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Natural pipes in blanket peatlands: major point sources for the release of carbon to the aquatic system

Running title: "Pipes: major peatland aquatic carbon sources"

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Abstract

Natural soil pipes, which have been widely reported in peatlands, have been shown to contribute significantly to total stream flow. Here, using measurements from eight pipe outlets, we consider the role of natural pipes in the transport of fluvial carbon within a 17.4-ha blanket-peat-covered catchment. Concentrations of dissolved and particulate organic carbon (DOC and POC) from pipe waters varied greatly between pipes and over time, ranging between 5.3 and 180.6 mg L^{-1} for DOC and 0.08 and 220 mg L^{-1} for POC. Pipes were important pathways for peatland fluvial carbon export, with fluxes varying between 0.6 and 67.8 kg yr^{-1} (DOC) and 0.1 and 14.4 kg yr^{-1} (POC) for individual pipes. Pipe DOC flux was equivalent to 20 % of the annual DOC flux from the stream outlet while the POC flux from pipes was equivalent to 56 % of the annual stream POC flux. The proportion of different forms of aquatic carbon to total aquatic carbon flux varied between pipes, with DOC ranging between 80.0 and 91.2 %, POC from 3.6 to 17.1 %, dissolved CO_2-C from 2.4 to 11.1 % and dissolved CH_4-C from 0.004 to 1.3 %. The total flux of dissolved CO_2-C and CH_4-C scaled up to all pipe outlets in the study catchment was estimated to be 89.4 and 3.6 kg yr^{-1} respectively. Overall, pipe outlets produced discharge equivalent to 14 % of the discharge in the stream but delivered an amount of aquatic carbon equivalent to 22 % of the aquatic carbon flux at the catchment outlet. Pipe densities in blanket peatlands are known to increase when peat is affected by drainage or drying. Hence, environmental change in many peatlands may lead to an increase in aquatic carbon fluxes from natural pipes, thereby influencing the peatland carbon balance and downstream ecological processes.

Introduction

It is estimated that around a third of the world's soil carbon is stored in peatlands, equivalent to two thirds of the atmospheric carbon pool (Limpens *et al.*, 2008). Recent research on carbon cycling within peatlands has focussed on relationships between gaseous and aquatic carbon fluxes and water-table position, temperature, plants, and microbes (Billett *et al.*, 2006, Cole *et al.*, 2002, McNeil & Waddington, 2003, Strack *et al.*, 2008, Worrall *et al.*, 2006). There are few data on the role that water movement through peatlands plays in the retention and release of particulate, dissolved, and gaseous forms of carbon. Until recently most of the work examining fluvial carbon exports from peatlands has focussed on concentrations and fluxes of the dominant component – dissolved organic carbon (DOC) – (Andersson & Nyberg, 2008, Billett *et al.*, 2006, Dawson *et al.*, 2002), with less attention given to particulate organic carbon (POC) fluxes (Evans & Warburton, 2007, Pawson *et al.*, 2008) or dissolved gaseous forms of carbon (Billett & Moore, 2008, Dinsmore *et al.*, 2010, Dinsmore *et al.*, 2009). Hence, there is a need to compile full aquatic carbon flux inventories for peatland systems that account for all source waters.

Macropores are known to be common hydrological pathways in peatlands (Baird, 1997, Holden, 2009). Natural soil pipes are large macropores, often many centimetres in diameter and several tens of metres in length, which may form branching networks. Pipes have been reported in most types of peatland around the world (Dittrich, 1952, Egglesmann, 1960, Glaser, 1998, Ingram, 1983, Rapson *et al.*, 2006, Rudolf & Firbas, 1927, Woo & DiCenzo, 1988), and have frequently been reported in blanket peatlands (e.g. Gunn, 2000, Holden, 2006, Holden & Burt, 2002b, Holden *et al.*, 2004, Jones, 1981, Jones *et al.*, 1997, Markov & Khoroshev, 1988, McCaig, 1983, Norrstrom & Jacks, 1996, Price, 1992, Rapson *et al.*, 2006, Thorp & Glanville, 2003).

Little is known about peatland pipe formation and enlargement processes, but it is thought that peatlands are suitable environments for pipe development because of the strong vertical and lateral gradients in hydraulic conductivity within peat and a plentiful water supply (Holden, 2005a, Holden & Burt, 2003a, Rosa & Larocque, 2008). Drying of peat resulting in crack formation during desiccation has previously been suggested as one mechanism for pipe initiation and pipe network expansion (Gilman & Newson, 1980, Jones, 2004) but plentiful rainfall is likely to be required to flow through the cracks to open them up and further erode them. Drainage of peat through open ditch networks has also been found to be associated with enhanced densities of soil pipes (Holden, 2005a, Holden, 2006). Therefore, it may be that environmental change that encourages peat desiccation such as warmer summers with more drought periods may encourage enhanced pipe development in these systems.

Pipes appear to be important sources of water for peatland streams. Maximum discharges of 0.7 to 10 L s^{-1} from single peat pipes have been reported (Chapman, 1994, Gilman & Newson, 1980, Holden & Burt, 2002b, Woo & DiCenzo, 1988). Pipe responses to rainfall tend to be ‘flashy’ (rapid hydrological response), suggesting good connectivity between pipes and surface and near-surface peat layers (Holden & Burt, 2002b; Smart et al., in press). Around 10 % of streamflow was derived from pipe networks in Little Dodgen Pot Sike, a deep blanket peat catchment in the North Pennines of England (Holden & Burt, 2002b), while Smart et al. (in press) found that pipes contributed 13.7 % of the discharge in the nearby Cottage Hill Sike catchment, the focus of the study described below. The relative contribution of pipeflow to stream flow compared to other water sources varies with antecedent conditions (Chapman, 1994, Holden & Burt, 2002b, Jones, 1990), and many pipes cease flowing during dry conditions (ephemeral pipes). At Cottage Hill Sike, the relative contribution of pipeflow to streamflow was found to be greatest at low flows when some of the continuously-flowing (perennial) pipes became relatively more important for maintaining streamflow (Smart et al., in press).

