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Variable source and age of different forms of carbon released from natural peatland pipes

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[1] We used the carbon isotope composition (^{14}C and δ^{13}C) to measure the source and age of DOC, POC, dissolved CO_2 and CH_4 (δ^{13}C only) released from three natural peat pipes and the downstream catchment outlet of a small peatland in northern England. Sampling under different hydrological extremes (high flows associated with storm events and low flows before or after storms) was used to explore variability in C sources as flow paths change over short periods of time. The δ^{13}C composition of organic C differed (δ^{13}C-DOC −28.6‰ to −27.6‰; δ^{13}C-POC −28.1‰ to −26.1‰) from that of the dissolved gases (δ^{13}C-CO_2 −20.5‰ to +1.1‰; δ^{13}C-CH_4 −67.7‰ to −42.0‰) and showed that C leaving the catchment was a mixture of shallow/deep pipe and non-pipe sources. The isotopic composition of the dissolved gases was more variable than DOC and POC, with individual pipes either showing ^{13}C enrichment or depletion during a storm event. The ^{14}C age of DOC was consistently modern at all sites; POC varied from modern to 653 years BP and evasion CO_2 from modern to 996 years BP. Differences in the isotopic composition of evasion CO_2 at pipe outlets do not explain the variability in δ^{13}C and ^{14}C at the catchment outlet and suggest that overland flow is likely to be an important source of CO_2. Our results also show that the sources of CO_2 and CH_4 are significantly more variable and dynamic than DOC and POC and that natural pipes vent old, deep peat CO_2 and POC (but not DOC) to the atmosphere.

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1. Introduction

[2] Soil pipes are significant subsurface structural features of peatlands and are known to occur in northern Europe, North America, Siberia, and the Southern Hemisphere [*Norrström and Jacks*, 1996; *Price*, 1992; *Rapson et al.*, 2006; *Thorp and Glanville*, 2003]. They have been widely recorded in UK blanket peats [e.g., *Holden and Burt*, 2002; *Holden*, 2005; *Jones et al.*, 1997], where it has been shown that peat drainage, surface drying and *Calluna vulgaris* L. (Hull.) encroachment are associated with increased pipe densities. Human action and environmental change can therefore potentially increase the number and size of pipes. Despite their widespread occurrence, there has been almost no research on the role of soil pipes in the release of C from peatlands and their potential to export C stored deep within the peat profile. Hence, it is important to understand and quantify the sources and amounts of different forms of C lost from peatlands via the pipe network and to investigate whether old, pre-bomb C is being released from deep peat sources.

[3] Globally, peatlands are estimated to store between 400 and 500 Gt C and play a significant role in greenhouse gas (GHG) exchange between the land surface and the atmosphere [*Gorham*, 1991; *Roulet*, 2000]. Peatland management and mismanagement (degradation) has had a major impact on their CO_2 sink and CH_4 source strength [e.g., *Gorham*, 1991; *Minkkinen et al.*, 2002]. Much of our understanding of C cycling and GHG fluxes associated with peatlands is based upon a knowledge of relationships between water table position, microbial community, temperature, plant type and management [*Billett et al.*, 2006a; *Cole et al.*, 2002; *McNeil and Waddington*, 2003; *Strack et al.*, 2008; *Worrall et al.*, 2006]. These factors affect components of the peatland C budget in different ways [e.g., *Dinsmore et al.*, 2010; *Koehler et al.*, 2011]. While pipes are known to be important in the delivery of water to peatland streams [e.g., *Holden and Burt*, 2002], there has been little work examining the role that water movement through peatlands plays in the retention and release of particulate and dissolved organic carbon (POC, DOC) and of dissolved gaseous carbon (CO_2

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and CH_4). Pipe-mediated C transport is likely to be temporally variable since it is known that the relative contribution of pipeflow to streamflow changes with antecedent conditions [*Holden and Burt*, 2002]. The dynamic hydrology associated with peatland pipes is also manifest in frequent changes in outlet morphology, appearance of new pipes and closure of existing pipes [*Holden et al.*, 2012].

[4] Natural soil pipes, which comprise inter-connecting macropores several centimeters in diameter and up to several hundred meters in length, typically form complex, undulating, branching subsurface networks that are potential pathways for water, dissolved gas, sediment and solute transport [*Holden et al.*, 2009]. Flow within individual pipes is either perennial (continuous) or ephemeral (responds only to storm events and therefore discontinuous). Pipe networks are also known to occur at a variety of depths within the soil profile [*Holden and Burt*, 2002] and have the potential to provide connectivity with both deep and shallow sources of water [*Holden*, 2004]. This has important implications in ombrotrophic peatlands where deep peat has traditionally been assumed to be a stable C store largely disconnected from the stream network.

[5] Radiocarbon (^{14}C) studies in northern temperate, boreal and subarctic peatlands show that the ^{14}C age of peats increases with depth down the soil profile [*Schiff et al.*, 1997; *Charman et al.*, 1999; *Chasar et al.*, 2000; *Palmer et al.*, 2001; *Raymond and Bauer*, 2001a, 2001b; *Billett et al.*, 2007; *Clymo and Bryant*, 2008]. The upper layers are dominated by peat ^{14}C ages that are modern (post-bomb) with peat typically several thousand years old in deeper layers [*Charman et al.*, 1999; *Chasar et al.*, 2000; *Palmer et al.*, 2001; *Clymo and Bryant*, 2008]. Soil solution DOC and gaseous forms of C also increase in age with depth. However, soil gases are generally younger than the peat at the same depth and, in most reported cases, soil solution DOC is younger still. Ages of gases reported in peatlands range from modern to 4330 years BP for CO_2 and modern to 4033 years for CH_4, while ages of DOC range from modern to 6970 years [*Charman et al.*, 1999; *Chasar et al.*, 2000; *Clymo and Bryant*, 2008; *Garnett et al.*, 2011]. Although there are a number of exceptions, peatland-derived stream water DOC generally produces a radiocarbon signature indicating a modern source. Studies of ^{14}C and stable carbon isotope ($\delta^{13}C$) suggest that the majority of the DOC is derived from the decomposition of recent soil organic matter [*Palmer et al.*, 2001; *Raymond and Bauer*, 2001a; *Billett et al.*, 2007; *Evans et al.*, 2007]. Stream water POC, however, is often much older with ages of up to 3710 years reported [*Striegl et al.*, 2007; *Billett et al.*, 2011]. *Billett et al.* [2007] found that DOC released from the stream system of four UK peatland catchments was young (modern to 202 years BP), while CO_2 being released (evaded or degassed) from the stream water surface was older, (modern to 1449 years BP), suggesting (in association with the $\delta^{13}C$ values) that the sources of fluvial DOC and CO_2 were in most cases different.

[6] Up to now there has been no study of the radiocarbon age of natural pipe waters in peatlands. In terms of C this is important because it is not only present in a variety of chemical forms in peats (DOC, POC, DIC (dissolved inorganic carbon), CO_2 and CH_4), but the age of C stored is known to increase with depth within the peat profile. It could be assumed that peatland pipes simply act as "benign" conduits for surface water transfer through the peat mass, although that is unlikely. We know that CO_2 and CH_4 concentrations in both soil solution and the soil atmosphere of shallow and deep peats are orders of magnitude higher than concentrations in the above-ground atmosphere [*Charman et al.*, 1999; *Clymo and Bryant*, 2008; *Hope et al.*, 2004; *Dinsmore et al.*, 2009]. Therefore, concentrations in pipe water are likely to be significantly higher than those in stream water. Pipeflow, supersaturated with CO_2 and CH_4, may degas rapidly once it leaves the pipe system due to lower ambient partial pressures [*Dinsmore et al.*, 2011]. In peatland systems this out-gassing in the drainage network potentially contributes a significant loss of terrestrially derived C to the atmosphere [*Hope et al.*, 2004]. It has been shown that peatland headwater streams are important zones of degassing [*Dawson et al.*, 2002], and concentrations of CO_2 vary over different temporal scales [*Dawson et al.*, 2001; *Dinsmore and Billett*, 2008]. Specific parts of peatland streams act as hot spots for degassing [*Billett and Moore*, 2008]; additional degassing (CO_2 and CH_4) hot spots have been identified in peatland gullies [*McNamara et al.*, 2008] and the riparian zone of DOC-rich streams [*Dinsmore et al.*, 2009]. Recent work by *Dinsmore et al.* [2011] has demonstrated the importance of pipe outgassing and shown that significant loss of greenhouse gases (CO_2, CH_4 and N_2O) occur from the pipe network to the atmosphere.

[7] Here we report isotopic measurements of DOC, POC, CO_2 ($\delta^{13}C$ and ^{14}C) and CH_4 ($\delta^{13}C$ only) released from three natural pipes and the downstream catchment outlet of a blanket bog at Moor House, Cumbria, UK. We hypothesize that:

[8] 1. Natural peat pipe waters contain C sourced from different depths/ages within the profile.

[9] 2. Dissolved, particulate and gaseous forms of C exported from peat pipes have different sources/ages.

[10] 3. Natural pipes contain a greater proportion of "old" C compared to the stream network.

[11] We tested these hypotheses by collecting samples of pipe and stream water under a range of hydrological conditions associated with spring, summer and autumn high flow events. Since upland peatland systems in the UK are characterized by a rapid rainfall-runoff response [*Holden and Burt*, 2003a] associated with changes in flow pathways and greater pipe flow, our aim was to target sampling at different parts of the storm hydrograph to see the greatest potential differences in carbon age/source.

2. Methods

2.1. Study Site

[12] Cottage Hill Sike (54°41′N, 2°23′W), located within the Moor House National Nature Reserve (Cumbria, northern England), has a catchment area of 17.4 ha and an altitudinal range of 545 to 580 m (Figure 1). The catchment is covered almost entirely by a thick ombrotrophic blanket peat (typically 3–4 m deep, maximum 8 m) that overlies a Quaternary clay-rich glacial till on Carboniferous Limestone bedrock. Cottage Hill Sike (CHS) is a headwater of the River Tees, which flows eastward and drains into the North Sea. The climate is subarctic oceanic, with a mean annual

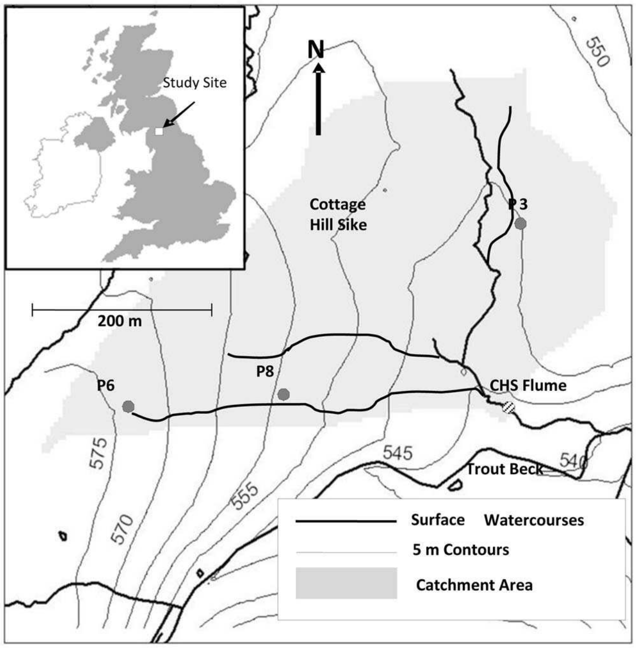

Figure 1. Location, site characteristics and sample locations in the Cottage Hill Sike catchment.

temperature of 5.3°C (1931–2006) and rainfall of 2012 mm yr^{-1} (1951–1980, 1991–2006) [*Holden and Rose*, 2011]. The catchment contains an ECN (Environmental Change Network) target monitoring site and is one of the CEH (Centre for Ecology and Hydrology) Carbon catchments. As part of the ECN, parameters such as vegetation composition, water table position and soil-water chemistry have been monitored under strict protocols since 1992 [*Sykes and Lane*, 1996]. Vegetation cover in the catchment is predominantly *Calluna vulgaris* and *Eriophorum vaginatum* L. with other species including *Empertrum nigrum* L. and *Sphagnum capillifolium* (Ehrh.) Hedw.

