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Abstract

The aquatic pathway is increasingly being recognised as an important component of catchment carbon and greenhouse gas (GHG) budgets, particularly in peatland systems due to their large carbon store and strong hydrological connectivity. In this study we present a complete 5-year dataset of all aquatic carbon and GHG species (POC, DOC, DIC, CO₂, CH₄, N₂O) from an ombrotrophic Scottish peatland. We show that short term variability in concentrations exists across all species and this is strongly linked to discharge. Seasonal cyclicality was only evident in DOC, CO₂ and CH₄ concentration; however temperature correlated with monthly means in all species except DIC. Whilst the temperature correlation with monthly DOC and POC concentrations appeared to be related to biological productivity in the terrestrial system, we suggest the temperature correlation with CO₂ and CH₄ was primarily due to in-stream temperature-dependent solubility. Interannual variability in total aquatic carbon concentration was strongly correlated with catchment GPP indicating a strong potential terrestrial aquatic linkage. DOC represented the largest aquatic carbon flux term ($19.3 \pm 4.59 \text{ g C m}^{-2} \text{ yr}^{-1}$), followed by CO₂ evasion ($10.0 \text{ g C m}^{-2} \text{ yr}^{-1}$). Despite an estimated contribution to the total aquatic carbon flux of between 8 - 48%, evasion estimates have the greatest uncertainty. Interannual variability in total aquatic carbon export was low in comparison with variability in terrestrial biosphere-atmosphere exchange, and could be explained primarily by temperature and precipitation. Our results therefore suggest that climatic change is likely to have a significant impact on annual carbon losses through the aquatic pathway, and as such aquatic exports are fundamental to the understanding of whole catchment responses to climate change.

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Introduction

Compared to other ecosystems peatlands store disproportionately large amounts of soil carbon and subsequently have a significant impact on the atmospheric carbon and greenhouse gas (GHG) pool and the earth's radiative balance [Frolking *et al.*, 2006]. The most widely accepted estimate of contemporary peatland carbon accumulation in the Northern Hemisphere is $-23 \text{ g C m}^{-2} \text{ yr}^{-1}$ [Gorham, 1991; reaffirmed by Nilsson *et al.*, 2008; and Roulet *et al.*, 2007]. However there is still significant uncertainty in both the value itself and the predicted rate of change in response to climatic and anthropogenic influences. Reducing the uncertainty in current estimates and predicting future changes in peatland sink/source strength is an important research challenge. Greatest uncertainty exists around the magnitude of the aquatic flux term [Billett *et al.*, 2010].

Our knowledge of peatlands systems is strongly bias towards soil-atmosphere fluxes, highlighting water table depth, temperature and plant functional group as important drivers of net ecosystem CO₂ exchange (NEE), and CH₄ uptake and emission [Bubier *et al.*, 2003; Dinsmore *et al.*, 2009b; Dinsmore *et al.*, 2009c; Gray *et al.*, in press; Lafleur *et al.*, 2005; Roulet *et al.*, 1993; Strack *et al.*, 2004]. However, Dinsmore *et al.* [2010] showed that 41% of carbon uptake via NEE at Auchencorth Moss, Scotland, was lost via the aquatic pathway, highlighting the importance of stream losses in the full catchment net ecosystem carbon balance (NECB). Similarly, losses through the aquatic pathway accounted for 51% of carbon uptake via NEE at Mer Bleue, Canada [Billett and Moore, 2008; Roulet *et al.*, 2007], and 34% of carbon uptake via NEE in a Swedish mire complex [Nilsson *et al.*, 2008].

The global surface area of streams and rivers has recently been estimated at between 485 000 and 662 000 km² (0.3-0.56% of total land surface area), with first order streams representing ~6% of this water surface area and 52% of total stream and river length [Downing *et al.*,

2012]. Therefore aquatic fluxes are not only important at a catchment scale but play an important role in global carbon and GHG cycling.

Our understanding of aquatic fluxes from peatlands is strongly biased towards DOC [Clark *et al.*, 2007; Hope *et al.*, 1994; McDowell and Likens, 1988]. DOC influences river water quality through the transport of complexed metals and nutrients and its effect on pH; it also represents a significant challenge to water supply companies who may have to remove DOC to meet drinking water quality standards [Clark *et al.*, 2005; Driscoll *et al.*, 1989; Hughes *et al.*, 1990; Qualls and Haines, 1991]. Particulate forms of organic carbon (POC) usually represent only a small proportion of the total aquatic flux, although POC can reach $<100 \text{ g C m}^{-2} \text{ yr}^{-1}$ in eroding systems [Evans *et al.*, 2006; Pawson *et al.*, 2008]. Therefore although POC is unlikely to represent a major flux within the NECB, changes in aquatic POC concentrations may provide an early indication of peatland degradation [Billett *et al.*, 2010]. POC fluxes tend to be highly variable and episodic in their rate of export [e.g. Dinsmore *et al.*, 2010; Dyson *et al.*, 2010], often linked to discreet high flow events, making them difficult to quantify unless sampling is carried out over long timescales. Dissolved inorganic carbon (DIC) is largely derived from the bedrock-soil system and controlled by processes such as weathering, decomposition of organic matter and root respiration, or produced in-stream as a result of either terrestrial or aquatic derived substrate decomposition [Billett *et al.*, 2007; Johnson *et al.*, 2007; Köhler *et al.*, 2002]. The in-stream speciation of DIC is strongly controlled by pH through the carbonate equilibrium system [Dodds and Whiles, 2010]. Therefore in peatland drainage waters where pH is typically low, the majority of DIC is likely to take the form of free CO_2 making it susceptible to evasion from the water surface.

Recent studies now recognise the importance of downstream export and evasion of CO_2 [Butman and Raymond, 2011; Dinsmore *et al.*, 2010; Huotari *et al.*, 2011; Nilsson *et al.*, 2008; Richey *et al.*, 2002; Wallin *et al.* 2011]; data on CH_4 and N_2O are less commonly

reported. CO₂ supersaturation is common to many natural drainage water systems, with CH₄ supersaturation linked primarily to peatlands [Aufdenkampe et al., 2011; Cole et al., 1994; Cole et al., 2007; Dawson et al. 2004; Kling et al., 1991; Richey et al., 2002]. Although N₂O supersaturation is less common, as a GHG with a 100-year global warming potential of 298 [IPCC, 2007], even small evasion losses could contribute significantly to catchment GHG budgets. Uncertainty in GHG exports comes primarily from two main sources, i) a lack of long-term studies which encapsulate enough of the temporal variability to accurately quantify concentrations in systems with complex hydrological regimes, and ii) a lack of direct measurements of gas transfer coefficients required to calculate evasive fluxes. Evasion of the dissolved gas component therefore remains a major source of uncertainty in catchment scale budgets. As many eddy covariance systems are set up to specifically exclude water bodies and stream channels from their footprint (as these introduce significant areas of spatial heterogeneity), evasion fluxes need to be quantified and included as independent flux terms in the NECB.