Although headwater peatland streams release significant amounts of DOC and POC (e.g. Billett *et al.* 2010) and are known to be supersaturated in gaseous forms of carbon (Dawson *et al.* 2004; Billett and Moore 2008), we know little about the role of pipes in exporting carbon from peatlands. While some pipe networks form at the interface of soil horizons (Jones, 1994, Jones & Crane, 1984), other networks may occur at a variety of depths within the soil profile (Holden & Burt, 2002b, Holden *et al.*, 2002) and are, therefore, potentially able to receive and convey water and carbon from throughout the peat profile. Pipe connectivity may be of great importance for transferring carbon and other substances in a number of environments such as ombrotrophic peatlands (Holden & Burt, 2003b) which have been thought to be dominated by surface and near-surface water and carbon exchange (Ingram, 1978, Ingram, 1983). Alternatively, pipes in relatively undisturbed peatlands may simply be 'benign' conduits for surface water transfer through the peat mass and there may be little exchange of water and carbon between pipes and the peat mass at depth.

Dinsmore *et al.* (2011) have shown that pipes in the peat at Cottage Hill Sike act as important sources to river water and the atmosphere of CO_2 and CH_4. The variability in concentrations and fluxes of dissolved gases between pipes was large, with mean concentrations in individual pipes ranging from 0.70 to 6.51 mg C L^{-1} of CO_2 and 0.90 to 897 µg C L^{-1} of CH_4. Total dissolved CO_2 and CH_4 fluxes from a subsample of eight pipe outlets were estimated to represent 3% and 38% of downstream export of the respective gases from the stream outlet whilst contributing only 2% of runoff. There was also strong evidence of rapid degassing from pipe waters at their outlets (Dinsmore *et al.*, 2011) suggesting that they act as point sources of greenhouse gas to the atmosphere. It is not known whether the pipes deliver a similar proportion of DOC and POC compared to their water contribution or, as with dissolved gases, whether the relative roles of pipes in transporting organic carbon is more important than their water contribution.

Holden *et al.* (2012) have shown that pipe outlets within the Cottage Hill Sike catchment over a 33-month period varied in size and shape through time. The cross-sectional area of 85 % of pipe outlets changed, 20 % of pipe outlet areas altered by more than 50 cm^2 (equivalent to a median 207 % change in area, including both increases and decreases, for this upper fifth of pipes) and one changed by 312 cm^2 (98 % reduction in size). Although pipe outlets may not be wholly representative of the internal morphology of pipe networks, the evidence of rapid morphological change does suggest that pipes may be important contributors of POC to blanket peatland stream systems. The aim of the work reported herein was to quantify not only the POC flux from the pipes but also to investigate the flux of DOC from pipes. As with the studies of Dinsmore *et al.* (2011), Smart *et al.* (in press) and Billett *et al.* (2012), we focused on the Cottage Hill Sike catchment in the North Pennines, England. We investigated i) the relative contribution of pipe DOC and POC export to total downstream losses, and, by using the dissolved gas flux data presented by Dinsmore *et al*. (2011), ii) the role of pipes in total aquatic carbon loss from the Cottage Hill Sike catchment.

Study Site

Cottage Hill Sike (54°41'N, 2°23'W) is within the Moor House World Biosphere Reserve in northern England (Figure 1). The reserve is located within the North Pennines, with most of the area higher than 450 m above mean sea level (amsl), and characterized by open and exposed plateaux and broad ridges which support moorland and montane habitats with few trees. The Cottage Hill Sike catchment has an altitude ranging from 545 m to 580 m amsl with a sub-arctic oceanic climate (Manley, 1936, Manley, 1942). The mean annual temperature between 1931 and 2006 at the Moor House weather station, located at 556 m amsl, 620 m southeast of the Cottage Hill Sike catchment outlet, was 5.3^{o}C. Between 1991 and 2006 the mean annual temperature was 5.8^{o}C (Holden & Rose, 2011). Mean annual precipitation was 2012 mm (records from 1951-1980 and 1991-2006). Precipitation is only slightly seasonal, with 57 % occurring in the winter-half year from October to March. A typical winter season will see several snowfall and melt events.

A high resolution topographic survey using real time kinematic GPS ground survey (with a horizontal precision of +/-1 cm and a vertical precision of +/-3 cm) was conducted on the catchment. This GPS survey focussed on the areas adjacent to the catchment perimeter where the location of the catchment divide was most uncertain. Using this technique the catchment area was found to be 17.4 ha which was lower than the previous estimate of 20 ha which is quoted in earlier papers for the catchment (e.g., Clark *et al.,* 2007). Figure 1 shows the catchment boundary determined by ground survey.