[13] Stream discharge is characterized by a rapid hydrological response to all rainfall or snowmelt events [*Clark et al.*, 2005]. Discharge at the outlet of the catchment is monitored continuously through a rated flume (CHS flume). Trout Beck (the mainstream in the area into which CHS drains) displays mean lag times of 2.8 h between peak rainfall and peak discharge [*Evans et al.*, 1999] and annual runoff coefficients of 70%–80%. Overland flow and shallow throughflow generally dominate runoff response at the site, with little apparent deeper flow through the peat matrix [*Holden and Burt*, 2003a].

[14] Stream water chemistry at Cottage Hill Sike is acidic and organic-rich with a mean (1993–2007) pH of 4.3, mean DOC concentration of 18.8 ± 8.7 (SD) mg L^{-1} and mean Ca concentration of 1.1 mg L^{-1} [*Tipping et al.*, 2010]. Soil water DOC concentrations sampled within the catchment by the Environmental Change Network (ECN) at 10 and 50 cm depth were 21.1 ± 4.4 and 16.9 ± 2.2 mg L^{-1} [*Adamson et al.*, 2001], respectively, with summer maxima of 25–50 mg L^{-1} [*Clark et al.*, 2005]. Mean annual DOC flux from the catchment (1992–2007) is high (23.4 g C m^{-2} yr^{-1}), with significant year-on-year variation [*Billett et al.*, 2010]. Previous isotopic studies carried out at the site showed that DOC at the catchment outlet was modern (i.e., carbon fixed post-1955 AD), while $\mathrm{CO_2}$ released (evaded) from the stream water surface was older (modern to 530 ± 35 years BP), suggesting that the sources of fluvial DOC and $\mathrm{CO_2}$ were different [*Billett et al.*, 2007]. In addition, *Tipping et al.* [2010] showed that stream water DOM (dissolved organic matter) was young (5 years old) and predominantly associated with surface peat, whereas groundwater DOM was 8,500 years old and likely derived from a source within the underlying glacial clay.

2.2. Sampling and Analysis

[15] We aimed to collect samples for isotopic analysis of DOC, POC, $\mathrm{CO_2}$ and $\mathrm{CH_4}$ over a range of hydrological conditions by sampling pre-storm (base flow), rising limb, high flow and the receding limb of storms at different times of year. We succeeded in sampling pipe water during major high flow events in April and November and a minor rainfall event in August 2009. Samples collected in all three storms were sent for stable isotope (δ^{13}C) analysis at the NERC Life Sciences Mass Spectrometry Facility (LSMSF-Lancaster, UK); those collected in August and November were also sent to the NERC Radiocarbon Facility (RCF-East Kilbride, UK) for ^{14}C analysis. A mean of 84 pipe outlets have been mapped in CHS [*Holden et al.*, 2012]. Of these, several have been more intensively studied for their hydrology and hydrochemistry [*Dinsmore et al.*, 2011; *Holden et al.*, 2012; *Smart et al.*, 2012; J. Holden et al., Natural pipes in blanket peatlands: Major point sources for the release of carbon to the aquatic system, submitted to *Global Change Biology*, 2012]. Of these pipes (24 ephemeral; 60 perennial) we selected three to represent different pipe types and pipe outlet depths below the peat surface (depths ranged from 15 cm to 200 cm below the surface). These were P3 (perennially flowing, pipe outlet 25 cm from the peat surface), P6 (perennially flowing, pipe outlet 100 cm from the peat surface) and P8 (ephemerally flowing, pipe outlet 160 cm from the peat surface). The naming of the three pipes is consistent with that used in other papers from the site; for more information on pipe distribution and morphology, see *Holden et al.* [2012] and *Smart et al.* [2012]. Our sampling strategy was therefore based on three continuously monitored pipes plus the catchment outlet (CHS flume). An additional set of water samples from the same sites was collected for the determination of DOC, POC, $\mathrm{CO_2}$ and $\mathrm{CH_4}$ concentration and in situ measurements of pH, conductivity and temperature at the time of sampling.

[16] Between field sampling, sample preparation in the laboratory, and analysis, all water samples were stored at 4°C and in the dark following standard protocols (to minimize biological activity). For the determination of DOC and POC, samples were collected from free flowing water at the pipe outlet in acid-washed, 500 mL polypropylene sample bottles pre-rinsed with sample water. A Thermalox Total Carbon (TC) analyzer was used to measure DOC (precision ±0.1 mg C L^{-1}, detection limit 1.0 mg C L^{-1}). Samples were acidified and sparged with $\mathrm{O_2}$ to stabilize the sample and remove inorganic carbon. Acidified samples were run in duplicate (or triplicate if the coefficient of variation was >1%). Regular analysis of potassium hydrogen phthalate standards and a certified reference material (VKI QC WW4a) ensured the level of error was kept to a minimum.

Particulate organic carbon was determined indirectly by loss-on-ignition after filtration through 0.7 μm Whatman GF/F glass micro-fibre filters. The filtrate was dried at 105°C (24 h), ignited at 375°C (16 h); POC was calculated using a regression equation for non-calcareous soils [*Ball*, 1964; *Dawson et al.*, 2002].

[17] For the determination of δ^{13}C-DOC and δ^{13}C-POC, samples were collected in two acid-washed 500 mL polypropylene sample bottles per sample pre-rinsed three times with sample water. Prior to analysis for δ^{13}C of DOC and POC at LSMSF, 1 L samples were filtered through pre-ashed 0.70 μm GF/F filter papers on an acid-washed suction filtration system into acid-washed 1 L conical flasks. Filter papers were stored in 20 mL acid-washed glass vials at 4°C prior to ^{13}C analysis of POC at LSMSF. The pH of each sample filtrate was then determined in 500 mL aliquots, prior to being adjusted to pH 4 by addition of 2 M HCl. Samples were then sparged with CO_2-free N_2 for 20 min before the pH was raised to pH 7 by 0.2 M NaOH. 500 mL aliquots of sample were then placed in 1 L rotary evaporator flasks for evaporation at 40°C under vacuum. Samples were evaporated to near dryness (20–30 mL) before being transferred to a 100 mL rotary evaporator flask and evaporated to dryness. The dried DOC samples were then transferred to labeled 20 mL acid washed glass vials and stored at 4°C prior to δ^{13}C analysis at the LSMSF. Samples for the determination of δ^{13}C-DOC and δ^{13}C-POC were combusted using a Eurovector elemental analyzer. Resultant CO_2 from combustion was analyzed for δ^{13}C using an Isoprime Ltd "Isoprime" Isotope Ratio Mass Spectrometer (IRMS). Maximum standard deviation of duplicates for δ^{13}C was 0.16‰.

[18] For ^{14}C-DOC, 1 L of stream or pipe water was collected in acid-washed pre-rinsed glass bottles before storage and analysis at the NERC Radiocarbon Facility (NERC RCF). Because the concentration of POC is generally much lower than DOC, 10 L of sample was collected in an acid-washed 10 L sample aspirator for ^{14}C-POC analysis. This sample was filtered (using ashed 0.7 μm GF/F filters) and the filter contents (i.e., the POC) retained and sent to the NERC RCF, where the POC was removed from the filter and dried. Samples of DOC were filtered (through ashed GF/F filters), acidified to pH 4 by addition of 2 M HCl, and sparged by bubbling with CO_2-free N_2 gas. The samples were returned to pH 7 by addition of KOH solution, rotary evaporated and freeze-dried. For all DOC and POC samples, the total carbon in the dried sample material was cryogenically recovered as CO_2, following combustion inside an evacuated sealed quartz tube by heating with CuO, and stored in glass tubes prior to isotope analysis.

[19] Samples for the determination of dissolved CO_2 and CH_4 in stream or pipe water were collected using the headspace method [*Hope et al.*, 2004; *Billett and Moore*, 2008]. This involves equilibrating 40 mL of water with 20 mL of ambient atmosphere for 1 min underwater in a sealed 60 mL syringe and transferring the equilibrated saturated headspace sample to a gas-tight nylon syringe. Dissolved gas concentrations are calculated from the measured headspace and ambient concentrations using Henry's law, which requires additional measurements of water temperature, atmospheric pressure and elevation [*Hope et al.*, 1995]. On return to the laboratory at CEH Edinburgh headspace samples were analyzed on an HP5890 Series II gas chromatograph equipped with a FID and attached methanizer (detection limits: CO_2 199 ppmv, CH_4 1.26 ppmv). For the determination of δ^{13}C-CO_2 an additional headspace sample was collected in the same way described above, the only difference being that the headspace sample was transferred to an evacuated 20 mL exetainer using a hypodermic needle. To collect sufficient CH_4 for the determination of δ^{13}C we used three × 100 mL syringes, and in each syringe 60 mL of stream water was equilibrated with 40 mL of ambient air. The headspace from all three syringes was transferred to a dry 100 mL syringe in the field and the composite headspace injected into a sealed 100 mL evacuated glass Wheaton bottle through a self-sealing septum. Samples for the determination of δ^{13}C-CO_2 were directly introduced into the injection port of an Isoprime Ltd (Cheadle, UK) TraceGas pre-concentrator interfaced via an open split to an Isoprime Ltd isotope ratio mass spectrometer. All samples were analyzed to the United Kingdom Accreditation Scheme (UKAS) ISO17025 standard. Methane analysis was performed using the same instrument with the gas selectors set to CH_4 and a furnace tube in line. Methane was converted to CO_2 in a Pt/Ni furnace at 1050°C from which δ^{13}C measurements were then determined.

[20] Samples of dissolved CO_2 for C isotope analysis were collected in situ from selected peat depths (25, 30, 50 and 100 cm) in one profile ~20 m meters from the outlet to pipe P3 using a passive sampling method [*Garnett and Hardie*, 2009]. Stainless steel probes were inserted vertically (with minimal disturbance) to the required sampling depth. The end of the probes contained a hydrophobic gas permeable, water-impermeable filter (Accurel PP V8/2 HF, Membrana GmbH, Germany). The upper end of the probe remained above ground, and to this a quartz glass cartridge containing a zeolite molecular sieve [*Hardie et al.*, 2005] was attached. The molecular sieve passively adsorbs CO_2 and therefore sampled the atmosphere inside the probe, thus collecting CO_2 in the vicinity of the gas entry point to the probe. Probes were inserted on 20th August and removed on 11th November 2009. The molecular sieves were then returned to the NERC RCF, the CO_2 cryogenically recovered following heating (500°C) and stored in glass tubes until analysis.