The factors which influence concentration variability in the stream channel can be classified into two distinct categories: i) those which influence the concentration of solutes at their source, i.e. environmental factors such as temperature and soil moisture which control microbial and vegetation productivity, and ii) flowpath dynamics which control soil-stream connectivity. These two categories are likely to influence variability at different temporal scales. Whereas vegetation productivity is strongly seasonal, flow path variability occurs on a much shorter time scale in relation to individual precipitation or snowmelt events.

In this study we present the first complete 5-year time series of concentrations and fluxes of aquatic carbon and GHG species (POC, DOC, DIC, CO₂, CH₄ and N₂O) in a peatland stream. The study aims to analyse and explain temporal variability in concentrations and fluxes (both

downstream export and evasion) at weekly, seasonal and annual scales. Specifically, we aim to test the following hypotheses:

- 1) Concentration variability in instantaneous spot samples of all carbon and GHG species are primarily controlled by changes in the dominant hydrological flowpath and can therefore be explained by stream water discharge.
- 2) Concentrations of POC, DOC, CO₂, CH₄ and N₂O, which are linked to terrestrial vegetation and microbial productivity, will vary seasonally in relation to temperature patterns (a proxy for multiple seasonal variables including day length and photosynthetically active radiation). DIC derived primarily from ground water sources will not follow a temperature related seasonal pattern.
- 3) Exports of carbon and GHG will be greatest in late summer when both productivity and rainfall are high, and lowest in spring/early summer when source concentrations are depleted.
- 4) Significant interannual variability in export of all carbon and GHG species is related to differences in climatic variables.

Materials and Methods

Site description

Auchencorth Moss (55° 47' N, 03° 14' W) is a 3.4 km², low-lying (249-300 m), ombrotrophic peatland (histosols cover 85% of the catchment) in SE Scotland [Billett *et al.*, 2004]. The land-use is primarily low intensity sheep grazing with a small area of peat extraction in the southwest corner. The catchment vegetation consists of a patchy mix of grass (e.g. *Deschampsia flexuosa*) and sedges (e.g. *Eriophorum vaginatum* and *Juncus effusus*)

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covering a primarily Sphagnum base layer on a hummock/hollow microtopography; shrubs such as *Calluna vulgaris*, *Erica tetralix* and *Vaccinium myrtillus* are also present in the southern part of the catchment. Although hollows may become submerged after periods of intense rainfall, no permanent pools of standing water exist in the catchment. Peats, which range in depth from <0.5 m to >5 m, are underlain by glacial till and an Upper Carboniferous/Lower Devonian sequence of sandstones and shaly sandstones with minor limestone, mudstone, coal and clay layers [Billett *et al.*, 2004]. Annual mean water table depth in the catchment is 12.5 cm ranging from >55 below to 4.5 cm above the peat surface [Drewer *et al.*, 2010]. Mean water extractable DOC from 5 to 30 cm below the peat surface is 312 ± 15.9 (SE) $\mu\text{g C g}^{-1}$ dry soil and KCl extractable NO_3^- and NH_4^+ are 4.45 ± 0.48 (SE) and 21.8 ± 1.85 (SE) $\mu\text{g N g}^{-1}$ dry soil, respectively [Dinsmore *et al.*, 2010]. Total N deposition is $0.8 \text{ g N m}^{-2} \text{ yr}^{-1}$ [Drewer *et al.*, 2010].

The catchment drains NE through a series of natural tributaries and overgrown (>100 yr old) drainage ditches into the main stream channel, the Black Burn [Dinsmore *et al.*, 2010]. The total length of stream channel between the stream source and the catchment outlet, including both the main stem and tributaries, is 5.2 km with an average channel width of 0.65 m. The stream hydrograph is characterised by a rapid ('flashy') response to storm or snowmelt events.

Methods

Streamwater sampling was carried out approximately weekly on the Black Burn (55° 47' 41 N, 3° 14' 52 W) between January 2007 and December 2011. The following analysis is therefore based on a total of between 176 to 216 concentration measurements for each species (sample numbers differ due to difficulties in sample collection, sample loss or

contamination). On each sampling occasion a water sample was collected in a 300 mL glass bottle for analysis of POC, DOC and DIC and a headspace and ambient air sample collected in gas-tight syringes for analysis of CO₂, CH₄ and N₂O. As N₂O was only analysed on four occasions in 2008, that year is excluded from seasonal and annual analyses of N₂O. Stream water pH, temperature and electrical conductivity (EC) were also measured using hand-held devices in-situ on each sampling occasion.

Stream water samples were filtered within 24 hours of collection through pre-ashed (6 hours at 500°C), pre-weighed Whatman GF/F (0.7 µm pore size) filter papers. POC was calculated using loss-on-ignition, following the method of *Ball* [1964]. The filtrate was stored in the dark at 5°C until analysis within 2 weeks of sampling. The filtrate was analysed for DOC and DIC concentration using a Rosemount-Dohrmann DC-80 total organic C analyser (2007) or a PPM LABTOC Analyser (2008 onwards). Both instruments had a detection range of 0.1-4000 mg L⁻¹.

Dissolved CO₂, CH₄ and N₂O were calculated using the headspace technique [*Billett et al.*, 2004; *Dinsmore et al.*, 2010; *Kling et al.*, 1991]. A 40 mL water sample was equilibrated with 20 mL of ambient air at stream temperature by shaking vigorously under water for one minute; the equilibrated headspace was then transferred to a gas tight syringe and returned to the laboratory for analysis. On each sampling occasion two replicate headspace samples were collected alongside a separate sample of ambient air. Headspace samples were analysed within two weeks of collection on an HP5890 Series II gas chromatograph (Hewlett-Packard), with electron capture (ECD) and flame ionisation detectors (with attached methaniser) for N₂O and CH₄/CO₂, respectively. Detection limits for CO₂, CH₄ and N₂O were 7 ppmv, 84 ppbv and 8 ppbv, respectively. Concentrations of CO₂, CH₄ and N₂O dissolved in the stream water were calculated from the headspace and ambient concentrations using Henry's law [e.g. *Hope et al.*, 1995].