Blanket peat covers 98 % of the Cottage Hill Sike catchment (Adamson *et al.*, 1998, Miller *et al.*, 2001) up to thicknesses of 8 m, although typical peat depth is 3 to 4 m. Radiocarbon dating of basal peat in the catchment puts the age of initiation of peat formation at around 6500 year BP (Billett *et al.*, 2012). The peat within the catchment has not been drained with ditches or managed by burning (the latter being common in many upland UK peatlands). There has been a recent increase in *Sphagnum* cover in this area as the North Pennines recovers from the effects of historic atmospheric pollution (Evans & Warburton, 2007). The North Pennines experienced enhanced peatland erosion from the 1960s to the 1980s through water-driven gully development and wind erosion on flat hill tops, but damage was not as serious as in the English South Pennines which are closer to sources of industrial air pollution (implicated in the erosion – Evans & Warburton, 2007) and where erosion has been severe in many places. Cottage Hill Sike is a relatively uneroded catchment, although there may have been some stream headward incision and enhanced bank erosion on some of the tributaries between the 1960s and 1980s.

The underlying geology of Cottage Hill Sike is Carboniferous in age, with alternating strata of limestone, sandstone and shale, with intrusions of the Whin Sill dolerite. A poorly-drained overlying clay-rich fluvioglacial till led to the development of blanket peat (Johnson & Dunham, 1963). Slopes tend to be gentle, with 80 % of the catchment having slopes between 0 and 5^{o} (Grayson & Holden, 2012).

Vegetation cover within Cottage Hill Sike is most commonly *Calluna vulgaris* (L.) Hull., *Eriophorum vaginatum* L. with some *Empertrum nigrum* L. and *Sphagnum capillifolium* (Ehrh.) Hedw.. Water-table measurements on a uniform slope in the catchment show that the water table is within 5 cm of the surface for 83 % of the time and rarely falls to depths greater than 20 cm (Evans et al., 1999). The peat is acidic, with a pore-water pH of 3.6 to 4.3 (Adamson *et al*., 2001). The mean pH for Cottage Hill Sike streamwater was 4.34 between 1993 and 2007 (Tipping *et al*., 2010), with 4.01 and 4.75 being the 5^{th} and 95^{th} percentiles. Low pH, associated with a low mean Ca concentration of 1.1 mg L^{-1} (Tipping *et al*. 2010), suggests that there is little groundwater contribution from the mineral matter underlying the peat. Estimates of the annual DOC flux from Cottage Hill Sike for 1993 to 2007 range from 14.3 g C m^{-2} yr^{-1} (1995) to 32.7 g C m^{-2} yr^{-1} (2006) with an overall mean of 23.4 g C m^{-2} yr^{-1} (Billett *et al*., 2010). These values were based on weekly sampling, but may be underestimates because most DOC is likely to be transported during storms, which requires more intensive sampling (Clark *et al.*, 2007).

Materials and methods

A detailed catchment survey to locate and measure pipe outlets occurred on three occasions between August 2007 and April 2010 as described in Holden *et al*. (2012). Additionally, each pipe outlet was visited 12 further times during storms and dry periods between 2007 and 2010 to determine whether pipe discharge was continuous or ephemeral. A mean of 84 pipe outlets was identified across the catchment, with a mean of 24 pipes continuously-flowing and a mean of 60 ephemerally-flowing. The distinction between continuous and ephemeral pipes is partly qualitative, because, during the very driest conditions, flow from many of the continuously-flowing pipes was very low. Eight of the pipes (P1-P8; Figure 1) were chosen to provide a selection of typical pipes within the catchment as a whole (based on size of outlet, depth of pipe outlet relative to the peat surface and flow conditions) for continuous gauging. Pipe nomenclature is consistent with Dinsmore *et al.* (2011), Smart *et al.* (in press) and Billett *et al.* (2012). The outlets of these pipes ranged from 1 cm to 30 cm in diameter (Table 1). Further details on pipe geomorphology for all of the pipes in Cottage Hill Sike are given in Holden *et al*. (2012). The mean diameter of the pipe outlets in the catchment was 9.8 cm (standard error = 0.7 cm) ranging from 0.8 to 45 cm in diameter, the latter being the only case of a pipe outlet with a diameter larger than 30 cm. Flow from the pipes was gauged either using calibrated V-notch weirs and pressure transducers, or tipping bucket flow gauges, the latter for pipes where flows were thought to be lower (Holden & Burt, 2002b). Pipe discharge was monitored from December 2007 to December 2009.

Samples of pipe water were collected from each of the pipe outlets every two weeks except from those pipes that were not flowing at the time of sampling. Because blanket peatland streams have very flashy hydrological regimes, most two-weekly visits would coincide with low flow periods (Clark *et al.*, 2007). Therefore, five of the pipes (P2, P3, P6, P7 and P8) were randomly chosen to be fitted with ISCO 6712C auto-samplers. These operated during storm events, and collected water samples from the pipe outlets at 15-60 minute intervals. For an eight-week period from 24 April 2008 the auto-sampler at P6 collected samples at 24-hour intervals.

Flow at the catchment outlet (Figure 1) was gauged using a glass-fiber reinforced plastic flume, and weekly water samples from the flume were collected by staff from the UK's Environmental Change Network (ECN) who operate a soil sampling plot within the catchment (Figure 1). Additional stream water samples were collected during storms using an ISCO 6712C auto-sampler.

All water samples were analysed for DOC, after filtering to 0.45 µm, using a Thermalox Total Carbon (TC) analyser, which has a precision of ± 0.1 mg C L^{-1} and a lower detection limit of 1.0 mg C L^{-1}. Prior to analysis, samples were acidified and sparged with oxygen in order to stabilise the sample and to remove any inorganic carbon. The acidified samples were then run through the TC analyser in duplicate (or triplicate if the coefficient of variation was > 1%), with the DOC concentration determined by a seven-point calibration curve created using the standard DOC calibration compound, potassium hydrogen phthalate (KHP). Regular analysis of KHP standards and use of a certified reference material, VKI QC WW4A, also minimised error. Samples were stored at 4^{o}C for between 24 hrs and 1 week prior to analysis.