[21] Further supporting age data were provided by radiocarbon analysis of two basal peats (2.4–2.6 m) from a site at the western edge of the CHS catchment (100 m west of pipe P6; see Figure 1) collected on 26 July 2000. Samples were acid-washed (2 M HCl) to remove potentially mobile carbon, dried, and converted to CO_2 in a combustion "bomb" in an atmosphere of high pressure oxygen. The CO_2 was cryogenically recovered then converted to benzene, and the ^{14}C measured by liquid scintillation counting (on a Quantulus 1220, LKB Wallac, Finland).

[22] Carbon dioxide lost by evasion from the water surface to the atmosphere was sampled from the pipe outlets and the stream for isotopic analysis using a sealed opaque floating chamber connected to a zeolite molecular sieve sampling system [*Hardie et al.*, 2005; *Billett et al.*, 2006b]. Evaded (degassed) CO_2 is trapped by the molecular sieve after purging the original atmospheric CO_2 from the floating headspace. Sampling time is a function of evasion rate which is dependent on gas transfer rate at the water surface (enhanced by turbulence) and the pCO_2 of the water. We aimed to trap 5–15 mL of CO_2 to provide a suitable volume

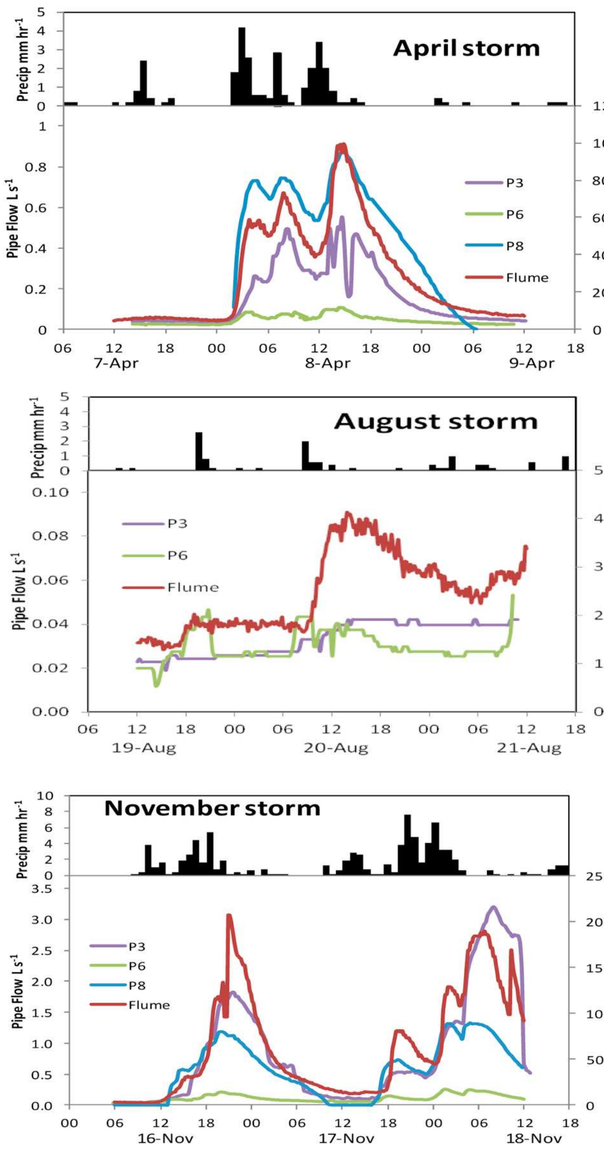

Figure 2. Storm hydrographs (L s^{-1}) and rainfall rates (mm hr^{-1}) for the three pipes (P3, P6, P8) and the CHS flume during the April, August and November storms. No discharge was produced by P8 during the August storm.

for ^{14}C analysis by accelerator mass spectrometry (AMS). Sample times in this study varied from 30 min at CHS flume to 19 h at pipe P3. After trapping the evaded CO_2, the molecular sieve cartridges were returned to the NERC RCF and the CO_2 recovered using the same procedures as used for the ^{14}C analysis of dissolved peat CO_2 [see *Hardie et al.*, 2005; this study].

[23] For all samples analyzed for radiocarbon, an aliquot of the recovered CO_2 was first used to determine δ^{13}C (relative to the Vienna-PDB standard) by isotope IRMS (VG Optima, Micromass, UK). The remaining CO_2 was converted to graphite by Fe-Zn reduction [*Slota et al.*, 1987] and passed to the Scottish Universities Environmental Research Centre (SUERC) for ^{14}C measurement by AMS. Following conventions, ^{14}C results were normalized to δ^{13}C −25‰ and expressed as % modern and conventional radiocarbon ages (years BP; where 0 BP = 1950 AD) with $\pm 1\ \sigma$ analytical confidence. A correction was made to the evasion isotope values to account for the fact that the CO_2 had degassed into a closed chamber. As described by *Billett and Garnett* [2010], this adjustment is used to calculate the isotopic composition of the evasion CO_2-C if it had been degassing directly into the free atmosphere rather than the chamber. However, for the current samples, the correction made only a small difference to most results. During passive sampling, isotopic fractionation occurs which has been quantified to be ∼4‰ [*Garnett and Hardie*, 2009]. The δ^{13}C values for dissolved CO_2 in peat were therefore adjusted to account for this effect (^{14}C results did not require this correction as following convention they were normalized to a δ^{13}C of −25‰).

[24] Hourly rainfall was recorded in a tipping bucket rain gauge at the ECN weather station approximately one kilometre from the study site. Discharge at the outlets of the three pipes was measured using continuously recording Trafag DL/N type pressure transducers with data loggers, installed in stilling wells located within rated V notch weir boxes which collected discharge from pipe outlets; discharge at the CHS flume was recorded continuously using a logging pressure transducer (In Situ Level Troll 300) situated directly upstream of the flume.

[25] Possible differences in chemical species between sites and between the isotopic signature of different forms of C were evaluated using one-way ANOVA followed by Tukey's multiple comparison test to examine which individual mean values differ significantly from others.

3. Results

3.1. Storm Hydrology

[26] The most intense of the three storms occurred in November when 78.4 mm of rain fell in 44 h. The precipitation profile had two major peaks which resulted in a rapid runoff response as flow at CHS flume increased from 4 to 207 L s^{-1} (Figure 2). The intensity of the November storm was demonstrated by the exceedence value relative to the complete 2009 flow record at CHS flume; peak flow in the November event was only exceeded 0.3% of the time. Similarly the April storm was double-peaked but of lower intensity (24.8 mm of precipitation in 33 h) resulting in a rise in discharge from 4 to 99 L s^{-1} at CHS flume. The exceedence value of this storm was 2.3%. The August event was of a smaller magnitude (10.8 mm of precipitation in 44 h) and, due to a combination of drier antecedent conditions and low rainfall intensity, we only measured a rise in discharge from 1 to 4 L s^{-1} at the catchment outlet. The exceedence value of the August event was 34.8%. In all three events the rainfall-runoff response lag time (the time between onset of rainfall and a rise in water level at CHS flume) was approximately 1 h.

[27] Of the two continuously flowing pipes, P6 was the less hydrologically responsive. Discharge increased from 0.02 to 0.25 L s^{-1} during the November storm and from 0.02 to 0.11 L s^{-1} during the April storm. In contrast, P3 recorded much higher flows with an increase from 0.03 to a maximum of 3.21 L s^{-1} in November and from 0.04 to 0.55 L s^{-1} in April. During the August event, discharge at the two continuously flowing perennial pipes remained at 0.02–0.04

Table 1. Basic Mean Chemical Characteristics (Minimum and Maximum Values in Parentheses) of P3, P6, P8 and the Outlet Flume During the Three Storm Events

	P3 (n = 18)	P6 (n = 18)	P8[a] (n = 8)	Flume (n = 18)
DOC (mg L^{-1})	33.29[a][b] (5.60–124.93)	35.12[a] (7.21–85.05)	60.55[a] (6.38–142.84)	32.82[a] (12.20–51.30)
POC (mg L^{-1})	2.89[a] (0.09–23.60)	2.60[a] (0.72–9.81)	1.20[a] (0.18–2.72)	0.86[a] (0.36–1.73)
CO_2-C (mg L^{-1})	1.42[ab] (0.46–2.91)	2.41[a] (0.58–10.99)	0.78[b] (0.70–0.95)	1.48[ab] (0.44–3.45)
CH_4-C (μg L^{-1})	3.71[b] (0.37–11.75)	215.80[a] (13.36–1132.14)	4.79[b] (0.37–6.81)	2.00[b] (0.02–4.53)
pH	4.16[a] (3.99–4.32)	4.22[a] (4.01–4.42)	4.17[a] (4.09–4.24)	4.22[a] (4.12–4.36)
Cond (μS cm^{-1})	37[a] (25–45)	37[a] (25–46)	41[a] (31–50)	37[a] (26–45)
Temp (°C)	7.15[a] (3.52–13.91)	6.55[a] (3.53–12.06)	4.67[a] (3.71–5.52)	7.12[a] (3.49–13.27)

[a] Pipe P8 flowed only during the April and November events.

[b] Mean values that do not share the same bracketed letter(s) are significantly different (Tukey's multicomparison test).

L s^{-1}; there was no flow from the ephemeral pipe (P8). In the intense November storm P8 exhibited two distinct periods of discharge which were closely related to precipitation intensity; a maximum flow of 1.32 L s^{-1} was recorded during the second storm peak. In the April storm P8 recorded the highest flows of all the pipes reaching 0.87 L s^{-1} soon after the second precipitation peak. The storm hydrographs of pipes P3 and P8 were similar in shape to that at CHS flume.

3.2. Spatial Differences in Chemical and Isotopic Concentrations Between Sites

[28] Although mean DOC concentrations at the two continuously flowing pipes (P3 and P6), the ephemeral pipe (P8) and the CHS flume were not statistically different (Table 1), the mean concentration at P8 was almost double those at the other three sites. Likewise POC concentrations were not significantly different at the four sample sites. Highest CO_2 concentrations were observed at P6 and lowest at P8; the differences between these two pipes were statistically significant. Mean CH_4 concentration at P6 was between 45 and 108 times higher and significantly different from the other three sites. No significant differences existed between pH, conductivity and temperature at the four sites when data from all the storm events were pooled.

[29] The mean δ^{13}C value of DOC released from P3 was statistically more ^{13}C depleted than the DOC from other sites (Table 2). In contrast DOC at the flume was significantly more ^{13}C enriched; P6 and P8 had similar δ^{13}C-DOC values. P3 and P6 had similar δ^{13}C-POC values and were significantly more ^{13}C depleted than POC from P8 and CHS flume. The most ^{13}C enriched dissolved (and evaded) CO_2 was associated with P6, whereas P3 was significantly depleted in ^{13}C compared to the other sites. For CH_4 the most ^{13}C depleted mean values were at P6 and P8, while CH_4 measured at CHS flume was the most ^{13}C enriched. P3 had a significantly different δ^{13}C-CH_4 value from the other sites.

[30] A comparison between the δ^{13}C signature of different forms of C at each of the four sites (Table 2, statistics not shown) demonstrated that the isotopic composition of both DOC and POC associated with each pipe and CHS flume was statistically similar. However, differences between the δ^{13}C composition of CO_2, CH_4 and evasion CO_2 were statistically significant showing that at each site the gaseous forms of C had a unique δ^{13}C signature.