Stream height was measured at 10-min intervals at the sampling site using a Druck PDCR 1830 series pressure transducer from 2007 until April 2009. After April 2009, water height was also measured approximately 2 km downstream on an In Situ Inc. Level Troll® pressure transducer with atmospheric correction from a BaroTroll® sensor located above the water surface. Stage height readings from both pressure transducers were converted to discharge at the sampling site using manually calibrated rating curves ($r^2 > 0.90$) based on dilution gauging measurements.

Meteorological data including air pressure, air temperature, rainfall and water table depth were measured at a flux tower located approximately 400 m from the stream water sampling site (M. Coyle, unpublished results, 2012).

Data analysis

Instantaneous concentrations are expressed in units of mg L^{-1} or $\mu\text{g L}^{-1}$ with datasets summarised using the arithmetic mean \pm standard error, median, range and flow weighted mean concentrations (FWMC). FWMC was calculated using equation 1 where c_i is the instantaneous concentration, q_i is the instantaneous discharge and t_i is the time step between subsequent concentration measurements.

$$(1) \text{ FWMC} = \frac{\sum(c_i \times t_i \times q_i)}{\sum(t_i \times q_i)}$$

Where average pH values are presented, these are based on the average H^+ ion concentration reconverted back to a pH value on the logarithmic scale. All datasets were tested for autocorrelation and 1^o autocorrelation residuals used in further analysis where appropriate.

This removed autocorrelation and allowed the statistical assumption of independence to be met.

Seasonal and interannual variability are displayed using box-plot diagrams where the box represents the interquartile range with a line showing median concentration. Whiskers extend to the highest/lowest data values within the upper/lower limit defined as 1.5 times the interquartile range. Outliers are defined as any data point beyond the upper/lower whisker limit; maximum and minimum outlier values are also plotted.

Time series deconstruction was carried out on mean monthly concentrations (Minitab® version 16) using an additive model. The resulting seasonal indices were normalised to range between -1 and 1 and are plotted beneath seasonal box-plots. Seasonal cyclicity, i.e. the presence of a smooth seasonal cycle rather than random variability from one month to the next, was tested using an autocorrelation function on the seasonal indices. Where the seasonal index in a particular month was correlated with the seasonal index in the previous month, this is considered evidence of a smooth seasonal cycle. Mean annual deseasonalised residual concentrations were normalised between 0 and 1 and are shown in a separate plate beneath each annual box-plot to illustrate trend. Trends were statistically analysed using linear regression of seasonally corrected concentration against time.

Concentration discharge relationships are plotted with r^2 and P-values representing the results from linear regression analysis. Drivers of variability at weekly, monthly and annual time scales were explored using Spearman's rank correlations of concentration against discharge, rainfall, water table depth, stream temperature, soil temperature, pH and EC.

Analysis of downstream export and water-atmosphere evasion are carried out on seasonal and annual timescales. Where annual values are shown this refers to the calendar year (1st January to 31st December) allowing for easy comparison to other catchment fluxes presented in the

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literature. However, seasons are based on the hydrological year in which the winter season runs from 1st October to 31st March and the summer season 1st April to 30th September [Gordon *et al.*, 2004]. Here we split the seasons further to prevent one season running across two calendar years and therefore follow the nomenclature; early winter (October, November, December), late winter (January, February, March), early summer (April, May, June) and late summer (July, August, September).

Downstream export was calculated using Walling and Webb [1985] 'Method 5' described in equation (2) where C_i is the instantaneous concentration associated with Q_i the instantaneous discharge, Q_r is the mean discharge for the full study period, and n is the number of instantaneous samples analysed. Standard error of the mean load was calculated using equation (3) [Hope *et al.*, 1997] where F is the total annual discharge and C_F is the flow-weighted mean concentration. The variance of C_F was estimated using equation (4) where Q_n is the sum of all the individual Q_i values. Downstream exports are expressed in units of $\text{g m}^{-2} \text{yr}^{-1}$ (or derivatives thereof) scaled to the catchment area of 3.4 km^2 .

$$(2) \text{ Load} = Q_r \times \frac{\sum_{i=1}^n [C_i \times Q_i]}{\sum_{i=1}^n Q_i}$$

$$(3) \text{ SE} = F \times \text{var}(C_F)$$

$$(4) \text{ var}(C_F) = \left[\sum (C_i - C_F)^2 \times \frac{Q_i}{Q_n} \right] \times \sum \frac{Q_i^2}{Q_n^2}$$

Water-atmosphere evasion of CO_2 , CH_4 and N_2O were calculated using the interfacial mass transfer equation [Borges *et al.*, 2004; Dinsmore *et al.*, 2009a] described for CO_2 in equation

(5) where k_{CO_2} is the gas transfer velocity, α is the gas and temperature specific solubility coefficient and Δp_{CO_2} is the difference in partial pressure between the surface water and the atmosphere.

$$(5) \quad F_{CO_2} = k_{CO_2} \alpha \Delta p_{CO_2}$$

Solubility coefficients for CO₂, CH₄ and N₂O were derived from *Weiss* [1974], *Wiesenburg and Guinasso* [1979] and *Weiss and Price* [1980], respectively. Gas transfer coefficients for CO₂ and CH₄ were calculated by *Billett and Harvey* [2012], at the same sampling site as this study (referred to as AUCH-DOWN), using the volatile conservative gas tracer (propane) method. For this study we use median, minimum and maximum gas transfer velocities of 0.056 (0.013-0.0134) min⁻¹ and 0.062 (0.014-0.151) min⁻¹ for CO₂ and CH₄, respectively, converted to gas transfer velocities by multiplication with the average reach depth of 0.16 m [*Billett and Harvey*, 2012]. The gas transfer velocity for N₂O (k_{N_2O}) was calculated using equation (6) [*Jones and Mulholland*, 1998] where d_{CO_2} and d_{N_2O} are temperature dependent gas diffusion coefficients for CO₂ and N₂O respectively and n is a coefficient which describes the characteristics of water turbulence. Here we use the value of n = 0.5 which is considered typical for upland streams [*Billett and Harvey*, 2012; *Wallin et al.*, 2011].

$$(6) \quad \frac{k_{N_2O}}{k_{CO_2}} = \left(\frac{d_{N_2O}}{d_{CO_2}} \right)^n$$

Equation (5) was applied using water-air concentration gradients calculated from the median water and median atmospheric partial pressures of individual gases over the specific time periods being analysed.