POC was derived via loss on ignition of filtrates from 500 mL water samples. Samples were filtered through pre-ashed (500 ^{o}C), pre-weighed 0.7µm Whatman GF/F glass micro-fibre filters using suction filtration equipment. The filtrate was dried at 105 ^{o}C for 24 hours, weighed, and then ignited at 375 ^{o}C for 16 hours in a muffle furnace and re-weighed (Dawson *et al.,* 2002). POC was then calculated using a regression equation for non-calcareous soils (Ball, 1964).

During the early stages of the monitoring programme, very high and/or very low pipe flows were not captured by some of the flow gauges. Subsequent adjustments to the instrumentation had to be made to ensure that the full range of pipe flows was recorded. During the latter stages of monitoring, some equipment failure occurred due to frost/ice damage. Hence, the flow records for different pipes are of different lengths (Table 1). However, the pipe-flow record is complete for all pipes (except P1 – see below) for the 12-month period starting on 24 April 2008. In order to avoid any seasonal bias we largely focus on the results for this 12-month period, and summary results for April 2008-9 are provided in Table 1. However, because previous results for annual fluxes from Cottage Hill Sike have been reported on a calendar-year basis (Billett *et al.*, 2010), we also present some of the summary results for calendar years where appropriate. Results from the full monitoring period for each pipe are also presented in Table 1. The logger for P1 frequently broke and only 54 % of its discharge record is complete. However, because the logger breakage occurred randomly across the discharge range (based on examination of rainfall and discharge at the stream and from other pipes), we were able to use its discharge record to produce an annual DOC and POC flux for the pipe.

Routine samples collected every two weeks in combination with storm samples were used to derive fluxes of carbon. Total and annual fluxes of DOC and POC for each pipe and for the stream were calculated using the following equation (Verhoff *et al.*, 1980, Walling & Webb, 1985):

$$\text{Flux} = \frac{K.\sum_{i=1}^{n}(Q_i.C_i)}{\sum_{i=1}^{n}Q_i}.Q_r$$

[equation 1]

where K is a conversion factor to scale units to annual catchment values, 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. Dinsmore *et al*. (2011) used equation 1 to calculate CO_2 and CH_4 fluxes from the pipes. These data were combined with data on DOC and POC fluxes to produce the overall aquatic carbon export for each of the monitored pipes.

Upscaling from the monitored pipes to the 84 pipe outlets identified in the catchment was done separately for ephemeral pipes and continuously-flowing pipes using the two mean flux values which were multiplied across the number of ephemerally-(60) or continuously- (24) flowing pipes to estimate the overall contribution that pipes make to the stream carbon flux. Volume-weighted mean concentrations of POC and DOC were calculated by summing the concentration × discharge products for each sampling occasion and dividing them by the sum of the discharge values recorded during the sampling period.

Following the method of Jones (1997), Smart *et al.* (in press) calculated an approximate 'maximum dynamic contributing area' for each of the study pipes by using data from over 100 storms. Because pipes do not have clear topographic catchment areas, Jones (1997) advocated using storm discharge and rainfall data and assuming a runoff coefficient of 1 to derive the maximum dynamic contributing area. The maximum calculated area for each pipe during the study was determined and was then used to estimate approximate area-weighted aquatic carbon fluxes for each pipe.

Results

Meteorological conditions

For the 12 months from 24 April 2008 precipitation at Cottage Hill Sike was 2105 mm, some 5 % higher than the long-term average. Stream runoff was 1758 mm (rainfall to runoff ratio of 83%). The maximum hourly rainfall intensity for the 12 months from 24 April 2008 was 11.6 mm on 1 August, with peak stream discharge recorded during a snowmelt event in February 2009. As noted above, previous studies have examined DOC and POC fluxes for Cottage Hill Sike on a calendar-year basis. Additionally, pipe water samples were collected through to December 2009 to support annual flux calculations and to examine storm response behaviour. Therefore, it is also useful to report climate conditions for the 2008 and 2009 calendar years. A total of 2616 mm fell on the catchment in 2008 with a mean annual temperature of 5.5^{o}C, slightly lower than the 1991-2006 average (Holden & Rose, 2011). In 2009 the catchment received 2173 mm of precipitation, with a peak hourly intensity of 18 mm on 1 July and a mean annual temperature of 5.6^{o}C.

DOC and POC concentrations

Over the period December 2007 to December 2009 the concentration of DOC in pipe water collected during storm sampling and regular fortnightly sampling ranged from 5.3 to 180.6 mg L^{-1}, while for POC the range was very similar at 0.08 to 220 mg L^{-1}. The range of concentrations for the stream was 5.3 to 89.9 mg L^{-1} for DOC and 0.1 to 25.5 mg L^{-1} for POC. These data show that, while the maximum stream-water DOC concentration was around half that observed in pipe water, the maximum stream-water POC concentration was eight times lower than that observed in pipe water samples suggesting that pipe-stream transfer of carbon is more effective for DOC than for POC.

Using Spearman's Rank correlation there were no significant associations between discharge and DOC or POC concentrations or between POC and DOC concentrations for any of the sampling points including the stream (all $p > 0.05$). Water samples were separated into two groups: those taken when discharge was above mean flow and those taken when discharge was below mean flow. We found that median DOC concentrations were greater for all pipes when discharge was above mean flow (Figure 2). Volume-weighted mean DOC concentrations were also greater for all pipes for discharges above the mean when compared to discharges below the mean (Figure 2, open circles). For POC, the median concentrations in pipe waters were significantly greater at high flows compared to low flows in all but two cases. Volume-weighted mean POC concentration was greater at high flow for four pipes (P4, P5, P6, P8) than when discharge was below the mean value (Figure 2).