[31] Table 3 shows the ^{14}C enrichment of DOC, POC and evasion CO_2 for the August and November storm events. The overall (August + November) mean ^{14}C enrichment of DOC samples collected was significantly higher at P3 (114.22% modern) and P6 (114.30% modern) compared to CHS flume (111.21% modern). For POC pipe P6 was significantly more ^{14}C depleted (99.61% modern) compared to P3 (107.09% modern) and CHS flume (105.58% modern). Likewise, P6 was associated with the most ^{14}C depleted evasion CO_2 (mean 94.57% modern), although this was not significantly different from the value at CHS flume (97.74% modern). Evasion CO_2 at P3, however, was significantly more ^{14}C-enriched than the other two sites.

[32] We compared the ^{14}C values of DOC, POC and evasion CO_2 at individual sites and found that both at P3 and P6 DOC was significantly ^{14}C enriched compared to both evasion CO_2 and POC. At CHS flume, however, the mean ^{14}C enrichment of all three forms of C was significantly different. We collected insufficient carbon for ^{14}C analysis of the ephemeral pipe (P8) to make the same type of comparison.

[33] Isotope analysis of dissolved CO_2 passively sampled down the peat profile at P3 showed that between 25 and 100 cm CO_2 became progressively more ^{13}C enriched and ^{14}C depleted (Table 4). The oldest CO_2 was collected at 100 cm and corresponded to a radiocarbon age of 448 ± 37 years BP. The 2 basal peat samples from the western edge of the catchment sampled in 2000 were dated at

Table 2. Mean δ^{13}C Values (Minimum and Maximum Values in Parentheses) of Various Carbon Species Collected During the Three Storm Events

	P3 (n = 12–18)	P6 (n = 13–18)	P8 (n = 8)	Flume (n = 14–18)
δ^{13}C-DOC	−28.3[c][a] (−28.6 to −28.1)	−28.2[b] (−28.4 to −27.8)	−28.1[b] (−28.2 to −28.0)	−27.9[a] (−28.1 to −27.6)
δ^{13}C-POC	−27.2[b] (−28.1 to −26.5)	−27.1[b] (−28.0 to −26.6)	−26.4[a] (−27.0 to −26.2)	−26.6[a] (−27.3 to −26.1)
δ^{13}C-CO_2	−17.4[c] (−20.5 to −12.4)	−4. 9[a] (−13.5 to 1.1)	−14.6[bc] (−16.2 to −13.7)	−14.5[b] (−16.7 to −11.4)
δ^{13}C-CH_4	−54.1[b] (−60.1 to −47.9)	−64.2[c] (−67.7 to −61.6)	−61.9[c] (−67.3 to −49.1)	−46.7[a] (−53.1 to −42.0)
δ^{13}C-evasion CO_2	−23.4[b] (−26.7 to −18.1)	−8.8[a] (−16.5 to −1.4)	−19.8 (*one value only*)	−19.2[b] (−20.7 to −14.9)

[a] Mean values that do not share the same bracketed letter(s) are significantly different (Tukey's multicomparison test). Seven to eight samples of evasion CO_2 were collected from each of P3, P6 and P8. The statistical comparison shown here is between sites, not between C species.

Table 3. Mean ^{14}C Enrichment (% Modern) Values (Minimum and Maximum Values in Parentheses) of DOC, POC and Evasion CO_2 Collected From Three Pipes and the Catchment Outlet During the August and November Storm Events

	P3	P6	P8	Flume
		August		
DOC	115.31 (115.00–115.89)	115.54 (113.97–116.71)	ns	111.48 (111.08–112.01)
POC	106.46 (103.31–110.24)	96.54 (93.27–102.67)	ns	103.94 (103.24–104.68)
CO_2-C	109.13 (107.41–110.19)	89.21 (88.34–90.17)	ns	98.04 (96.01–99.53)
		November		
DOC	113.41 (112.48–114.20)	113.37 (110.99–115.08)	114.6 (113.37–115.83)	111.1 (109.9–112.0)
POC	107.47 (102.68–109.47)	101.45(92.21–107.75)	111.21 (110.89–111.52)	106.57 (102.64–108.87)
CO_2-C	106.54 (104.61–107.38)	98.59 (92.43–104.09)	106.45[a]	97.77 (95.98–100.42)

[a] One sample.

6396 ± 46 (Publication Code SRR-6613) and 6511 ± 50 years BP (Publication Code SRR-6614).

3.3. Temporal Changes in Chemical and Isotopic Concentrations During Storm Events

[34] During the April storm, DOC concentrations from the three pipes were variable and high and showed no consistent temporal trend over the hydrograph period. Concentrations of DOC in the more intense November storm were much lower and showed a decline in all three pipes over the event period (Figure 3). δ^{13}C-DOC values were variable and inconsistent during both storms.

[35] During the April storm event POC concentrations peaked at the same time on the rising limb of the storm hydrograph at CHS flume and all three pipes (Figure 4). Generally higher POC concentrations were recorded in the more intense November storm with P3 releasing very high POC concentrations during the low-flow period between the two discharge peaks. Like the δ^{13}C values of DOC, there were no consistent temporal trends in δ^{13}C-POC during the two storms.

[36] In the April and November storms the onset of rising stream and pipe discharge was associated with a rapid drop in dissolved CO_2 concentration (Figure 5); thereafter, concentrations recovered slightly (April) or remained consistently low (November). Our data also showed that over the course of both storm events the often distinct pre-storm differences between CO_2 concentrations at all four sampling sites became less clear as flows increased. P6 exhibited significant changes in δ^{13}C-CO_2 during both storms, with pre-storm (base flow) values of −0.1‰ and −0.9‰ changing to −13.5‰ and −11.8‰ during the high discharge period indicating progressive ^{13}C depletion. The δ^{13}C-CO_2 values of P3, P8 and CHS flume were less variable over the course of both storms (−11.4‰ to −18.6‰) and in the November storm showed a trend of increasing ^{13}C enrichment over time.

[37] In all three pipes, CH_4 concentrations dropped at the start of the storms and remained relatively low throughout the storm; these changes were clearer in the November event (Figure 6). While distinct differences existed between individual pipes and CHS flume, only P3 exhibited a consistent trend of increasing ^{13}C enrichment over time.

[38] The most complete set of radiocarbon data was collected for the November storm (Figure 7) and showed that at CHS flume and P3, changes in ^{14}C-DOC and ^{14}C-POC were similar. During the pre-storm period POC produced from P6 was ^{14}C depleted; it became rapidly ^{14}C enriched at the start of the November storm and then more depleted at the end of the storm. Evasion ^{14}C-CO_2 values changed little at P3 over the course of the storm. However, pre-storm evasion ^{14}C-CO_2 values were depleted at both P6 and CHS flume. At the onset of the storm, values became more ^{14}C enriched before declining in the case of CHS flume and enriching further in the case of P6.

[39] We do not show temporal changes in isotopic composition during the August event because changes in discharge were minimal (Figure 2). The δ^{13}C signature of DOC and POC at the three remaining sites (P3, P6 and CHS flume) varied only slightly (0.2–0.6‰) over the sampling period, although at P6 there was a larger change (2.1‰). Evasion and dissolved CO_2 were more variable, particularly at P6 where we recorded the most ^{13}C enriched sample (+1.1‰ dissolved CO_2) at summer base flow before the start of the small storm. This changed to −3.9‰ on the receding limb of the short event. Likewise, dissolved CH_4 values were more variable than DOC or POC, with changes of up to 6.8‰ during the course of the event.

[40] The radiocarbon age of DOC and POC samples collected during the August event was generally modern, although at P6 we measured POC ages of 526 ± 37 and 559 ± 37 years BP at base flow and peak flow, respectively. Evasion CO_2 ages were most ^{14}C depleted at base flow with ages varying from 996 ± 38 to 831 ± 38 years BP at P6 and

Table 4. Isotopic Signature of CO_2 Collected at a Range of Peat Depths (25–100 cm) at Site P3 by Passive Sampling[a]

Peat Depth (cm)	^{14}C Enrichment (% Modern ± 1σ)	Conventional Radiocarbon Age	$\delta^{13}C_{(VPDB)}$ (±0.1‰)	Publication Code
25	102.86 +/− 0.45	modern	−22.8 (−18.8)	SUERC-28812
30	101.22 +/− 0.47	modern	−15.9 (−11.9)	SUERC-28811
50	98.79 +/− 0.43	98 +/− 35	−10.8 (−6.8)	SUERC-28810
100	94.58 +/− 0.44	448 +/− 37	−2.3 (+1.7)	SUERC-28809

[a] NB: δ^{13}C values outside parentheses are measured values, and those in parentheses are representative of the dissolved CO_2 (having been corrected for 4‰ isotopic fractionation during passive trapping [see *Garnett and Hardie*, 2009]).

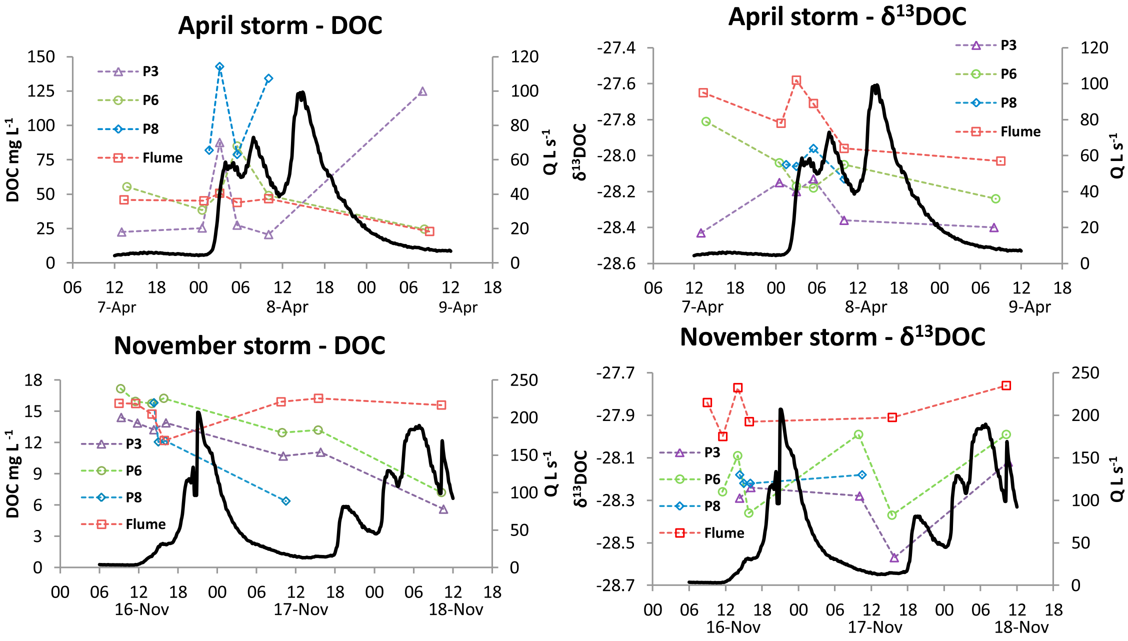

Figure 3. Temporal changes in DOC concentration and δ^{13}C-DOC for the three pipes (P3, P6, P8) and the CHS flume during the April and November storm events. Flow (solid line) is presented for CHS flume only.

327 ± 37 to 38 ± 37 years BP at CHS flume; radiocarbon ages at P3 were all modern.

4. Discussion

[41] The use of carbon isotopic geochemistry in headwater regions is a powerful tool to investigate catchment processes that control the source and age of C in the freshwater environment. In contrast, isotopic measurements in major river systems are often difficult to interpret because of their size and complexity [e.g., *Raymond and Bauer*, 2001a]. Here, δ^{13}C and ^{14}C measurements of C released at the catchment outlet (CHS flume) and from three pipes can be individually related to specific parts (in the case of pipes, depth-variable, micro-catchments) of the peatland itself.