Results

Discharge over the measurement period was “flashy” with a rapid response to precipitation events and a seasonal cycle characterised by low flows in June (Figure 1a). Daily mean discharge ranged from 0.95-1815 L s⁻¹ with a median of 25.9 L s⁻¹ (Table 1). Stream water temperature displayed a very clear seasonal pattern with highs of approximately 14°C in late July and lows of <1°C in early January (Figure 1b), and was negatively correlated with discharge ($r = -0.23$, $P < 0.01$). pH averaged 4.68 over the full measurement period with maxima and minima of 7.07 and 3.50, respectively (Table 1). EC showed clear interannual differences; mean EC excluding 2010 was 52.0 $\mu\text{S cm}^{-1}$, compared to the 2010 mean of 108 $\mu\text{S cm}^{-1}$.

Rainfall was highest in 2008 and lowest in 2010 (Figure 2a), however these values do not include snowfall which was significant in 2010. Based on an average rainfall:runoff ratio in the years excluding 2010 of 69%, total precipitation in 2010 was estimated as 1072 mm. Based on total precipitation rather than rainfall alone, 2011 was the driest year. Lowest annual mean discharge was recorded in 2007, followed by 2011, 2009, 2010 and 2008, respectively. 2011 was the warmest year (biased by high August-October temperatures) and 2010 was the coolest year (biased by abnormally low January-March temperatures) (Figure 2b).

Aquatic carbon and GHG concentrations

Of the carbon species measured DOC had the highest FWMC, followed by DIC, POC, CO₂ and CH₄; N₂O had a FWMC of 0.36 $\mu\text{g N L}^{-1}$ (Table 1). Concentrations in all species were highly variable (Figure 3) with coefficients of variation (CV) highest for POC and DIC and

lowest for CO₂ (Table 1). Although the explained variance was low, all species displayed significant relationships between concentrations and log-transformed (Ln) discharge (Figure 4); relationships were positive for POC and DOC, negative for DIC, CO₂, CH₄ and N₂O.

Clear seasonal cycles were evident in DOC ($r = 0.67$, $P < 0.05$), CO₂ ($r = 0.61$, $P < 0.05$) and CH₄ ($r = 0.74$, $P < 0.01$) concentrations (Figure 5). Annual DOC and CH₄ highs were observed in August (based on seasonal indices), whereas CO₂ concentrations reached an annual high in June. Seasonal indices for POC, DIC and N₂O were highly variable throughout the year with no clear annual cycle.

Interannual variability was evident in all carbon and GHG species concentrations (Figure 6). Variability was greatest in mean annual DIC concentrations (CV= 0.42), followed by POC (CV 0.26), DOC (CV 0.16), N₂O (CV 0.13), CO₂ (CV 0.09) and CH₄ (CV 0.04), respectively. The only species to exhibit significant trends in concentration over time were CO₂ ($r^2 = 0.05$, $p < 0.05$) and N₂O ($r^2 = 0.14$, $p < 0.01$), both of which showed a decline over the sampling period.

Table 2 highlights groups of species which vary temporally in a similar nature. Strong positive correlations were found between CO₂, CH₄ and DIC. DOC and POC were positively intercorrelated and negatively correlated with CO₂, CH₄ and DIC. No correlation was observed between N₂O and the DOC/POC grouping, although it was negatively correlated to the DIC/CO₂/CH₄ grouping.

Spearman's rank correlation, which was carried out to determine the primary driver of variability across different time scales, showed that all C and GHG species (instantaneous spot samples) were significantly correlated with at least five of the seven parameters listed (Figure 7). Discharge was a significant driver of all species and DIC, CO₂ and CH₄ showed additional negative correlations with water table depth; DIC also showed a positive

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correlation with rainfall. All species were again correlated with soil and stream temperature, pH and EC, however the sign of the relationship was species specific. For POC, DOC and DIC the correlation with soil temperature was greater than that with stream temperature; the opposite was true for the GHGs.

Monthly mean soil temperature was the only variable found to explain monthly mean POC concentrations; annual concentrations were strongly positively correlated with stream water temperature and negatively with soil temperature. Monthly mean DOC concentrations were weakly positively correlated with both discharge and rainfall, and both soil and stream water temperature were related to high DOC concentrations during mid-summer (Figure 5).

Discharge was not significantly correlated with mean monthly DIC concentration, which was instead associated with low water table and high EC. The best predictor of annual DIC concentration was again EC. CO₂ and CH₄ concentrations showed similar monthly correlations with the greatest influence being water table depth or stream temperature. Mean monthly N₂O concentrations were negatively correlated with stream temperature; interannual variability was controlled primarily by rainfall.

Aquatic carbon and GHG fluxes

Over the full five year period the greatest aquatic carbon flux was downstream export of DOC (19.3 g C m⁻² yr⁻¹) which accounted for 54.3% of total aquatic carbon losses (25.5 g C m⁻² yr⁻¹); CO₂ evasion was the second largest carbon flux (10.0 g C m⁻² yr⁻¹) accounting for 28.1% of total aquatic carbon loss (Table 3). GHG evasion from the water surface was dominated by CO₂ which accounted for 97.1% of total GHG losses (42.2 g CO₂-eq m⁻² yr⁻¹) presented as CO₂-eq based on a 100 yr time horizon [IPCC, 2007]. Comparing downstream

versus evasive fluxes, 71.6% of total aquatic carbon was transported downstream whereas 89.3% of GHGs were evaded from the water surface.

When split into seasons based on hydrological year, greatest total carbon export (downstream export plus evasion) was observed in late summer (Figure 8a). Early summer was the period with both lowest carbon export and lowest mean discharge. Downstream export of DOC represented the largest aquatic carbon flux in all seasons except early summer, when CO₂ evasion represented the greatest flux (Table 4). DIC was the next largest flux term with greatest export during early winter (0.50 g m⁻² month⁻¹); POC export was greatest in late summer (0.27 g m⁻² month⁻¹). CH₄ export was < 0.01 g m⁻² month⁻¹ in all seasons, but peaked in late summer. Export variability between seasons was greatest for POC (CV 0.84), followed by DIC (CV 0.79) and DOC (CV 0.61); seasonal coefficients of variation were <0.5 for all 3 GHG species.

Over the five year period 2007 had the greatest total carbon export, dropping sequentially until 2011 (Figure 8b), this relates primarily to a decreasing trend in DOC export. Using a 2010 precipitation value of 1072 mm, >99% of the interannual variability in DOC export could be explained using an interaction term between annual precipitation and mean annual temperature (P < 0.01); years with high DOC export corresponded to years that were warmer and wetter (Figure 2).