Concentrations of DOC and POC were highest from pipe P8 (Figure 2). Pooling data from the ephemeral and perennial pipes showed that mean DOC concentrations were similar between the two pipe types (30.5 and 27.9 mg L^{-1} respectively, with standard errors of 0.6 and 0.4 mg L^{-1}). However, the mean POC concentration of the ephemeral pipe water was more than twice that of the perennial pipes (5.4 and 2.2 mg L^{-1} respectively, with standard errors of 0.6 and 0.1 mg L^{-1}).

The interquartile range of DOC concentration was larger for six of the eight pipes compared to the stream. DOC concentrations in pipe water fluctuated widely during storms (Figures 3 and 4), and apparent exhaustion of DOC supply was rarely evident. Temporal variability in pipe water DOC concentrations was also present during low-flow periods. For example, in P6, DOC concentrations changed from 25 mg L^{-1} to 87 mg L^{-1} and then to 45 mg L^{-1} on three consecutive days during low flow in late May 2008 (Figure 5).

Pipe-water POC concentrations most commonly peaked on the rising limb of storm hydrographs (Figure 4). However, for P6 (Figure 5), there was evidence of episodic pulses of relatively high concentrations of POC that were not coincident with changes in pipe-water discharge. The interquartile range for mean POC concentration was larger for seven of the eight pipes (i.e., not P3) than for the stream. Examination of the daily time-series for P6 (Figure 5) shows that POC concentrations tended to be low during or immediately after high flow events (e.g., 24 and 25 April 2008). Because P6 maintained its water discharge between rainfall events (often accounting for as much as 1 to 2 % of total stream discharge during baseflow periods, Smart *et al.* in press) it provided a regular supply of POC to the stream during baseflow.

Aquatic carbon fluxes

Using equation 1 and the two-weekly stream water data, we estimated the total DOC and POC flux for Cottage Hill Sike in calendar year 2008 (enabling comparisons to be made with other calendar years for the site) to be 36.5 and 2.4 g C m^{-2} yr^{-1}, respectively. In 2009, which was a drier year, the values were 29.7 and 1.9 g m^{-2} yr^{-1}, respectively. However, these values were much lower than the fluxes determined when values of DOC and POC from storm events were also included in the analysis. Combining the regular and storm water samples, DOC and POC fluxes for the stream were 63.4 g m^{-2} yr^{-1} DOC and 3.0 g m^{-2} yr^{-1} POC (2008) and 51.5 g m^{-2} yr^{-1} DOC and 2.4 g m^{-2} yr^{-1} POC (2009).

The DOC and POC fluxes were highly variable between pipes (Table 1). DOC fluxes varied by more than a factor of 100, and POC fluxes by more than a factor of 140. For the 12 months from 24 April 2008, the total DOC yield from individual pipes ranged from 0.6 kg to 67.8 kg, while the POC flux varied from 0.1 kg to 14.4 kg. The total DOC flux from the eight monitored pipes was equivalent to 2.1 % of the DOC flux from the catchment outlet. These results suggest that, when scaled to the 84 pipe outlets across the Cottage Hill Sike catchment, the pipes could be responsible for an estimated 20 % of DOC leaving the catchment via the stream, provided there is no storage of DOC in the stream bed and banks or loss to the atmosphere. The total POC flux from the monitored pipes alone was equivalent to 5.2 % of the POC leaving the catchment in the stream. The POC flux from all pipes in the catchment was estimated to be equivalent to 56 % of that leaving the catchment in stream flow.

Table 1 includes dissolved gas fluxes for the pipes based on data collected by Dinsmore *et al.* (2011) but recalculated for the 12 months from 24 April 2008. The aquatic carbon fluxes from the pipes are dominated by DOC, which represents 84.7 % of the total carbon flux. However, DOC is even more important within the stream, representing 92.5 % of the total downstream aquatic carbon flux. The relative importance of different forms of aquatic carbon to the total flux from individual pipes varied from 80.0 to 91.2 % (DOC), 3.6 to 17.1 % (POC), 2.4 to 11.1 % (dissolved CO_2-C) and 0.004 to 1.3 % (dissolved CH_4-C). The flux values for gaseous forms of carbon do not, however, include the evasion flux from the water surface to the atmosphere, which is known to be significant from individual pipes (Dinsmore *et al.*, 2011). Overall, pipes in Cottage Hill Sike were estimated to provide about 22 % of the aquatic downstream carbon flux that is eventually lost from the catchment at the stream outlet.

The maximum dynamic contributing area was estimated for each pipe by Smart et al. (in press). These estimates enable an approximation of the area-weighted carbon flux from each pipe outlet. The values for pipes P1 to P8 were 7, 12, 12, 8, 9, 12, 19 and 26 g C m^{-2} yr^{-1} respectively. All of the pipes therefore have lower area-weighted aquatic carbon fluxes than the stream (57 g C m^{-2} yr^{-1}) for the 12 months from 24 April 2008 although, because the pipe area-weighted fluxes are based on maximum dynamic contributing area, they represent minimum area weighted fluxes.

