep water and soil CO$_2$ concentrations.

Where significant positive lags were found for concentration against an explanatory variable, the dataset was adjusted before further analysis was carried out. Where significant negative lags were found, as for surface water CO$_2$ versus conductivity (lag $= -4.5$ hours), the variable was omitted from further calculations. Variables which could potentially drive CO$_2$ cycles were therefore separated and modelled independently from variables responding to CO$_2$ changes.

The remaining variables along with autocorrelation terms of up to order 2 were then used to model CO$_2$ concentrations with stepwise regression (Table I). The best model for surface water CO$_2$ concentration included autocorrelation factors up to order 2, positive coefficients for short-wave variation and air temperature and negative coefficients for adjusted short-wave radiation and surface water temperature ($r^2 = 0.97$). Deep water concentrations could be modelled ($r^2 = 0.98$) using short-wave radiation as the only independent variable.

Stepwise regression was also used to model CH$_4$ concentrations from 10 cm and 60 cm depths (Table II) with the addition of DOC as an independent variable. Autoregressive terms were not included as no significant autocorrelation was found in the CH$_4$ dataset. Emissions throughout July and August could be modelled using the variables 24-hour antecedent rainfall and
adjusted shortwave radiation \( r^2 = 0.73 \). Diurnal CH\(_4\) concentrations in the surface water from 30–31 July were modelled using both surface and deep water temperature \( r^2 = 0.78 \). Using the complete dataset, both summer and diurnal variation in CH\(_4\) could be modelled from rainfall, radiation and adjusted radiation with \( r^2 = 0.63 \).

### Table I. Results from stepwise regression on July and August CO\(_2\) concentrations (water CO\(_2\) concentrations are expressed in units of mg l\(^{-1}\), soil concentrations are in volume fractions, ppmv)

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Independent variables</th>
<th>Lag (hrs)</th>
<th>Coefficient</th>
<th>t value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Surface water CO(_2) (total ( r^2 = 0.97 ))</td>
<td>Intercept</td>
<td>—</td>
<td>4.6 ( \times ) 10(^{-2})</td>
<td>3.51</td>
<td>&lt;0.01</td>
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<tr>
<td></td>
<td>Autoregressive term (first-order)</td>
<td>—</td>
<td>1.64</td>
<td>66.8</td>
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<td></td>
<td>Autoregressive term (second-order)</td>
<td>—</td>
<td>0.66</td>
<td>-21.7</td>
<td>&lt;0.01</td>
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<tr>
<td></td>
<td>Short-wave radiation</td>
<td>3.5</td>
<td>7.2 ( \times ) 10(^{-5})</td>
<td>-3.7</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Air temperature</td>
<td>0</td>
<td>1.1 ( \times ) 10(^{-4})</td>
<td>3.2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Adjusted short-wave radiation</td>
<td>3.5</td>
<td>1.5 ( \times ) 10(^{-4})</td>
<td>-2.7</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Surface water temperature</td>
<td>4.5</td>
<td>1.5 ( \times ) 10(^{-3})</td>
<td>-2.7</td>
<td>0.01</td>
</tr>
<tr>
<td>(b) Deep water CO(_2) (total ( r^2 = 0.97 ))</td>
<td>Intercept</td>
<td>—</td>
<td>0.39</td>
<td>2.11</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Autoregressive term (first-order)</td>
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<td>0.99</td>
<td>211.1</td>
<td>&lt;0.01</td>
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<tr>
<td></td>
<td>Short-wave radiation</td>
<td>0</td>
<td>7.5 ( \times ) 10(^{-5})</td>
<td>2.4</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### Table II. Results from stepwise regression on July and August CH\(_4\) concentrations (water CH\(_4\) concentrations are expressed in units of mg l\(^{-1}\), soil concentrations are in volume fractions ppmv)

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Independent variables</th>
<th>Coefficient</th>
<th>t value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Surface water CH(_4) July/August dataset (total ( r^2 = 0.73 ))</td>
<td>Intercept</td>
<td>-0.2518</td>
<td>-0.32</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>Antecedent rainfall (24hr)</td>
<td>0.30</td>
<td>4.20</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Adjusted short-wave radiation</td>
<td>0.0064</td>
<td>2.24</td>
<td>0.05</td>
</tr>
<tr>
<td>Hourly dataset (total ( r^2 = 0.78 ))</td>
<td>Intercept</td>
<td>-2.26</td>
<td>-3.72</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Temperature (surface water)</td>
<td>-0.83</td>
<td>-6.11</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Temperature (deep water)</td>
<td>13.61</td>
<td>3.96</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Full dataset (total ( r^2 = 0.63 ))</td>
<td>Intercept</td>
<td>0.70</td>
<td>4.77</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Antecedent rainfall (24hr)</td>
<td>0.25</td>
<td>4.73</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Short-wave radiation</td>
<td>0.0032</td>
<td>2.97</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Adjusted short-wave radiation</td>
<td>-0.0061</td>
<td>-1.98</td>
<td>0.05</td>
</tr>
<tr>
<td>(b) Deep water CH(_4) July/August dataset (total ( r^2 = 0.66 ))</td>
<td>Intercept</td>
<td>1159</td>
<td>113</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Deep water CO(_2)</td>
<td>-113</td>
<td>-1.97</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>Water depth</td>
<td>-84</td>
<td>-1.97</td>
<td>0.09</td>
</tr>
<tr>
<td>Hourly dataset (total ( r^2 = 0.23 ))</td>
<td>Intercept</td>
<td>-285.4</td>
<td>-285.4</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Temperature (deep water)</td>
<td>16.1</td>
<td>2.78</td>
<td>&lt;0.01</td>
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</tbody>
</table>