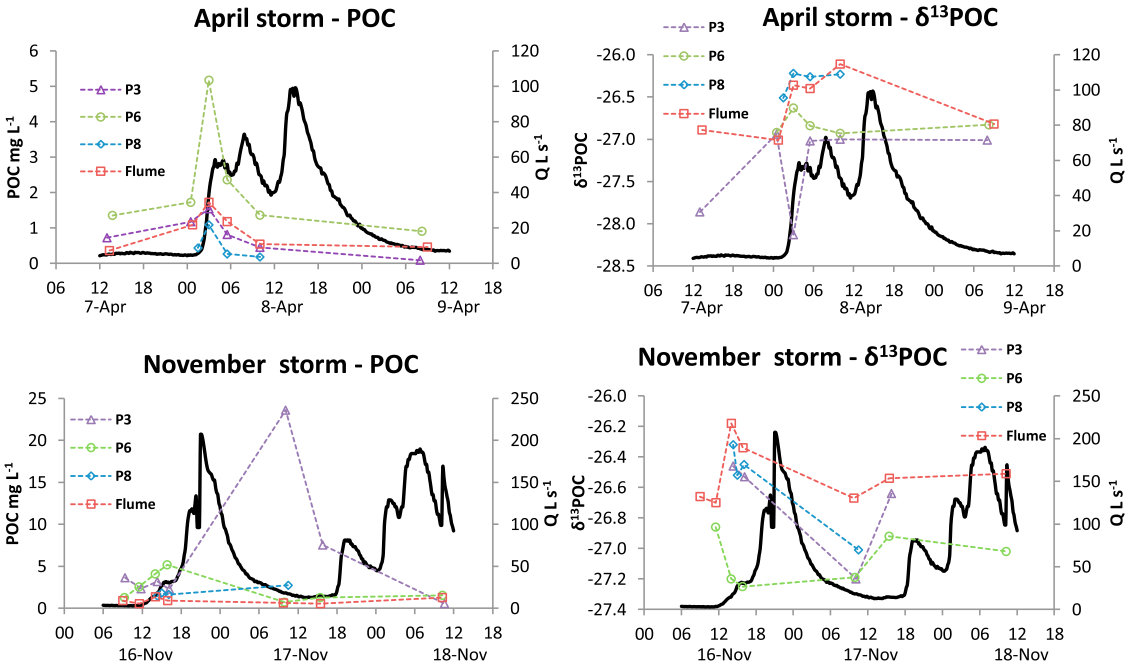

Figure 4. Temporal changes in POC concentration and δ^{13}C-POC for the three pipes (P3, P6, P8) and the CHS flume during the April and November storm events. Flow (solid line) is presented for CHS flume only.

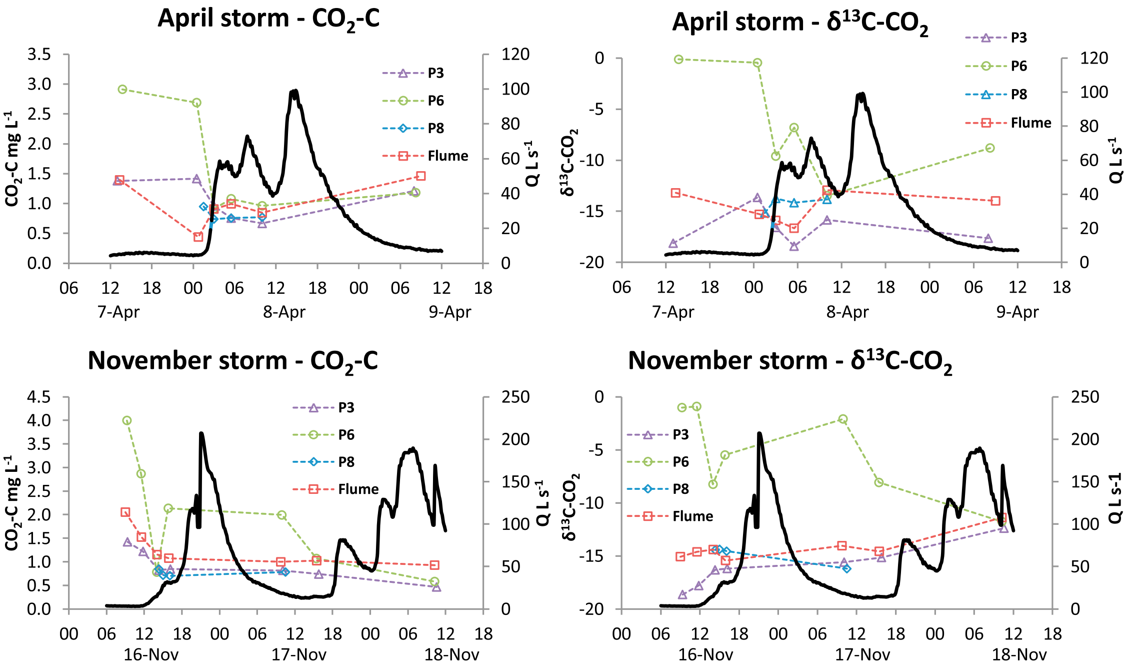

Figure 5. Temporal changes in CO$_2$-C concentration and δ^{13}C-CO$_2$ for the three pipes (P3, P6, P8) and the CHS flume during the April and November storm events. Flow (solid line) is presented for CHS flume only.

We sampled under different hydrological extremes (high and low flows associated with storm events) to explore variability in C sources as flow paths change over short time periods. P3 and P8 were hydrologically more responsive than P6 and, collectively, all three pipes were more responsive to rainfall events than the catchment outlet. While pipe water DOC and POC concentrations were similar across all the sample sites, concentrations were higher than those recorded in the soil solution at the site [*Adamson et al.*, 2001], demonstrating the importance of peatland pipes as conduits for carbon flow. Dissolved gas concentrations were more variable across the sites with P6 in particular enriched in both CO$_2$ and CH$_4$ [see also *Dinsmore et al.*, 2011].

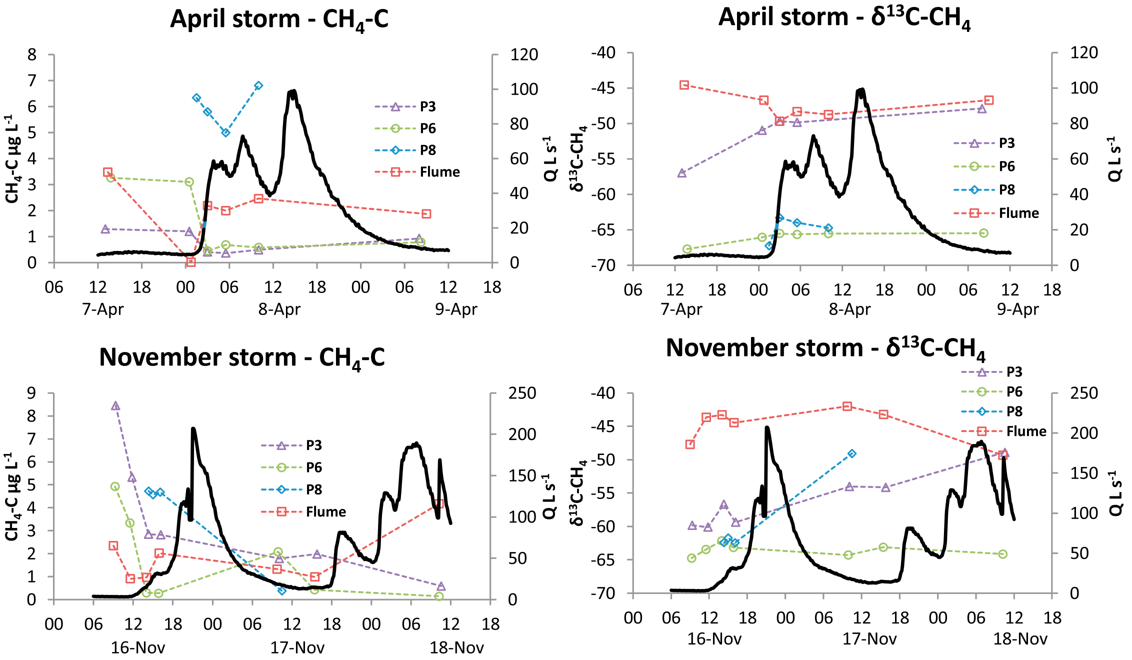

Figure 6. Temporal changes in CH$_4$-C concentration and δ^{13}C-CH$_4$ for the three pipes (P3, P6, P8) and the CHS flume during the April and November storm events. Flow (solid line) is presented for CHS flume only.

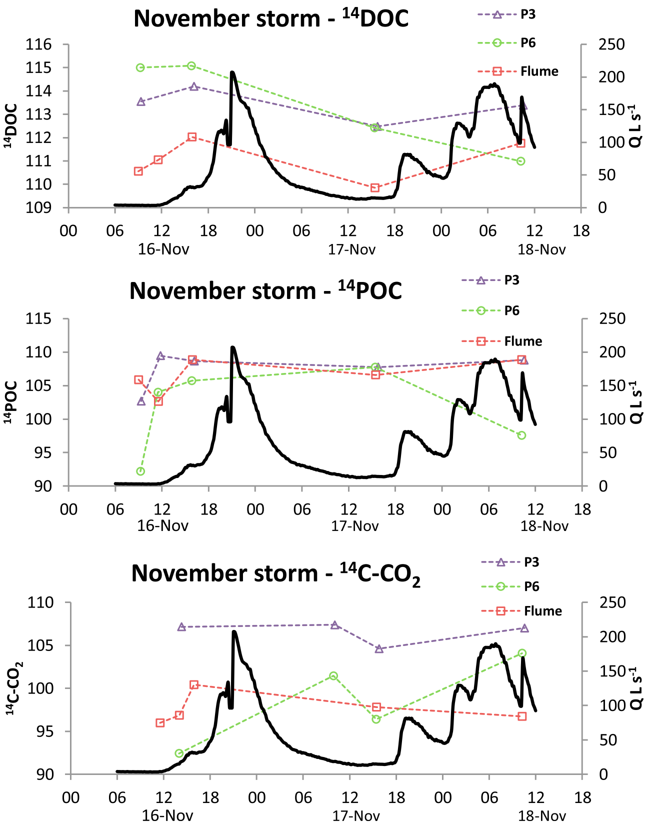

Figure 7. Temporal changes in ^{14}C enrichment (% modern) of DOC, POC and evasion CO_2 for the two pipes (P3, P6) and the CHS flume during the November storm event. Flow (solid line) is presented for CHS flume only.

4.1. Source and Age of DOC and POC

[42] A small but significant difference in δ^{13}C-DOC and δ^{13}C-POC between the pipes and CHS flume showed that water leaving the catchment was more ^{13}C enriched compared to water derived from the two continuously flowing pipes (P3 and P6). Biological processing of organic C in aquatic systems would lead to ^{13}C enrichment of both DOC and POC as it is transported from the pipe system through the drainage network to the catchment outlet. However, water transfer times (which are typically likely to be <2 h) from pipe outlet to CHS flume are unlikely to be sufficient for in-stream processing to account for this difference in δ^{13}C-DOC and δ^{13}C-POC between perennial pipe water and stream water.