Discussion

The concentration of DOC from pipe outlets varied widely during storm events (see also Chapman 1994), fluctuating through time even when discharge was falling steadily (e.g. Figure 4). However, a general dilution effect was observed during higher flow periods indicative of source limitation or dilution by rainwater and/or overland flow. Even between storms, DOC concentrations were highly variable in individual pipes (Figure 5). Clark *et al.* (2008) measured DOC concentrations from pore waters in the upper 50 cm of the peat profile within the study catchment at daily intervals during October 2002, and found little daily variability at any measured depth for periods between storms. Our observation of more dynamic DOC concentrations in pipe water may suggest that there are frequent changes to source waters for pipes and that the pipes do not obtain their source waters from one depth alone within the peat. The carbon source may change through time as discharge varies and as preferential flow networks connect to or disconnect from the pipe. Interestingly, this suggestion is not supported by isotopic ($\delta^{13}C$ and ^{14}C) analysis of DOC from the pipe system at Cottage Hill Sike, which shows that both the source and age of DOC is relatively consistent between pipes and changes little during individual storm events (Billett *et* *al*. 2012). Therefore, alternative mechanisms may be responsible for the wide fluctuations in DOC from pipe waters which may be related to variability in production as well as transport. It may be possible that for the same depth, different sources of DOC or parts of the upper peat are being accessed (e.g., sedge root exudates, decomposition products from *Sphagnum*, decomposition products from *Calluna*). This idea is consistent with the isotopic data because these sources would be of similar isotopic ages. Such mechanisms require further investigation.

Despite the flashy response of pipe outlets to rainfall, Smart et al. (in press) found that pipes tended to have more subdued hydrograph recessions than the stream, demonstrating that more prolonged drainage into pipe systems from the surrounding peat was common. P3 had the narrowest range of DOC and POC concentrations during high flow events (Figure 2) suggesting good connectivity between the pipe and water sources near or at the peat surface. However, at low flows the variability in DOC and POC concentrations in P3 was similar to that of other pipes. Indeed, the estimated area-weighted aquatic carbon flux for P3 was similar to that for the other monitored pipes.

The fluctuations in pipe DOC concentrations during storms may be explained by pipe networks containing many small U-shaped bends or “sumps” (Holden, 2004). Some of the sumps within the pipe network may contain water, which over longer low-flow periods has attained high concentrations of DOC produced by oxidation of pipe wall material or from drainage water percolating from the surrounding peat. As the pipe network becomes hydrologically-connected during the storm event different parts of the network may contribute more or less DOC to runoff. It may also be that there are different water sources contributing to the pipe flows at different points in time. However, it should be noted that Billett *et al.* (2012) found that most DOC produced by peat pipes within the catchment was isotopically modern, and further work is required to explain the temporal variability in DOC produced by pipe outlets.

Stream fluxes of DOC at Cottage Hill Sike estimated in our study for 2008 (63.4 g C m^{-2} yr^{-1}) and 2009 (51.5 g C m^{-2} yr^{-1}) were larger than those previously reported for the site for any year since the start of the long-term record in 1993 (Billett *et al.*, 2010, Clark *et al.*, 2007). There are three possible reasons for these larger flux values. First, the earlier (lower) flux values were based on a slightly larger catchment area for Cottage Hill Sike (20 ha) compared to our more accurate value of 17.4 ha based on the GPS survey. Correcting for catchment size increases the earlier published values by 13 %. However, that alone still places 2008 and 2009 as the two highest flux years in the record. Secondly, in combination, 2008 and 2009 produced the wettest two-year period in the long-term DOC flux record. Rainfall exerts a dominant control on DOC fluxes within the catchment (Clark *et al.*, 2007). Thirdly, and most importantly, the use of auto-samplers allowed high flow events to be routinely sampled. Incorporating high-flow measurements resulted in the estimated annual flux of DOC and POC from Cottage Hill Sike increasing by 73 % and 26 %, respectively, compared to the use of weekly routine samples alone. Our results strongly suggest that reliance on weekly or fortnightly sampling results in a major underestimate of DOC and POC flux from blanket peatlands. The published DOC flux estimates from Cottage Hill Sike of 14 to 33 g C m^{-2} yr^{-1} have previously been thought of as normal for peatlands (Billett *et al.*, 2004). It may be that storm sampling across a wider range of peatlands will result in consistently higher flux estimates. If we did not use the revised catchment area and did not include storm samples in our flux calculation, then DOC fluxes for 2008 and 2009 would be 31.8 and 27.7 g C m^{-2} yr^{-1} which is within the range of values previously reported for the catchment. It should also be noted that, because we did not have auto-samplers installed on P1, P4 and P5, it is also very likely that the DOC and POC fluxes for these pipes are underestimates.

At 3.0 and 2.4 g C m^{-2} yr^{-1}, the POC flux from the stream at Cottage Hill Sike was not especially high, and is fairly typical of relatively undisturbed peatlands (e.g. Dinsmore *et al.*, 2010), but is lower than actively-eroding systems (Pawson *et al.*, 2008). The relative contribution of DOC and POC to total peatland aquatic carbon flux appears to be similar to estimates for other sites (Dawson *et al.*, 2002, Hope *et al.*, 1997). However, it should be recognised that, because our study included storm sampling, the results may not be strictly comparable to many earlier studies which excluded storm sampling. POC concentrations in the ephemeral pipes were more than twice those of the perennial pipes (5.4 and 2.2 mg L^{-1} respectively) indicating that, during dry periods, POC builds up and is released during storms, or that these pipes erode more during the storms themselves. POC build up does not appear to occur in continuously-flowing pipes. Nevertheless, at low flows some continuously-flowing pipes provided a regular supply of POC and at higher concentrations than found in the stream. It is also important to note that the relative contribution of pipe-water discharge to streamflow was greatest at low flows in the catchment (Smart *et al.,* in press). POC delivery to streams in peatlands has traditionally been thought to occur only via overland flow, stream erosion or deposition from wind-blown sources (Crisp & Robson, 1979). We have, through direct measurement, shown that pipes are an additional source of POC that may be important under both high and low flow conditions. The discharge of POC at pipe outlets was equivalent to a large proportion of the POC being lost by the stream. However, it is likely that some of the sediment leaving pipes does not initially reach the stream but is deposited close to the pipe outlet. This sediment-trapping results in the familiar sediment yield problem (Walling, 1983) whereby deposition and reworking of sediment means that the volume of sediment transported towards river banks at any given time may not equal the volume of sediment being removed by the river. POC discharged from a pipe outlet may be subject to more rapid oxidation and decomposition than if it had remained within the peat itself, although this will depend on the nature (recalcitrance or quality) of the POC. The fluxes of POC from the pipe outlets also suggest that these systems are not benign and that active erosion is taking place within the peat mass. This hypothesis is supported by observations of changes in pipe outlet morphology in the study catchment over time (Holden *et al.*, 2012).