Figure 7. Continuous CO\(_2\) concentrations in soil, air and surface water over a 4 day period illustrating lag in CO\(_2\) cycles (note separate axis for surface water concentrations).

Evasion from water surface

Mean instantaneous CO\(_2\) evasion from the water surface, calculated from the continuous NDIR sensor data over the summer period, was 165 \( \pm \) 28.8 \( \mu \text{g m}^{-2} \text{s}^{-1} \) (Table III). From the spot headspace measurements, mean CO\(_2\) evasion was 86.2 \( \pm \) 52.1 \( \mu \text{g m}^{-2} \text{s}^{-1} \). These correspond to C losses of 44.9 \( \pm \) 7.86 \( \mu \text{g C m}^{-2} \text{s}^{-1} \) and
23.7 ± 14.2 µg C m⁻² s⁻¹, respectively. As direct measurements of CH₄ could not be made continuously, concentrations were predicted at half-hourly intervals for the whole 2 months using the full dataset model and environmental variables measured continuously during July and August. Using these modelled values, the mean summer instantaneous CH₄ evasion rate from the water surface was 0.59 µg m⁻² s⁻¹. The standard error in the evasion calculations as a result of the modelled CH₄ concentrations equates to ±0.09 µg m⁻² s⁻¹. This value, in addition to the 95% confidence interval of the mean evasion rate (±0.33), gives a total standard error in the summer CH₄ flux of ±0.42 µg m⁻² s⁻¹. Using only the spot sampled headspace measurements, the mean instantaneous CH₄ flux is calculated as 0.35 ± 0.20 µg m⁻² s⁻¹. These values correspond to instantaneous C losses of 0.44 ± 0.25 µg C m⁻² s⁻¹ and 0.26 ± 0.15 µg C m⁻² s⁻¹ for the modelled and headspace methods, respectively.

**DISCUSSION**

**GHG concentrations in the aquatic system**

Surface waters at Mer Bleue were consistently and highly supersaturated in CO₂ and CH₄ with respect to the atmosphere. The mean summer CO₂ concentration measured using the headspace technique (pCO₂ = 11786 ± 4838 µatm) was just over 70% of that calculated from the NDIR sensors (pCO₂ = 16268 ± 1700 µatm). However, considering the large confidence intervals associated with both measurements, this difference is not statistically significant. The depth profile experiments showed significant stratification in CO₂ concentrations (Figure 3), with concentrations increasing with depth. Although every effort was made to minimize mixing within the water column during sampling, a degree of mixing is inevitable and may have caused an increase in variation and decrease in the magnitude of the headspace CO₂ concentrations. Mixing within the water column is likely to be greater when headspace samples are collected from depth. This may also partly explain the much larger discrepancy between measurement methods at 60 cm.

A similar method comparison was carried out using data collected from the Black Burn, a small peatland draining stream in south east Scotland (K.J. Dinsmore, unpublished data). Mean pCO₂ concentrations measured using the 2 different methods in the Black Burn were much more similar than those from Mer Bleue (Headspace: 4330 ± 468 µatm; NDIR: 4007 ± 326 µatm). The Black Burn is a shallow, turbulent stream with a well-mixed water column; water disturbance during manual sampling is therefore unlikely to affect measured pCO₂ concentrations. This adds further support to the suggestion that the large differences observed between the two measurement methods at Mer Bleue are primarily due to disturbance within the water column during headspace sampling.

The method comparison also suggested that the influence of daytime sampling could lead to a ∼3.5% overestimation in the mean headspace concentration. From the direct method comparison, headspace concentrations at 10 cm depth were approximately 30% less than NDIR concentrations. The discrepancy in the July and August means is therefore likely to be due primarily to differences in measurement method rather than differences in sampling frequency.