Of all measured carbon and GHG fluxes, DIC export displayed the largest interannual variability (CV 0.98), linked primarily to high DIC concentrations in 2010. This was closely followed by POC (CV 0.92) which ranged from 0.44 g C m⁻² yr⁻¹ in 2011 to 4.49 g C m⁻² yr⁻¹ in 2010. N₂O and DOC export showed similar interannual variability (CV 0.48 and 0.35, respectively).

Discussion

Comparison of carbon and GHG concentrations and fluxes

The relative contribution of the individual species (DOC > DIC > CO₂ > POC > CH₄) to total streamwater carbon concentration was consistent with earlier work by *Billett et al.* [2004] at the same site. Mean carbon concentration in 1996-1998 was $47.5 \pm 1.4 \text{ mg C L}^{-1}$ compared to $38.4 \pm 1.73 \text{ mg C L}^{-1}$ in this study, the primary difference being a 10.2 mg C L^{-1} decrease in DOC concentration. Average DOC concentrations across 13 different UK peatland systems range from $\sim 3.4\text{-}25.5 \text{ mg C L}^{-1}$ [*Billett et al.*, 2010; *Daniels et al.*, 2012; *Hope et al.*, 2001]; examples from non-UK sites include $2.7\text{-}11.5 \text{ mg C L}^{-1}$ in Glencar, Ireland [*Koehler et al.*, 2009], $20.0\text{-}76.6 \text{ mg C L}^{-1}$ in Mer Bleue, Canada [*Roulet et al.*,], 25.3 mg C L^{-1} (TOC) from Degerö Stormyr in N Sweden [*Nilsson et al.*, 2008], and 21 and 33 mg C L^{-1} (TOC) from two sites in N Karelia, Finland [*Dyson et al.*, 2010]. DOC concentrations from Auchencorth Moss are therefore within the range of previously measured catchments.

CO₂ and CH₄ were consistently supersaturated throughout the measurement period with mean concentrations of 2.40 and 0.006 mg L^{-1} , respectively. Concentrations of both gases were lower than those measured at Mer Bleue, Canada [*Dinsmore et al.*, 2009a] and Degerö Stormyr, Sweden [*Nilsson et al.*, 2008], yet much closer to the ranges presented by *Hope et al.* [2001] for a peatland in NE Scotland ($0.29\text{-}1.86 \text{ mg CO}_2\text{-C L}^{-1}$; $<0.01\text{-}0.02 \text{ mg CH}_4\text{-C L}^{-1}$). Carbon and GHG fluxes for 2007 and 2008 were previously reported from the same study site in *Dinsmore et al.* [2010]. Having further refined the discharge rating curve, in particular the high-flow discharge calculation, mean annual aquatic carbon export (2007-2008) changed from 31.1 to $33.6 \text{ g C m}^{-2} \text{ yr}^{-1}$, and mean annual CO₂ and CH₄ evasion from 12.7 to $9.25 \text{ g C m}^{-2} \text{ yr}^{-1}$. The total mean annual catchment-scale aquatic carbon loss over the full 5-year measurement period was $35.6 \text{ g C m}^{-2} \text{ yr}^{-1}$, equating to a total GHG loss (based on 100-yr

GWP and including N₂O) of 42.2 g CO₂-eq m⁻² yr⁻¹. This is very similar to the total carbon loss of 35.0 g C m⁻² yr⁻¹ calculated by *Billett et al.* [2004] for the same catchment from 1996 to 1998, although the proportions of the overall flux comprising CO₂ evasion and DOC export were different. Other literature estimates of total aquatic carbon loss from peatlands include 41.4 g C m⁻² yr⁻¹ in the Brocky Burn catchment, NE Scotland [*Hope et al.*, 2001] and 21.3 g C m⁻² yr⁻¹ from Mer Bleue, Ontario [*Billett and Moore*, 2008; *Roulet et al.*, 2007].

The ratio of CO₂ and CH₄ evasion to total downstream carbon export in the Brocky Burn and Mer Bleue drainage waters were 0.52 and 0.17, respectively [*Billett and Moore*, 2008; *Hope et al.*, 2001], compared to 0.15 in the Black Burn in 1996-1998 (*Billett et al.* 2004) and 0.40 during this study (2007-2011). Upscaling evasion measurements from short study reaches, over a limited flow range leads to significant variability and uncertainty in catchment scale flux estimates. This is reflected in the large GHG evasion ranges given in this study. Another source of uncertainty in the evasion estimates is the total water surface area within the catchment. In this study we have used a more accurate, updated estimate of 3371 m², instead of an initial estimate of 1820 m² [*Billett et al.*, 2004]. Adjusting their evasion estimate (1996-98) of 4.6 g C m⁻² yr⁻¹ to the updated water surface area, gave an evasion flux of 8.6 g C m⁻² yr⁻¹ significantly closer to the 10.1 g C m⁻² yr⁻¹ for the period 2007-11. This gives a total evasion:export ratio of 0.28 and significantly improves our confidence in the long-term catchment-scale value.

Seasonal and interannual variability in carbon and GHG concentrations and fluxes

DOC concentrations followed a seasonal cycle with concentrations reaching an annual high in August. This led to high variability in exports between seasons with peak export occurring in late summer (August- October) when high concentrations coincided with high discharge. Exports earlier in the summer were restricted by low mean seasonal discharge.

Instantaneous DOC concentrations were driven by hydrological parameters linking high stream water DOC to shallow flow pathways. Temperature was significantly related to both instantaneous and average monthly DOC concentrations, suggesting the seasonal cycle was linked to biological productivity. Biological activity is known to follow a similar seasonal cycle to temperature, driven by environmental parameters such as day length and photosynthetically active radiation [e.g. *Frolking et al.*, 2002]. A greater correlation with soil compared to stream temperature supports our hypothesis that DOC is allochthonous and therefore linked to productivity within the soil-plant system rather than in-stream processing.

Interannual variability in DOC export was low relative to the other aquatic carbon species, although due to the magnitude of the DOC flux it strongly controlled total carbon export. Hence given that 99% of the interannual variability across the 5 study years was explained by the interaction between precipitation and air temperature, climatic change is likely to have a large impact on catchment-scale aquatic carbon losses. Furthermore, as the aquatic pathway itself represents a significant proportion of the total catchment NECB [*Billett and Moore*, 2008; *Dinsmore et al.*, 2010; *Nilsson et al.*, 2008; *Roulet et al.*, 2007], changes in DOC export may be fundamental in understanding the full catchment response to climate change.