P8 produced the largest annual carbon flux of any of the pipes. Its large carbon yield is despite it being an ephemeral pipe. P3 was a continuously-flowing pipe and provided an aquatic carbon flux very similar to that of P8. Thus, despite having different flow regimes, these two pipes were both potentially important point sources of aquatic carbon. P3 and P6 also produced significant quantities of dissolved gaseous carbon. However, there was no association between dissolved gas concentration and DOC or POC concentration (data not shown), nor any association between DOC and POC concentration within pipe waters. The lack of associations between DOC, POC and dissolved gas concentrations suggests the sources for each form of carbon delivered by these pipes were different. This difference in source was confirmed by $\delta^{13}C$ and ^{14}C analysis which showed that sources of dissolved gases (CO_2 and CH_4)

were more variable than DOC and POC both between pipes and within pipes (Billett *et al.*, 2012). Natural pipes in the Cottage Hill Sike catchment released CO_2 and POC of a range of ages (modern – 996 year BP), whereas DOC was consistently modern in age. This suggests that carbon transport and delivery through peatland pipe networks to the surface is highly dynamic and differs for individual carbon species.

At a catchment scale we estimated that pipe outlets produced a water discharge equivalent to 14 % of the discharge in the stream system (Smart *et al.*, in press). If pipes acted as a benign pathway for carbon, in that they are not different to other features in the catchment in terms of erosion, peat decomposition and so on, we would expect them to produce an equivalent of around 14 % of the aquatic carbon that is exported by the stream system. However, the pipes produced aquatic carbon equivalent to 22 % of that which leaves the catchment outlet as well as an unknown amount of gaseous carbon which is lost to the atmosphere by evasion (Dinsmore *et al.* 2011). In addition, the high yields of POC from pipe outlets point to active erosion on pipe walls or adjacent macropores demonstrating that pipes are not benign features of peatlands.

One further area for investigation is the composition of pipe-exported POC and DOC which may be different from that derived from other flowpaths. Some types of peat-derived carbon may be more recalcitrant than others and therefore contribute differently to greenhouse gas budgets via downstream processing. We have shown that pipes act as dynamic sources of carbon in blanket peatlands, rather than as benign conduits, and recommend further study on the effect of pipes on carbon dynamics in a range of peatlands.

Pipes are natural features of peatlands and have been observed in the palaeo record (Thorp & Glanville, 2003). However, management activities, such as drainage of blanket peatlands, and climatic influences such as drought, can enhance pipe development (Holden, 2005a, Holden, 2005c, Holden & Burt, 2002a). Here we have shown that pipes represent important pathways for catchment losses of aquatic carbon. Therefore, any management or climatic 'stress' that increases pipe density is also likely to affect aquatic carbon losses and the catchment greenhouse gas balance.

This study has provided the first comprehensive set of observations on the role of natural pipes in the transport of carbon in peatlands. At the 17.4-ha blanket peatland study site in the North Pennines of England, pipes were found to be important components of the peatland carbon system. It is estimated that pipes transport organic carbon (DOC and POC) equivalent to 20 % of that exported by the stream. Including gaseous inorganic species, pipes contributed 22 % of the total carbon exported by the stream. The two-layered acrotelm-catotelm model of peatlands (Ingram, 1978, Ivanov, 1981) is often used by peatland scientists to describe hydrological and ecological conditions within peatlands. However, many of the pipes we studied were deep within the peat and their role in preferentially exporting water and carbon further highlights the inadequacy of the acrotelm-catotelm concept to describe the hydrological functioning of peatlands (Holden, 2005b, Morris *et al.*, 2011). Anthropogenic, environmental and climatic processes that encourage pipe development in peatlands are likely to have a disproportionally large impact on carbon fluxes and losses to the aquatic system.

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Table 1. Annual export of fluvial carbon from pipes and the stream in the Cottage Hill Sike catchment