A similar study carried out by Billett and Moore (2008) using a small number of headspace spot samples found a mean epCO₂ value of 24.1 ± 10.9 (n = 3) at the same pond site between July and August 2005 (M.F. Billett, unpublished data). This is within the 95% confidence limits of the mean epCO₂ calculated from headspace measurements in this study (31.5 ± 12.9). Since 2005, when Billett and Moore carried out their study, water levels have dropped allowing wetland vegetation to encroach on the pond. As water levels rose again due to beaver activity the vegetation became immersed. By the summer of 2007 when this study was carried out, the pond contained much more plant and algal life than in 2005. The increase in plant and algal respiration is likely
to be the primary cause of the higher dissolved CO₂ levels found in 2007. In the same study by Billett and Moore (2008), mean ePCO₂ between July and August 2005 was 1310 ± 2732 \(n = 3\), compared to 3210 ± 1589 in July and August 2007 (this study). Again, as seen from the overlapping confidence intervals, variation was high and the difference in ePCO₂ between 2005 and 2007 was not statistically significant.

**Controls on aquatic GHG concentrations**

A number of studies have suggested that dissolved CO₂ in aquatic systems is allochthonous in nature, produced within the soil system and transported via ground water or through-flow to surface water courses (Kling et al., 1991; Hope et al., 1997; Palmer et al., 2001; Worrall et al., 2005). In the cross-correlation analyses, soil concentrations were seen to lag behind water concentrations indicating that it is unlikely CO₂ produced in the adjacent peat is influencing concentrations in the water column. It is more likely that the correlation between soil and water column concentrations is the result of a common driving variable e.g. temperature which was seen to be important in driving surface water cycles (Table I). The observed lag might then be explained by the different thermal properties of soil and water.

The key drivers of aquatic CO₂ cycles in surface water at Mer Bleue during this study appeared to be short-wave radiation, adjusted shortwave radiation and both air and surface water temperature. These factors suggest a biological control on concentrations through aquatic plants or algae, both of which were visibly plentiful in the pond. The influence of aquatic plant and algae is once again seen in the shape of the diurnal cycles. The double peaks seen in the surface waters were absent in the deep water cycles where light does not penetrate, and are likely to result from high photosynthetic rates during peak daylight hours. We hypothesize that CO₂ is produced by both autotrophic and heterotrophic respiration, similar to findings from studies on the Amazon basin (Richey et al., 2002; Mayorga et al., 2005). Considering the low soil-water connectivity at Mer Bleue, it is likely that autochthonous DOC forms the primary substrate for CO₂ production, making this system comparable to many northern lake systems (Karlsson et al., 2007). During higher flow periods, such as snow melt, the C dynamics are likely to change significantly to more closely resemble the functioning of river ecosystems with dissolved CO₂ being flushed into the water course from adjacent peat. Hence the system may be dynamic, with seasonal variation in the form of the ecosystem functioning reflected in the sources of CO₂ and DOC. Longer term measurements are needed to test this hypothesis.

Diurnal variation in CH₄ concentrations during this study appeared to be driven primarily by the temperature cycle. The longer term summer dataset responded to both short-wave radiation in the water column and rainfall. As with the CO₂, CH₄ concentrations showed significant stratification in the water column with higher concentrations below approximately 40 cm. Although not statistically significant, on a number of occasions a drop in the CH₄ concentration in the soil atmosphere wells can be seen to coincide with a rainfall event, especially at site 2 on the edge of the pond. The increased flow of water during rainfall may flush CH₄ from the adjacent soil or pond fringes, where high CH₄ concentrations were measured (Figure 4), into the open water. Alternatively, the physical turbulence caused by heavy rainfall may be enough to raise surface water concentrations by mixing with deeper water containing higher concentrations of CH₄.

**GHG release from the aquatic system**

CO₂ evasion rates per unit area of water surface, based on headspace samples and NDIR sensors, were 86.2 µg m⁻² s⁻¹ and 164.7 µg m⁻² s⁻¹, respectively. The NDIR sensor provided a more direct measurement than the headspace technique and was not subject to sampling disturbance; it is therefore likely to be the most reliable method. Both the above values are at the upper end of evasion rates reported in the literature for rivers and lakes. Kling et al. (1991) calculated mean CO₂ evasion for arctic tundra rivers and lakes as 3-62 ± 1.53 µg m⁻² s⁻¹ and 10-6 ± 1-68 µg m⁻² s⁻¹ respectively. Evasion from the Hudson River, New York, ranged from 8-19 to 18-8 µg m⁻² s⁻¹ (Raymond et al., 1997). Evasion rates for the Brocky Burn and Black Burn, streams draining two separate Scottish peatland catchments, were more similar to the Mer Bleue rates than other non-peatland sites geographically closer to Mer Bleue. Evasion at Brocky Burn ranged from 76-4 µg m⁻² s⁻¹ in the lower reaches to 1213 µg m⁻² s⁻¹ closer to its source (Hope et al., 2001). Evasion from the Black Burn ranged from 162 µg m⁻² s⁻¹ to 1098 µg m⁻² s⁻¹ (Billett et al., 2004).