[43] We found that POC was consistently enriched in ^{13}C by 1.0‰–1.5‰ compared to DOC. Likewise, *Guo and MacDonald* [2006] found that the δ^{13}C value of size fractionated organic matter in water from the Yukon River changed from −27.9‰ (low molecular weight DOM) to −26.2‰ (high molecular weight particulate organic matter, >0.45 μm). Our DOC and POC data are consistent with a common source (derivation from C3 plants) followed by further transformation and decomposition of soil organic matter. *Guo and MacDonald* [2006] also recognized that the different δ^{13}C values suggested an age difference between the various size fractions, as CO_2 sequestered by vegetation derived from the modern atmosphere (which includes a substantial component of CO_2 derived from combustion of fossil fuels) would have a δ^{13}C signature ~1.5‰ depleted relative to CO_2 sequestered by plants in the preindustrial era. This is consistent with our ^{14}C data for DOC and POC with P6 producing the oldest organic carbon (up to 559 years BP).

[44] The isotopic data therefore showed that, while the sources (implied from δ^{13}C values) of both DOC and POC produced in the CHS catchment were consistent across a range of flow conditions, the age (^{14}C enrichment) of POC varied significantly (Table 3), both being more or less ^{14}C enriched compared to the contemporary atmosphere (^{14}C concentration of atmosphere in 2009 estimated to be ~105% modern, based on *Levin et al.*, 2008). Interestingly, all DOC samples were significantly more enriched in ^{14}C compared to the atmospheric CO_2 in the year of sampling (2009), indicating that a substantial component of the carbon in DOC had been fixed from the atmosphere within the last ~50 years. While acknowledging that we cannot completely exclude the possibility that C fixed pre-bomb contributed to DOC, if we make the simplifying assumption that DOC was derived only from carbon fixed after the AD 1963 bomb-^{14}C peak, then we can estimate "mean" ages for the DOC, based on the recent declining trend in the atmospheric level of ^{14}C [e.g., *Levin et al.*, 2008]. Thus, mean ^{14}C concentrations for DOC from P3 and P6 (~114% modern) suggested a mean age of ~18 years since carbon fixation, clearly older than a mean age of ~13 years for DOC measured at CHS flume (~111% modern).

4.2. Source and Age of CO_2 and CH_4

[45] The δ^{13}C signature of dissolved CO_2 and CH_4 released from the two continuously flowing pipes was distinctly different from the catchment outlet. P6 was characterized by highly ^{13}C enriched CO_2 and highly depleted CH_4, whereas flow from P3 was ^{13}C depleted for both gases compared to stream water. A comparison between δ^{13}C-CO_2 (evasion) with δ^{13}C-CO_2 (dissolved) showed a ~4‰ enrichment in the dissolved phase (Figure 8), demonstrating that preferential loss of the lighter isotope of C occurred across the water-air interface during degassing [see also *Zhang et al.*, 1995; *Doctor et al.*, 2008].

[46] During storms we found that the clearest change in δ^{13}C-CO_2 occurred in P6, with a significant shift toward ^{13}C depletion at higher flows. Isotopic depth profiling in peats generally shows that CO_2 becomes more ^{13}C enriched with increasing depth from ca. −20‰ to ca. +10‰ [*Clymo and Bryant*, 2008, Figure 5]; similar ^{13}C enrichment trends have also been measured by *Aravena et al.* [1993] and *Charman et al.* [1999]. *Steinmann et al.* [2008] found that δ^{13}C-DIC (a surrogate for CO_2) changed from −21.7‰ at 50 cm depth to +8.8‰ at 6 m depth in a peat profile. This suggests that CO_2 in pipe water from P6 changed from a deep to a shallow source during storms. However, this pattern was not observed at other sites; in the April storm there was no change in δ^{13}C-CO_2 in P3, P8 and CHS flume, whereas in the November storm there was a gradual ^{13}C enrichment of CO_2 during the event period at both P3 and CHS flume. Measurements of down profile changes in δ^{13}C-CO_2 made at P3 suggested that CO_2 reaching the pipe outlet (δ^{13}C-CO_2 −20.5‰ to −12.4‰) was derived from up to ~25–30 cm depth. The most ^{13}C depleted (shallowest) CO_2 was released from P3 during the summer (August) event.

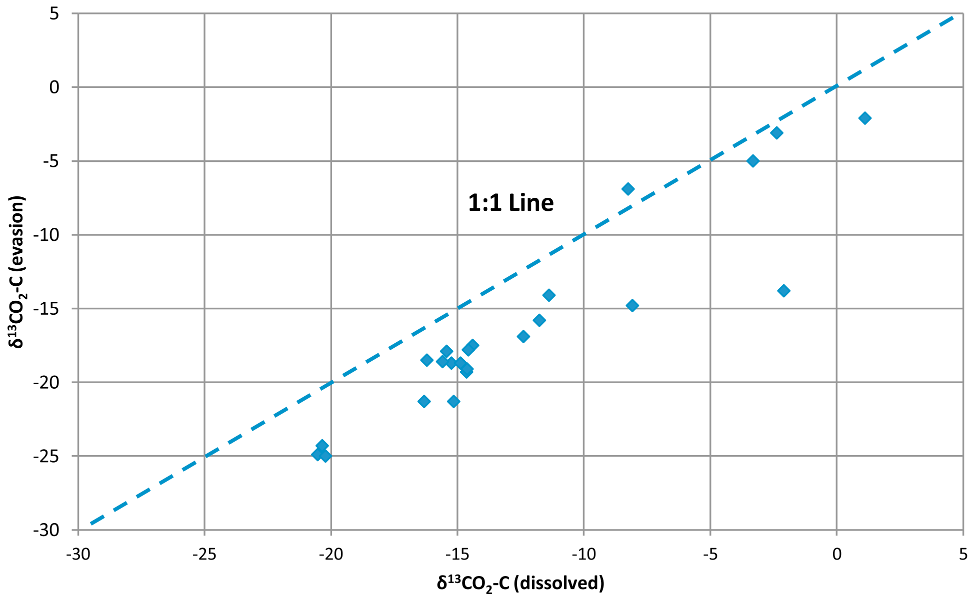

Figure 8. Relationship between the δ^{13}C value of evasion and dissolved CO_2 of samples collected during the August and November storm events.

During the most intense storm (November) we measured progressive ^{13}C enrichment of CO_2 at P3 during the event (a change from –18.6‰ to -12.4‰), suggesting an increasing contribution of CO_2 from deeper within the peat profile. P3 therefore behaved differently from P6, the latter exhibiting progressive ^{13}C depletion during the November event consistent with increasing dominance of near-surface CO_2 sources. *Waldron et al.* [2007], working in a catchment rich in organo-mineral soils and peats, described variations in stream water DIC as a combination of a ^{13}C-depleted (δ^{13}C-DIC ~ -22‰), low-flow end-member and a more ^{13}C-enriched (δ^{13}C-DIC ~ -10‰ to -6‰) high-flow end-member, produced primarily from CO_2 derived from the respiration of C3 vegetation (-28‰) and anaerobic fermentation of peat (-14‰ to $+10$‰). A similar mixing model would explain the changes in the shallow pipe (P3) and the CHS flume, but not the deep pipe (P6).

[47] The range in δ^{13}C-CH_4 values in the CHS catchment is typical of Northern Hemisphere lakes and wetlands (-64‰ to -58‰; *Walter et al.*, 2008) and suggests the dominant source is from acetate fermentation, producing values in the range -65‰ to -50‰ [*Hornibrook et al.*, 1997]. Values of δ^{13}C-CO_2 ranging from +8.6‰ to +9.2‰ have been measured at 4 m depth in Scottish peatlands [*Clymo and Bryant*, 2008; *Garnett and Hardie*, 2009] and it is known that fermentation processes in deep peats can produce highly ^{13}C enriched CO_2. Pathways for methanogenesis (CO_2 reduction or acetate fermentation) in peatlands can be identified by calculating an α_C value, where α_C = (δ^{13}C-CO_2 + 1000)/(δ^{13}C-CH_4 + 1000). Values of 1.03–1.07 from the pipes and outlet of the CHS catchment strongly suggest that acetate fermentation (characterized by α_C values >0.95) is the most important pathway for CH_4 production [*Whiticar et al.*, 1986] at the study site. While *Clymo and Bryant* [2008] and *Garnett et al.* [2011] found relatively little change in α_C with depth, *Steinmann et al.* [2008] and *Hornibrook et al.* [1997] found that the α_C value increased from 1.02 at 5 cm depth to 1.07 at 600 cm depth. We found that P6 had the highest α_C values (1.06–1.07) compared to the other perennial pipe (P3) (1.04–1.05) and the more variable (1.03–1.06) ephemeral pipe (P8). Although we do not know how α_C varies with depth in the CHS catchment, these data may suggest that dissolved gases in P6 were derived from a deep source, P3 from a shallow source and P8 from several sources across a range of depths.

[48] The most depleted δ^{13}C-CH_4 value we measured was -67.7‰ from P6, which is close to the most ^{13}C depleted CH_4 value recorded by *Clymo and Bryant* [2008] in a raised bog in southwest Scotland. The most negative δ^{13}C-CH_4 values were often (but not exclusively) associated with deeper water sources in the pre-storm, low-flow period and support results from CH_4 isotope peat depth profiling at other sites, which showed that δ^{13}C-CH_4 becomes more negative with depth [*Hornibrook et al.*, 1997; *Steinmann et al.*, 2008]. *Clymo and Bryant* [2008], however, found that CH_4 became more ^{13}C enriched at depth. *Waldron et al.* [1999], *Chasar et al.* [2000] and *Hornibrook et al.* [2000] found relatively small or non-existent changes with depth, presumably because of inconsistent and changing hydrological gradients within the profile affecting the reducing environment and the movement of dissolved gases at different depths. This led *Steinmann et al.* [2008] to conclude that isotopic composition could not be used to separate CH_4 bursts in peat bogs originating from near-surface or deep sources.

[49] Although the δ^{13}C values of DOC and POC showed that they are isotopically similar and, like many other studies [e.g., *Billett et al.*, 2007], are derived from decomposition associated with C3 plants, the sources of dissolved and evaded CO_2 and CH_4 were distinctly different (Table 2). Pipe P6 was consistently highly depleted in ^{13}C-CH_4, and had a wide range of ^{13}C-CO_2 enriched values relative to the other pipes and CHS flume (Figure 9). Our stormflow sampling showed that the most ^{13}C-CO_2 depleted samples at P6 occurred at highest flows as water tables rise within the catchment. At this point the ^{13}C-CO_2 signal of P6 became

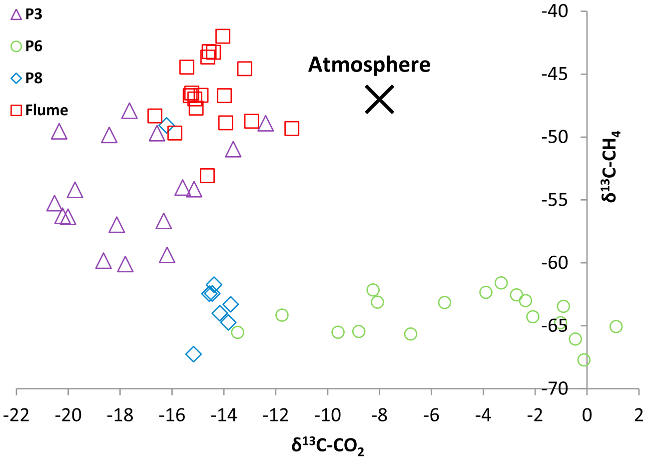

Figure 9. Relationship between the $\delta^{13}C$ isotopic composition of dissolved CO_2 and CH_4 for the three pipes (P3, P6, P8) and the CHS flume during the three storm events.

more like that of the ephemeral pipe (P8) and the CHS flume. The most ^{13}C depleted CO_2 measurements were associated with the shallow perennial pipe (P3), whereas the most ^{13}C enriched CH_4 samples were at the catchment outlet. The contemporary atmosphere in 2009 ($\delta^{13}C\text{-}CO_2$ = ca. −8‰, $\delta^{13}C\text{-}CH_4$ = ca. −47‰) was isotopically distinct from the dissolved gas samples (Figure 9).