Temporal variability in weekly concentrations were highest for POC and this translated into high variability in both seasonal and interannual exports. Although POC represented a mean of 7.5% of the total organic carbon export this varied seasonally and ranged from 11.0% in early winter to 3.5% in early summer. A positive correlation between instantaneous POC concentration and discharge, and negative correlation with pH and EC both indicate a strong dependence on hydrologic flow pathways. As pH and EC were lowest during high-flow conditions, high streamwater POC concentrations were likely associated with shallow or surface soil water sources.

We also found that POC was positively correlated with both soil and stream temperature. The average lag-time between rainfall and discharge peaks in the catchment was 7.5 ± 0.9 hours [Dinsmore and Billett, 2008] indicating a relatively short water residence time in the catchment during high flow conditions. Therefore any changes in terrestrial source concentrations (linked to changes in soil temperature) will be quickly translated into changes in aquatic concentration changes when associated with high rainfall events. The correlation between POC and temperature therefore indicates a biological driver linked to POC production within the catchment. We did not however see a seasonal cycle in POC concentrations; this was most likely masked by the high variability associated with discharge/flow path dynamics. Temperature was also strongly correlated with interannual variability in POC concentrations. However the correlation was negative with stream and positive with soil temperature, indicating a more complex set of drivers than we were able to consider here.

DIC, CO₂ and CH₄ concentrations showed significant inter-correlation and a high degree of similarity in their drivers across all time scales. Negative correlations with water table depth and discharge, alongside positive correlations with temperature, pH and EC in the instantaneous datasets, all suggest sources associated with deeper flow pathways. Similar correlations with discharge and water table were also seen in the monthly dataset, however water table became the strongest driver indicating the importance of integrating current and antecedent hydrological conditions. As hypothesised, there was no seasonal temperature driver of DIC concentrations, which indicates a disconnect from surface biological processes. The seasonal correlation of CO₂ and CH₄ with stream rather than soil temperature, suggests that in-stream temperature dependent solubility (rather than terrestrial biological productivity) was the primary driver of seasonal concentrations. Isotopic data from this site has shown that CO₂ is both significantly older and sourced from greater depths within the

peatland than DOC [Billett *et al.*, 2007]. Garnett *et al.* [2012] also found a strong seasonal cycle in the radiocarbon age of dissolved CO₂ in the Black Burn, with older CO₂ associated with deep water tables. However, they found no seasonality or discharge correlation with $\delta^{13}\text{CO}_2$, indicating that the source material was relatively consistent and characteristic of decomposition of C3 plant material. Since streamwater CO₂ is not linked to young DOC, is driven largely by in-stream temperature dependent solubility, and does not contain a significant geological signature, we conclude that the primary source of streamwater CO₂ in Black Burn is decomposition of organic carbon relatively deep within the soil profile. However, this will not necessary be true for all peatlands. For example, an isotopic study by Billett *et al.* [2012] found that root/soil respiration was a likely source of evasion CO₂ in forested Finnish catchments.

CH₄ was highly seasonal with concentrations reaching a maximum in August, correlating strongly with the seasonal cycle in stream temperature. CH₄ also showed strong negative correlations with discharge suggesting linkage to deep flow pathways associated with higher source concentrations. The drivers of CH₄ and CO₂ across all temporal scales were very similar, suggesting commonality in catchment CO₂ and CH₄ sources.

Despite high concentrations, downstream export in all species was lowest in early summer due to low discharge, and in many cases, highest in late summer when high concentrations coincided with high discharge. Evasion therefore became proportionally more important during summer months. No studies have yet considered seasonality in headwater gas transfer coefficients. However it is likely that these will be highly variable during summer as low turbulence stream flow is interspersed with periodic bursts of evasion associated with storm flow events, which release supersaturated gases which have built up within the water column. Clearly more work is required to consider seasonality and temporal dynamics in evasion fluxes.

Terrestrial NEE has been measured in the catchment continuously using eddy covariance techniques since 2002 [Helfter, in prep]. The direction and strength of prevailing wind in relation to the Black Burn stream channel means that except for very rare occasions, the footprint of the eddy covariance system does not include the stream channel. To consider the link between the terrestrial and aquatic systems further, a set of simple correlations were carried out comparing annual NEE, and its individual components, gross primary productivity (GPP) and ecosystem respiration (ER), with total annual aquatic carbon flux and the annual in-stream FWMC of total carbon. NEE did not correlate significantly with either aquatic carbon fluxes or concentrations; however a very strong correlation ($r^2 = 0.98$, $P < 0.01$) was found between GPP and annual FWMC of total carbon in the stream. This supports the concept that the streamwater carbon signal integrates heterogeneous terrestrial processes and as such may provide a useful, and easily measured, indicator of change within the catchment [Billett *et al.*, 2010].

Implications for catchment scale carbon and GHG budgets

Over the 5 years of this study total annual catchment carbon loss via the aquatic pathway averaged $35.6 \text{ g C m}^{-2} \text{ yr}^{-1}$, of which $10.1 \text{ g C m}^{-2} \text{ yr}^{-1}$ was lost directly to the atmosphere via evasion of CO_2 and CH_4 . In terms of GHG equivalents, direct evasion was responsible for $37.7 \text{ g CO}_2\text{-eq m}^{-2} \text{ yr}^{-1}$ with a further $4.50 \text{ g CO}_2\text{-eq m}^{-2} \text{ yr}^{-1}$ exported downstream and likely to be evaded outside the catchment area. CO_2 was by far the most important GHG representing >97% of GHG evasion. A very similar ratio (96%) is seen in the relative magnitude of CO_2 to the total terrestrial GHG fluxes at Auchencorth Moss based on values for the period 2006-08 [Dinsmore *et al.*, 2010]. NEE over the period 2007-2010, coinciding with the aquatic measurements, was $-72.8 \text{ g C m}^{-2} \text{ yr}^{-1}$ [Helfter, in prep]. Based on these

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measurements the aquatic pathway accounted for an average carbon loss equivalent to 49% of total uptake by NEE. This refined estimate is higher than the 41% previously quoted in *Dinsmore et al.* [2010] for the period 2006- 2007.

The annual CV in total aquatic export from 2007-2011 was 0.22 (downstream export 0.31; evasion 0.09) compared to a CV in NEE from 2007-2010 of 0.64. Hence aquatic exports of carbon appear to be much more annually consistent than NEE. However, as with seasonal fluxes, the lack of time-specific gas transfer coefficients is likely to mask some of the interannual variability in our evasion estimates. *Billett et al.* [2007] showed that DOC tended to be relatively young in age, however this included DOC fixed since 1955, and here we suggest that the primary source of evaded CO₂ (the second largest aquatic flux) is deep within the soil profile and relatively disconnected from surface processes. Hence stream export is a good integrator of carbon fixed over multiple years. Integration over multiple years and across a large heterogeneous landscape (the catchment), in addition to greater interannual stability could potentially make aquatic carbon flux monitoring a more robust indicator of long term change in catchment carbon turnover than NEE measurements (where high variability may mask step changes). This is a hypothesis that requires further testing against similar long-term datasets.