Mean CH₄ evasion from the water surface was calculated as 0.59 µg m⁻² s⁻¹ and 0.32 µg m⁻² s⁻¹ from the modelled and headspace data, respectively. CH₄ evasion rates in Arctic rivers and lakes and the Hudson River have been measured as 0.07 µg m⁻² s⁻¹ and 0.09 µg m⁻² s⁻¹, respectively (Kling et al., 1992; Raymond et al., 1997). In Brocky Burn, evasion rates reached 4.81 µg m⁻² s⁻¹ in the upper stream sections. In Black Burn, the mean CH₄ evasion rate was 2.12 µg m⁻² s⁻¹ (Billett et al., 2004; Hope et al., 2001). Although evasion from Mer Bleue surface water is at the upper end of all CH₄ rates reported in the literature, it is low in comparison with other peatland sites.

In terms of the relative importance of C evasion to the total catchment budget it is important to accurately assess the proportion of open water in the system. In this instance an estimated value of 0-5% open water in the 4.8 km² catchment is used (Billett and Moore, 2008). Evasion rates have been extrapolated to
In conclusion, the study showed extremely high concentrations of both dissolved gaseous C and DOC in the drainage waters of Mer Bleue during the summer season. The high temporal resolution obtained using NDIR sensors allowed us to examine in much more detail the patterns of CO$_2$ concentration in the water column. Clear diurnal cycles were evident both in the surface water and near the sediment-water interface. Our results suggest a strong influence of aquatic plants and algae on CO$_2$ concentrations, and relatively weak soil-stream connectivity. We conclude that during the study period aquatic CO$_2$ is most likely produced via \textit{in situ} respiration. Diurnal cycling was also seen in CH$_4$ concentrations, which could be modelled using rainfall and short-wave radiation ($r^2 = 0.63$). During summer months at Mer Bleue, CO$_2$ production by \textit{in situ} respiration is more closely related to the C dynamics of Amazonian drainage systems (Mayorga \textit{et al.}, 2005) or northern lakes (Kling \textit{et al.}, 1991; Karlsson \textit{et al.}, 2007). This contrasts to the way many northern river systems function, where CO$_2$ is produced predominantly within the adjacent peat (Billett \textit{et al.}, 2004; Dawson \textit{et al.}, 2004; Hope \textit{et al.}, 2004).

High summer concentrations of both CO$_2$ and CH$_4$ led to extremely high estimated evasion rates at Mer Bleue where many northern river systems function, where CO$_2$ is produced predominantly within the adjacent peat (Billett \textit{et al.}, 2004; Dawson \textit{et al.}, 2004; Hope \textit{et al.}, 2004).

CONCLUSIONS

In conclusion, the study showed extremely high concentrations of both dissolved gaseous C and DOC in the drainage waters of Mer Bleue during the summer season. The high temporal resolution obtained using NDIR sensors allowed us to examine in much more detail the patterns of CO$_2$ concentration in the water column. Clear diurnal cycles were evident both in the surface water and near the sediment-water interface. Our results suggest a strong influence of aquatic plants and algae on CO$_2$ concentrations, and relatively weak soil-stream connectivity. We conclude that during the study period aquatic CO$_2$ is most likely produced via \textit{in situ} respiration. Diurnal cycling was also seen in CH$_4$ concentrations, which could be modelled using rainfall and short-wave radiation ($r^2 = 0.63$). During summer months at Mer Bleue, CO$_2$ production by \textit{in situ} respiration is more closely related to the C dynamics of Amazonian drainage systems (Mayorga \textit{et al.}, 2005) or northern lakes (Kling \textit{et al.}, 1991; Karlsson \textit{et al.}, 2007). This contrasts to the way many northern river systems function, where CO$_2$ is produced predominantly within the adjacent peat (Billett \textit{et al.}, 2004; Dawson \textit{et al.}, 2004; Hope \textit{et al.}, 2004).

High summer concentrations of both CO$_2$ and CH$_4$ led to extremely high estimated evasion rates at Mer Bleue.
BLEU PEATLAND. PER UNIT AREA, SUMMER SURFACE WATER CO2 EVASION WAS ~2.5 TIMES HIGHER THAN CO2 UPTAKE VIA NEE. ONLY WHEN PERCENT OPEN WATER IN THE CATCHMENT IS TAKEN INTO ACCOUNT DOES THIS BECOME LESS IMPORTANT. WITHIN THE ECO SYSTEM, SURFACE DRAINAGE WATER THEREFORE REPRESENTS A SIGNIFICANT HOTSPOT FOR GHG EMISSIONS, WHICH IS OFTEN OVERLOOKED WHEN STUDIES RELY SOLELY ON FLOW TOWER MEASUREMENTS.

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