[50] The isotopic signature of evaded CO_2 ranged from relatively ^{13}C enriched/^{14}C depleted values associated with P6, to ^{13}C depleted/^{14}C enriched values associated with P3 (Figure 10). We also found a significant relationship between ^{14}C enrichment and $\delta^{13}C$ of evasion CO_2 collected at the pipe outlets ($r^2 = 0.92$, $p < 0.001$). The overall isotopic trend associated with pipe water CO_2 suggested that it was composed of a simple mixture of deep, old groundwater (produced from weathering or anaerobic fermentation) and shallower, young (plant-derived) CO_2 not dissimilar from pipe DOC, with the relative importance of the different sources changing in response to hydrological conditions (Figure 10). Our long-term (18 month) data set showed that pipe water derived from P6 had a higher mean pH and conductivity than P3 and P8, as well as significantly elevated CO_2, CH_4 and N_2O concentrations [*Dinsmore et al.*, 2011]. Because P6 also produced the oldest CO_2 and POC compared to the other two pipes, both the geochemical and isotopic evidence points toward the pipe tapping deep peat carbon even though the pipe is only at 100 cm depth at its outlet in a peat face. The other perennial pipe (P3) and the ephemeral pipe (P8) have all the geochemical and isotopic characteristics of shallow pipes with good connectivity to near surface carbon, even though the latter has the deepest pipe outlet [*Holden et al.*, 2012].

[51] The isotopic values of evasion CO_2 at CHS flume clearly do not lie on the trend line associated with the three pipes (Figure 10), suggesting that an additional (more ^{13}C and/or ^{14}C depleted) source contributes to evasion CO_2-C at CHS flume. Elevated Ca concentrations can occur under extreme low flow conditions at CHS, but during high flows, a geogenic (carbonate-derived) additional CO_2 source is less likely. Additionally, the fact that mean pH and conductivity at CHS flume was similar or lower than the three pipes, also suggests an additional geogenic CO_2 source is unlikely [*Dinsmore et al.*, 2011]. Isotopic fractionation during CO_2 evasion between the pipe outlets and the CHS flume would lead to preferential loss of ^{12}C and ^{13}C enrichment, rather than ^{13}C depletion (Figure 10). We believe the most likely explanation for the presence of more ^{13}C and/or ^{14}C depleted evasion CO_2 at the CHS flume is a contribution from overland flow/atmospheric CO_2, which might be expected to have an isotopic signature of $\delta^{13}C$ = ca. −27‰ and ^{14}C = ca. 105% modern (if derived from atmospheric CO_2 and/or the decomposition of organic matter on/near the peat surface). The fact that the isotopic composition of evasion CO_2 at

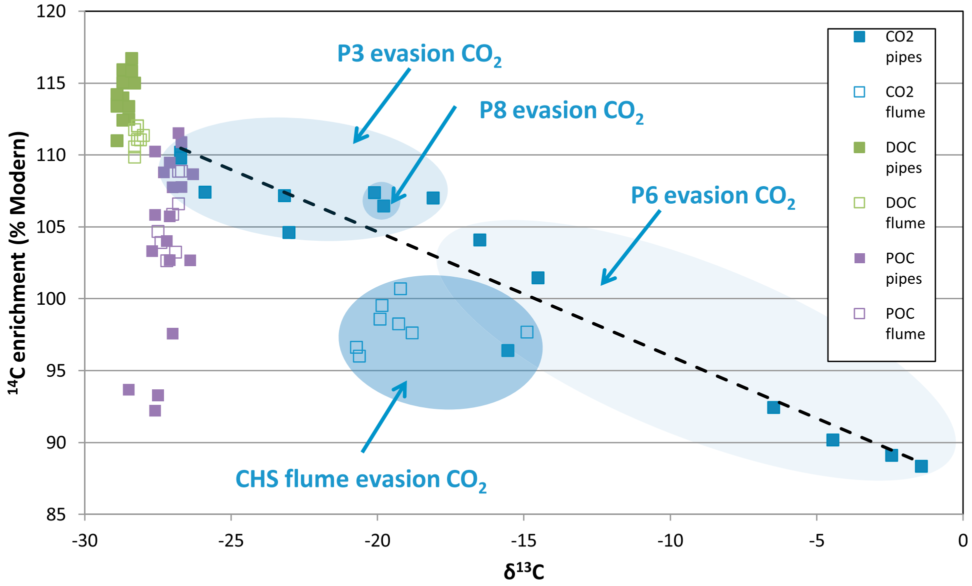

Figure 10. Relationship between ^{14}C enrichment (% modern) and $\delta^{13}C$ of DOC, POC and evaded CO_2-C for the three pipes (P3, P6, P8) and the CHS flume during the August and November storm event. The dashed line shows the relationship for evasion CO_2-C associated with the three pipes.

CHS flume does not vary as much as the pipes, suggests that a relatively small proportion of pipe CO_2 reaches the flume (most is lost by evasion) or is diluted by non-pipe sources, such as overland flow. The isotopic evidence for evasion CO_2 therefore supports the findings of Holden et al. (submitted manuscript, 2012), who made measurements of pipe C fluxes within the study catchment, and estimated that pipe outlets delivered to the surface 22% of the C that leaves the catchment outlet.

5. Conclusions

[52] Isotopic measurements at a peatland site in northern England showed that the age and source of C released from pipes into the drainage network is highly dynamic in space and time. This is particularly true for POC and the dissolved gases (CO_2 and CH_4) and suggests that $\delta^{13}C$ and ^{14}C composition is a sensitive indicator of changes in hydrological pathway in peat systems. We found that individual pipes showed contrasting ^{13}C enrichment trends and clearly tap both shallow (near-surface) and deep sources of CO_2 and CH_4 within the catchment. In contrast, pipes did not receive deep DOC suggesting that, while connectivity exists for the gaseous C phase, it does not exist for the dissolved C phase. We also found that C leaving the catchment was a mixture of pipe and non-pipe sources.

[53] The radiocarbon age data showed that, although all DOC and the majority of POC was modern, evasion CO_2 was more age variable The oldest POC (maximum 652 years BP) and CO_2 (maximum 822 years BP) was produced from pipe P6, which showed all the geochemical and isotopic characteristics of tapping deep peat C. Various studies have recorded significant increases in soil C, CO_2 and DOC age with depth [e.g., *Clymo and Bryant*, 2008]. At the peat surface (pipe outlets) and in the stream we found evidence for old soil C (POC) and CO_2, but not DOC. This finding suggests that the transport pathways in peat that link gaseous, dissolved and particulate C to the surface are different. The observed differences for DOC and POC are less easy to explain, since aged DOC has been routinely measured in deep peats [*Clymo and Bryant*, 2008; *Garnett et al.*, 2011]. Since the isotopic signature is potentially a mixture of different sources we suggest that the amount of young DOC produced primarily from near-surface decomposing peat is so large that it masks the presence of any older deep peat DOC in the pipe system; this effect is not seen for CO_2 because young gaseous C produced close to the peat surface will be lost directly to the atmosphere. Although we did not seek to measure "old" or "new" water, our findings do support the overall conclusion by *Jones* [2004] that the proportions of event and pre-event water vary from storm to storm and pipe to pipe within a single catchment.

[54] Natural pipes therefore play a dynamic (short-term) and changing (long-term) role in peatland C loss. The isotopic evidence presented here shows that pipes produce C derived from both shallow and deep sources in ombrotrophic bogs, supporting earlier suggestions [*Holden and Burt*, 2003b] that the traditional acrotelm-catotelm model for ombrotophic bogs [*Ingram*, 1978], whereby fluxes are mainly considered within an upper, shallow, active acrotelm zone, is inappropriate when considering C transfer from peat to the aquatic system.

Appendix A

[55] Table A1 contains a table showing the $\delta^{13}C$ values of DOC, POC, CO_2 and CH_4 of samples collected from the

Table A1. $\delta^{13}C$ Values of DOC, POC, CO_2 and CH_4 Samples

Site	Date and Time (dd/mm/yr)	$\delta^{13}C$-DOC	$\delta^{13}C$-POC	$\delta^{13}C$-CO_2	$\delta^{13}C$-CH_4
P3	07/04/09 1300	−28.43	−27.86	−18.13	−56.96
P3	08/04/09 0030	−28.15	−26.94	−13.64	−50.96
P3	08/04/09 0300	−28.20	−28.13	−16.58	−49.69
P3	08/04/09 0530	−28.13	−27.02	−18.42	−49.83
P3	08/04/09 1000	−28.36	−27.00	−15.85	ns
P3	09/04/09 0800	−28.40	−27.01	−17.64	−47.9
P6	07/04/09 1345	−27.81	ns[a]	−0.12	−67.71
P6	08/04/09 0030	−28.04	−26.92	−0.45	−66.05
P6	08/04/09 0300	−28.17	−26.63	−9.6	−65.51
P6	08/04/09 0530	−28.18	−26.84	−6.8	−65.65
P6	08/04/09 1000	−28.05	−26.93	−13.47	−65.52
P6	09/04/09 0815	−28.24	−26.83	−8.8	−65.45
P8	08/04/09 0130	−28.05	−26.51	−15.17	−67.25
P8	08/04/09 0300	−28.06	−26.22	−13.74	−63.29
P8	08/04/09 0530	−27.96	−26.26	−14.16	−64
P8	08/04/09 1000	−28.13	−26.23	−13.83	−64.73
CHS	07/04/09 1320	−27.65	−26.89	−13.2	−44.57
CHS	08/04/09 0045	−27.82	−27.01	−15.3	−46.71
CHS	08/04/09 0300	−27.58	−26.36	−15.89	−49.68
CHS	08/04/09 0530	−27.71	−26.40	−16.66	−48.32
CHS	08/04/09 1000	−27.96	−26.11	−12.93	−48.74
CHS	09/04/09 0900	−28.03	−26.82	−13.98	−46.71
P3	19/08/09 1635	ns	ns	−20.35	−49.54
P3	20/08/09 1115	ns	ns	−20.53	−55.25
P3	20/08/09 1330	ns	ns	−20.22	−56.25
P3	20/08/09 1500	−28.34	−27.55	−20.01	−56.33
P3	21/08/09 1030	−28.35	−27.45	−19.74	−54.19
P6	19/08/09 1535	ns	ns	1.12	−65.06
P6	20/08/09 1130	ns	ns	−2.37	−63.00
P6	20/08/09 1340	ns	ns	−3.31	−61.59
P6	20/08/09 1445	−28.27	−27.49	−2.72	−62.54
P6	21/08/09 0945	−28.22	−27.96	−3.90	−62.34
CHS	19/08/09 1610	ns	ns	−14.64	−53.07
CHS	20/08/09 1055	ns	ns	−15.24	−46.50
CHS	20/08/09 1310	ns	ns	−14.88	−46.68
CHS	20/08/09 1450	−27.89	−26.57	−15.12	−46.97
CHS	21/08/09 1045	−28.08	−27.31	−13.93	−48.87
P3	16/11/09 0920	ns	ns	−18.64	−59.82
P3	16/11/09 1150	ns	ns	−17.80	−60.09
P3	16/11/09 1420	−28.29	−26.46	−16.32	−56.66
P3	16/11/09 1610	−28.24	−26.53	−16.19	−59.36
P3	17/11/09 1005	−28.28	−27.20	−15.59	−54.01
P3	17/11/09 1550	−28.57	−26.64	−15.15	−54.14
P3	18/11/09 1035	−28.12	ns	−12.39	−48.90
P6	16/11/09 0915	ns	ns	−1.02	−64.75
P6	16/11/09 1130	−28.26	−26.86	−0.91	−63.45
P6	16/11/09 1400	−28.09	−27.20	−8.25	−62.15
P6	16/11/09 1550	−28.36	−27.25	−5.49	−63.15
P6	17/11/09 0955	−27.99	−27.19	−2.09	−64.28
P6	17/11/09 1525	−28.37	−26.92	−8.08	−63.12
P6	18/11/09 1015	−27.99	−27.02	−11.76	−64.15
P8	16/11/09 1420	−28.18	−26.32	−14.45	−62.43
P8	16/11/09 1500	−28.22	−26.52	−14.38	−61.73
P8	16/11/09 1605	−28.22	−26.45	−14.56	−62.45
P8	17/11/09 1030	−28.18	−27.01	−16.21	−49.07
CHS	16/11/09 0900	−27.84	−26.66	−15.07	−47.70
CHS	16/11/09 1135	−28.00	−26.70	−14.62	−43.64
CHS	16/11/09 1400	−27.77	−26.18	−14.40	−43.26
CHS	16/11/09 1555	−27.93	−26.34	−15.43	−44.44
CHS	17/11/09 0945	ns	−26.67	−14.04	−41.99
CHS	17/11/09 1530	−27.91	−26.54	−14.57	−43.21
CHS	18/11/09 1015	−27.76	−26.51	−11.38	−49.32