Conclusions

Temporal variability was evident in all carbon and GHG species concentrations across a range of time scales. As hypothesised, variability over short time scales in all species was strongly correlated to discharge, highlighting the importance of hydrological flow pathways through the catchment. In addition, seasonal cyclicality was observed in DOC, CO₂ and CH₄ concentrations, and a correlation between temperature and mean monthly concentrations was

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seen in all carbon and GHG species with the exception of DIC. In part this supports the hypothesis that all measured species with the exception of DIC will vary seasonally following temperature. However, as stream temperature was a stronger predictor of CO₂ and CH₄ concentration than soil temperature, we suggest the correlation is primarily due to in-stream temperature dependent solubility rather than terrestrial biological productivity. Although some CO₂ and CH₄ will be sourced from surface peat layers, the negative concentration-discharge relationship suggested the majority was from deeper sources with connectivity to surface biological processes only occurring during high flow events. Both POC and DOC concentrations showed significant inter-correlation and appear to be linked to surface flow paths and productivity in the soil-plant system. As hypothesised, total carbon export was greatest in late summer when high temperature and high runoff coincide, and lowest in early summer following a period of low winter productivity. Our results suggest that CO₂ evasion becomes proportionally more important in the early summer when evasion remains high and downstream carbon export is limited. As CO₂ evasion represented the 2nd largest aquatic C flux term within the catchment a better understanding of temporal variability in gas transfer coefficients is a future research priority.

We found a very strong positive correlation between aquatic concentrations and catchment GPP, indicating a strong linkage between the aquatic system and catchment productivity. The largest component of the aquatic flux was DOC (54.3% of total) followed by CO₂ evasion (28.1% of total). Annual DOC flux was strongly linked to precipitation and temperature with the greatest fluxes occurring in warmer and wetter years. Our results suggest that climatic change is likely to have a significant impact on annual carbon losses through the aquatic pathway, and as such aquatic exports are fundamental to the understanding of whole catchment responses to climate change.

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Tables

Table 1. Summary of hydrochemical parameters and concentrations over the 5 year measurement period where SE refers to the standard error of the mean, CV the coefficient of variation and FWM the flow weighted mean temperature, pH, EC or concentration.

	Mean (\pm SE)	CV	FWM	Median (Range)
Daily Mean Discharge ($L s^{-1}$)	70.6 \pm 3.25	1.88	---	25.9 (0.95-1815)
Water Temperature ($^{\circ}C$)	7.94 \pm 0.29	0.52	7.21	8.74 (0.00-16.7)
pH	4.68 \pm 1.12	0.16	4.58	5.76 (3.50- 7.07)
EC ($\mu S cm^{-1}$)	65.4 \pm 4.56	0.99	37.2	45.9 (6.40-463)
POC ($mg C L^{-1}$)	1.36 \pm 0.13	1.36	2.59	0.93 (0.00-17.8)
DOC ($mg C L^{-1}$)	28.4 \pm 1.07	0.51	28.4	24.4 (4.26-87.5)
DIC ($mg C L^{-1}$)	6.25 \pm 0.47	1.00	4.55	3.69 (0.00-35.1)
CO ₂ ($mg C L^{-1}$)	2.40 \pm 0.06	0.35	1.78	2.28 (0.46-5.09)
CH ₄ ($\mu g C L^{-1}$)	5.92 \pm 0.27	0.68	3.79	4.78 (0.65-28.6)
N ₂ O ($\mu g N L^{-1}$)	0.48 \pm 0.2	0.49	0.36	0.44 (0.12-2.41)

Table 2 Spearman's rank correlation matrix of measured carbon and GHG concentrations based on instantaneous spot samples. Results significant at $P < 0.05$ are indicated by *; results significant at $P < 0.01$ are indicated by **.

	POC	DOC	DIC	CO ₂ -C	CH ₄ -C
DOC	0.35**				
DIC	-0.17*	-0.40**			
CO ₂ -C	-0.19**	-0.17*	0.39**		
CH ₄ -C	---	---	0.41**	0.77**	
N ₂ O-N	---	---	-0.49**	-0.23**	-0.38**

Table 3 Annual downstream export and evasion of aquatic carbon and GHG fluxes (CO₂, CH₄ and N₂O) from 2007 to 2011, with SE and ranges shown for downstream export and evasion respectively. CO₂ equivalents are based on the most recent IPCC report [2007] equating to 25 and 298 for CH₄ and N₂O respectively.

	Downstream Export	Evasion
POC (g m ⁻² yr ⁻¹)	1.97 ± 0.23	---
DOC (g m ⁻² yr ⁻¹)	19.3 ± 4.59	---
DIC (g m ⁻² yr ⁻¹)	3.06 ± 1.75	---
CO ₂ -C (g m ⁻² yr ⁻¹)	1.17 ± 0.02	10.0 (2.33 - 24.0)
CH ₄ -C (mg m ⁻² yr ⁻¹)	2.50 ± <0.01	24.0 (5.41 - 58.3)
N ₂ O-N (mg m ⁻² yr ⁻¹)	0.26 ± <0.01	0.28 (0.06 - 0.66)
Total C (g C m ⁻² yr ⁻¹)	25.5	10.1
Total GHG (g CO ₂ -eq m ⁻² yr ⁻¹)	4.50	37.7

Table 4. Seasonal export of carbon and GHG species. Where ± terms are given these refer to SE. Bracketed terms after evasion estimates refer to the range calculated from minimum and maximum gas transfer coefficients. Seasons are defined based on the hydrological year as follows: Early Winter = Oct, Nov, Dec; Late Winter = Jan, Feb, Mar; Early Summer = Apr, May, Jun; Late Summer = Jul, Aug, Sep.