[a] The abbreviation "ns" stands for "no sample."

three pipes and the CHS flume and analyzed at the NERC Life Sciences Mass Spectrometry Facility.

Appendix B

[56] Table B1 contains a table showing ^{14}C enrichment, conventional radiocarbon ages and $\delta^{13}C$ values of DOC-C, POC-C and evasion CO_2-C of samples collected from the three pipes and the CHS flume and analyzed at the NERC Radiocarbon Facility. For evasion CO_2 (1) sample times marked the end of the collection period and (2) have not been corrected for the effect of degassing into the free atmosphere. Samples marked with an asterisk had CO_2 volumes lower than recommended when using molecular sieve cartridges (<4 mL); hence these values should be treated with caution.

Table B1. ^{14}C Enrichment, Conventional Radiocarbon Ages and $\delta^{13}C$ Values of DOC-C, POC-C and Evasion CO_2-C of Samples

Sample Type/Site	Date and Time (dd/mm/yr)	Publication Code	^{14}C Enrichment % Modern ± 1σ	Conventional Age (Years BP ± 1σ)	$\delta^{13}C_{VPDB}$‰ +/−0.1
Evasion CO_2 - P3	19/08/09 2000	SUERC-26041*	107.07 (0.49)	modern	−24.3
Evasion CO_2 - P3	20/08/09 0900	SUERC-26042	109.03 (0.51)	modern	−24.9
Evasion CO_2 - P3	20/08/09 1500	SUERC-26043	108.77 (0.51)	modern	−25.0
Evasion CO_2 - P6	19/08/09 1915	SUERC-26044	90.28 (0.43)	822 (38)	−2.1
Evasion CO_2 - P6	20/08/09 1230	SUERC-26045	90.82 (0.41)	774 (36)	−3.1
Evasion CO_2 - P6	20/08/09 1455	SUERC-26048*	91.72 (0.43)	694 (38)	−5.0
Evasion CO_2 - CHS	19/08/09 2000	SUERC-26049	96.55 (0.45)	282 (37)	−19.3
Evasion CO_2 - CHS	20/08/09 1300	SUERC-26050	98.79 (0.45)	98 (37)	−18.7
Evasion CO_2 - CHS	20/08/09 1500	SUERC-26051	99.73 (0.43)	21 (35)	−18.7
DOC-P3	19/08/09 1635	SUERC-26425	115.89 (0.53)	modern	−28.5
DOC-P3	20/08/09 1115	SUERC-26426	115.00 (0.53)	modern	−28.7
DOC-P3	20/08/09 1330	SUERC-26427	115.03 (0.53)	modern	−28.6
DOC-P6	19/08/09 1535	SUERC-26428	113.97 (0.50)	modern	−28.7
DOC-P6	20/08/09 1130	SUERC-26429	116.71 (0.54)	modern	−28.4
DOC-P6	20/08/09 1340	SUERC-26430	115.93 (0.51)	modern	−28.7
DOC-CHS	19/08/09 1610	SUERC-26431	112.01 (0.52)	modern	−28.2
DOC-CHS	20/08/09 1055	SUERC-26432	111.08 (0.51)	modern	−28.2
DOC-CHS	20/08/09 1310	SUERC-26435	111.36 (0.51)	modern	−28.0
POC-P3	19/08/09 1635	SUERC-27450	110.24 (0.51)	modern	−27.6
POC-P3	20/08/09 1115	SUERC-27451	105.83 (0.49)	modern	−27.6
POC-P3	20/08/09 1330	SUERC-27452	103.31 (0.45)	modern	−27.7
POC-P6	19/08/09 1535	SUERC-27453	93.67 (0.43)	526 (37)	−28.5
POC-P6	20/08/09 1130	SUERC-27454	102.67 (0.45)	modern	−26.4
POC-P6	20/08/09 1340	SUERC-27455	93.27 (0.44)	559 (37)	−27.5
POC-CHS	19/08/09 1610	SUERC-27456	104.68 (0.48)	modern	−27.5
POC-CHS	20/08/09 1055	SUERC-27457	103.91 (0.48)	modern	−27.4
POC-CHS	20/08/09 1310	SUERC-27460	103.24 (0.45)	modern	−26.9
Evasion CO_2 - P3	16/11/09 1700	SUERC-28149*	106.40 (0.50)	modern	−21.3
Evasion CO_2 - P3	17/11/09 1030	SUERC-28150	106.67 (0.50)	modern	−18.6
Evasion CO_2 - P3	17/11/09 1700	SUERC-28151*	104.55 (0.47)	modern	−21.3
Evasion CO_2 - P3	18/11/09 1200	SUERC-28152	106.44 (0.50)	modern	−16.9
Evasion CO_2 - P6	16/11/09 1530	SUERC-28160*	94.08 (0.41)	490 (35)	−6.9
Evasion CO_2 - P6	17/11/09 1115	SUERC-28161	101.80 (0.44)	modern	−13.8
Evasion CO_2 - P6	17/11/09 1610	SUERC-28162*	97.48 (0.45)	205 (37)	−14.8
Evasion CO_2 - P6	18/11/09 1045	SUERC-28163*	104.10 (0.45)	modern	−15.8
Evasion CO_2 - P8	17/11/09 1030	SUERC-28166*	105.94 (0.50)	modern	−18.5
Evasion CO_2 - CHS	16/11/09 1200	SUERC-28153	96.62 (0.45)	276 (38)	−19.1
Evasion CO_2 - CHS	16/11/09 1400	SUERC-28156	97.62 (0.46)	193 (38)	−17.5
Evasion CO_2 - CHS	16/11/09 1515	SUERC-28157	100.69 (0.44)	modern	−17.9
Evasion CO_2 - CHS	17/11/09 1700	SUERC-28158	98.25 (0.43)	142 (35)	−17.8
Evasion CO_2 - CHS	18/11/09 1220	SUERC-28159	97.68 (0.43)	188 (35)	−14.1
DOC-P3	16/11/09 0920	SUERC-30529	113.55 (0.52)	modern	−28.9
DOC-P3	16/11/09 1610	SUERC-30530	114.20 (0.50)	modern	−28.9
DOC-P3	17/11/09 1550	SUERC-30531	112.48 (0.49)	modern	−28.5
DOC-P3	18/11/09 1035	SUERC-30534	113.39 (0.50)	modern	−28.9
DOC-P6	16/11/09 0915	SUERC-30540	115.00 (0.50)	modern	−28.3
DOC-P6	16/11/09 1550	SUERC-30541	115.08 (0.50)	modern	−28.7
DOC-P6	17/11/09 1525	SUERC-30544	112.42 (0.49)	modern	−28.7
DOC-P6	18/11/09 1015	SUERC-30545	110.99 (0.51)	modern	−28.9
DOC-P8	16/11/09 1420	SUERC-30546	113.37 (0.52)	modern	−28.5
DOC-P8	16/11/09 1605	SUERC-30547	115.83 (0.53)	modern	−28.4
DOC-CHS	16/11/09 0900	SUERC-30535	110.56 (0.51)	modern	−28.3
DOC-CHS	16/11/09 1135	SUERC-30536	111.05 (0.48)	modern	−28.1
DOC-CHS	16/11/09 1555	SUERC-30537	112.03 (0.52)	modern	−28.2
DOC-CHS	17/11/09 1530	SUERC-30538	109.85 (0.48)	modern	−28.3
DOC-CHS	18/11/09 1015	-SUERC-30539	111.76 (0.51)	modern	−28.3
POC-P3	16/11/09 0920	SUERC-29750	102.68 (0.45)	modern	−27.1
POC-P3	16/11/09 1150	SUERC-29751	109.47 (0.50)	modern	−27.1

Table B1. (continued)

Sample Type/Site	Date and Time (dd/mm/yr)	Publication Code	^{14}C Enrichment % Modern ± 1σ	Conventional Age (Years BP ± 1σ)	$\delta^{13}C_{VPDB}$‰ +/−0.1
POC-P3	16/11/09 1610	SUERC-29752	108.66 (0.50)	modern	−26.3
POC-P3	17/11/09 1550	SUERC-29753	107.77 (0.50)	modern	−26.7
POC-P3	18/11/09 1035	SUERC-29754	108.79 (0.50)	modern	−27.3
POC-P6	16/11/09 0915	SUERC-29762	92.21 (0.40)	652 (35)	−27.6
POC-P6	16/11/09 1130	SUERC-29763	104.01 (0.46)	modern	−27.2
POC-P6	16/11/09 1550	SUERC-29764	105.73 (0.49)	modern	−27.1
POC-P6	17/11/09 1525	SUERC-29765	107.75 (0.50)	modern	−27.0
POC-P6	18/11/09 1015	SUERC-29766	97.57 (0.45)	197 (37)	−27.0
POC-P8	16/11/09 1420	SUERC-29767	110.89 (0.51)	modern	−26.7
POC-P8	16/11/09 1605	SUERC-29770	111.52(0.51)	modern	−26.8
POC-CHS	16/11/09 0900	SUERC-29755	105.87 (0.47)	modern	−27.0
POC-CHS	16/11/09 1135	SUERC-29756	102.64 (0.45)	modern	−27.2
POC-CHS	16/11/09 1555	SUERC-29757	108.86 (0.50)	modern	−26.8
POC-CHS	17/11/09 1530	SUERC-29760	106.6 (0.47)	modern	−26.8
POC-CHS	18/11/09 1015	SUERC-29761	108.87 (0.50)	modern	−26.7

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