	Early Winter	Late Winter	Early Summer	Late Summer
Mean Discharge (L s ⁻¹)	88.7 ± 16.3	79.1 ± 10.5	28.6 ± 7.91	82.7 ± 13.4
<i>Downstream Export</i>				
POC (g m ⁻² month ⁻¹)	0.21 ± 0.06	0.06 ± <0.01	0.02 ± <0.01	0.27 ± 0.12
DOC (g m ⁻² month ⁻¹)	1.70 ± 0.32	1.00 ± 0.14	0.52 ± 0.08	2.56 ± 3.49
DIC (g m ⁻² month ⁻¹)	0.50 ± 0.69	0.17 ± 0.06	0.10 ± 0.03	0.16 ± 0.26
CO ₂ -C (g m ⁻² month ⁻¹)	0.11 ± <0.01	0.10 ± <0.01	0.05 ± <0.01	0.11 ± 0.01
CH ₄ -C (mg m ⁻² month ⁻¹)	0.20 ± <0.01	0.14 ± <0.01	0.13 ± <0.01	0.31 ± <0.01
N ₂ O-N (mg m ⁻² month ⁻¹)	0.03 ± <0.01	0.03 ± <0.01	0.01 ± <0.01	0.02 ± <0.01
<i>Surface Water Evasion*</i>				
CO ₂ -C (g m ⁻² month ⁻¹)	0.74 (0.17-1.77)	0.57 (0.13-1.37)	0.99 (0.23-2.36)	1.04 (0.24-2.49)
CH ₄ -C (mg m ⁻² month ⁻¹)	1.75 (0.39-4.26)	1.05 (0.24-2.55)	2.62 (0.59-6.37)	3.44 (0.78-8.37)
N ₂ O-N (mg m ⁻² month ⁻¹)	0.01 (<0.01-0.03)	0.02 (0.01-0.05)	0.01 (<0.01-0.03)	0.04 (0.01-0.09)

* Due to data limitations, a single set of gas transfer coefficients is applied to calculate surface water evasion across all seasons. Therefore values do not represent the true seasonal variability and are included only as a comparison to downstream export to complete the aquatic carbon and GHG budget.

Table 5 Annual export of carbon and GHG species, stream temperature and discharge between 2007-11. Where \pm terms are given these refer to SE. Bracketed terms after evasion estimates refer to the range calculated from minimum and maximum gas transfer coefficients.

	2007	2008	2009	2010	2011
Mean Discharge ($L s^{-1}$)	60.8	95.5	64.1	78.6	62.7
<i>Downstream Export</i>					
POC ($g m^{-2} yr^{-1}$)	0.59 ± 0.02	4.49 ± 2.04	1.22 ± 0.11	2.28 ± 0.78	0.44 ± 0.01
DOC ($g m^{-2} yr^{-1}$)	27.5 ± 31.6	27.6 ± 14.6	17.9 ± 3.24	15.0 ± 4.65	12.4 ± 8.31
DIC ($g m^{-2} yr^{-1}$)	3.20 ± 2.33	0.68 ± 0.19	8.85 ± 10.1	2.27 ± 1.34	1.54 ± 0.34
CO ₂ -C ($g m^{-2} yr^{-1}$)	1.84 ± 0.04	1.21 ± 0.06	1.11 ± 0.02	1.23 ± 0.02	0.97 ± 0.01
CH ₄ -C ($mg m^{-2} yr^{-1}$)	$4.49 \pm <0.01$	$2.77 \pm <0.01$	$2.09 \pm <0.01$	$2.22 \pm <0.01$	$2.12 \pm <0.01$
N ₂ O-N ($mg m^{-2} yr^{-1}$)	$0.22 \pm <0.01$	$0.18 \pm <0.01$	$0.32 \pm <0.01$	$0.39 \pm <0.01$	$0.25 \pm <0.01$
<i>Surface water Evasion*</i>					
CO ₂ -C ($g m^{-2} yr^{-1}$)	10.20 (2.37-24.4)	8.26 (1.92-19.8)	10.5 (2.45-25.2)	9.91 (2.30-23.7)	9.91 (2.3-23.7)
CH ₄ -C ($mg m^{-2} yr^{-1}$)	24.1 (5.43-58.6)	19.22 (4.34-46.8)	25.5 (5.76-62.1)	24.6 (5.55-59.9)	26.2 (5.92-63.9)
N ₂ O-N ($mg m^{-2} yr^{-1}$)	-0.01 (-0.02-0.00)	---	0.17 (0.04-0.40)	0.20 (0.05-0.46)	0.27 (0.06-0.63)

* A single set of gas transfer coefficients is applied to calculate surface water evasion across all years. Therefore values do not represent the true interannual variability and are included only as a comparison to downstream export to complete the aquatic carbon and GHG budget.

Figures

Figure 1. Time series of a) daily mean discharge (grey line), b) temperature, c) pH and d) electrical EC in the Black Burn from January 2007 to December 2011. Solid black lines represent monthly moving averages (30 day window).

Figure 2. Interannual and seasonal variability in a) rainfall (snowfall not included) and b) mean air temperature. Seasons are based on the hydrological year running from 1st October to 30th September. Precipitation in late winter 2010 was exclusively snowfall.

Figure 3. Time series of instantaneous a) POC, b) DOC, c) DIC, d) CO₂, e) CH₄ and f) N₂O concentrations in the Black from January 2007 to December 2011. Solid black lines represent monthly moving averages (30 day window).

Figure 4. Concentration discharge relationships for a) POC, b) DOC, c) DIC, d) CO₂, e) CH₄ and f) N₂O in the Black Burn from January 2007 to December 2011. Note that in most cases axis are displayed on a logarithmic scale. r^2 and P values represent the results from regression analysis.

Figure 5. Boxplots showing monthly concentration distributions of a) POC, b) DOC, c) DIC, d) CO₂, e) CH₄ and f) N₂O in the Black Burn. Only maximum and minimum outliers are included. Normalised seasonal indices from time series deconstructions are presented in plates beneath each boxplot.

Figure 6. Boxplots showing annual concentration distributions in a) POC, b) DOC, c) DIC, d) CO₂, e) CH₄ and f) N₂O in the Black Burn. Only maximum and minimum outliers are included. Normalised trend indices from time series deconstructions are presented in plates beneath each boxplot.

Figure 7. Illustration of results from Spearman's rank correlations of carbon and GHG concentration against hydrochemical and meteorological variables at different time scales. Colour scale represents r values with the value also displayed within each box; positive concentrations are shown in red, negative in blue. Only results significant at $P < 0.05$ are included. Variable labels are defined as Q = Discharge, Rain = Rainfall, WT = Water table, Stream T = Stream temperature, Soil T = Soil temperature, pH and EC.

Figure 8. Bar charts of a) seasonal and b) interannual variability in carbon export separated into different carbon species; the dashed line represents changes in mean annual discharge over the described period. CH₄ and CO₂ bars include both downstream export and evasion. Seasons are based on the hydrological year and are defined as Early Winter (October, November, December), Late Winter (January, February, March), Early Summer (April, May, June) and Late Summer (July, August, September).