	[a]Flow type	Auto-sampler	Pipe outlet diameter cm	Depth from peat surface cm	Duration of flow measurement	Storms sampled	[b]Mean DOC kg yr^{-1}	[b]Mean POC kg yr^{-1}	[c]Study year DOC kg	[c]Study year POC kg	[cd]Study year CO_2-C kg	[cd]Study year CH_4-C kg	Study year total kg
Stream	C	Yes			01/1/08-31/12/09	Yes	9977.73	472.62	9133.13	432.62	311	1.02	9877.77
P1	E	No	10	47	13/2/08-20/5/09	No	0.97	0.08	1.1	0.09	0.03	0.00007	1.22
P2	E	Yes	3	75	14/1/08-16/6/09	Yes	0.89	0.14	1	0.16	0.06	0.00005	1.22
P3	C	Yes	30	25	14/12/07-01/12/09	Yes	67.12	2.69	66.05	2.64	3.71	0.00702	72.41
P4	E	No	3	60	14/12/07-16/6/09	No	0.52	0.05	0.58	0.05	0.03	0.00004	0.66
P5	E	No	1	100	13/2/08-20/5/09	No	0.53	0.1	0.56	0.11	0.03	0.00009	0.70
P6	C	Yes	15	100	14/12/07-01/12/09	Yes	27.33	1.98	26.14	1.9	3.55	0.41105	32.00
P7	C	Yes	6	30	23/4/08-11/11/09	Yes	16.08	2.52	13.23	2.08	0.67	0.00804	15.99
P8	E	Yes	10	160	23/4/08-1/12/09	Yes	77.43	16.47	67.77	14.41	2.01	0.01538	84.21
Pipe total							190.87	24.03	176.43	21.44	10.09	0.44174	208.40
Equivalent % of stream C output by monitored pipes							1.91	5.08	1.93	4.96	3.24	43.31	2.11
Equivalent stream C output by all pipes							1848.32	259.6	1695.5	230.84	89.36	3.60	2130.99
Equivalent % stream C output by all pipes							18.52	54.93	18.56	53.36	28.73	352.94	21.57

[a]Ephemeral or continuously-flowing pipe. [b]Based on the full period of flow measurement for each pipe. [c]Corrected for season by calculating for 24 April 2008 to 23 April 2009 (the ‘study year’). [d]Taken from data collected by Dinsmore *et al.* (2011).

Figure captions

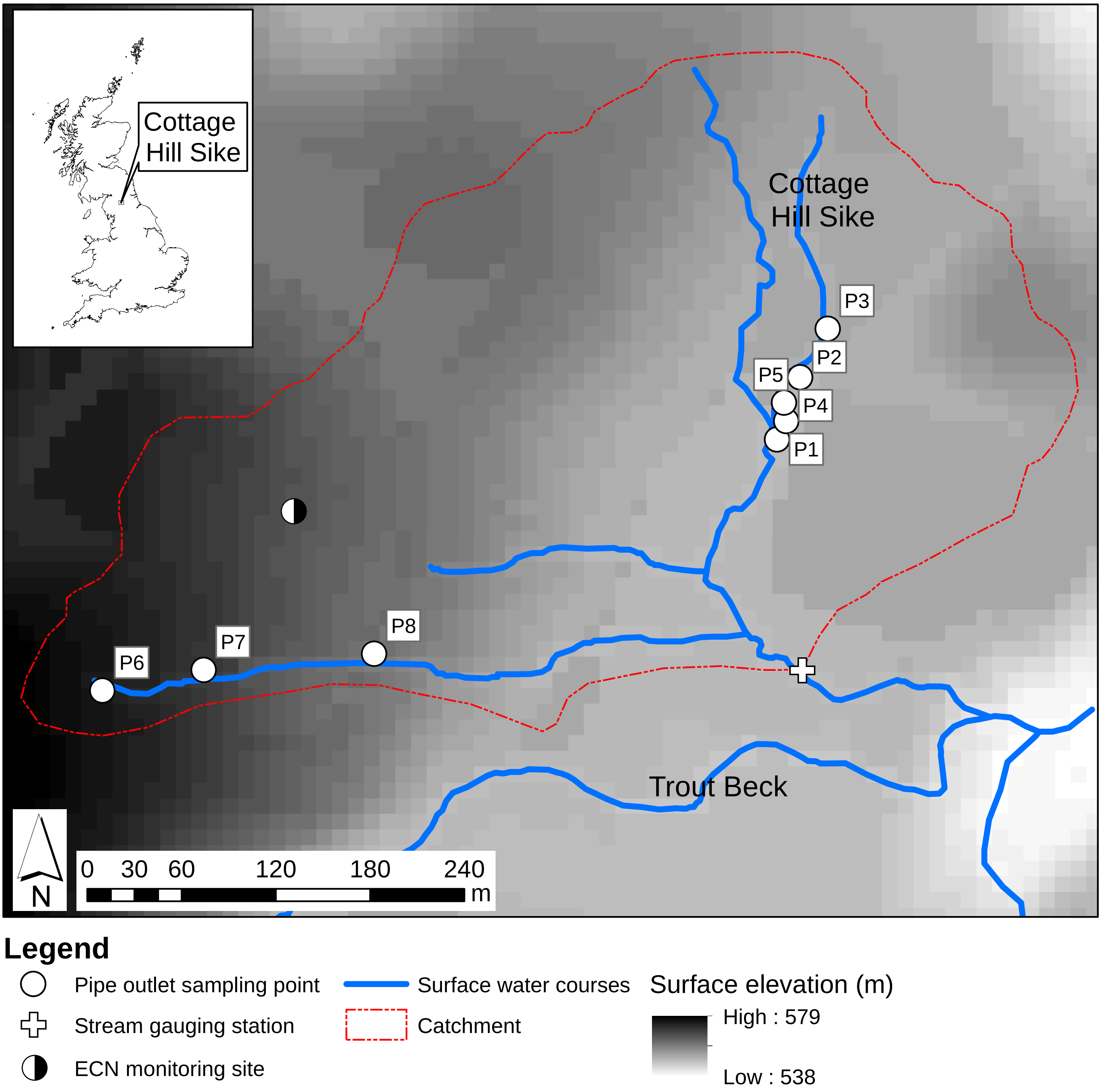
Figure 1. Map showing the location of Cottage Hill Sike and location of sampled pipes within the catchment.

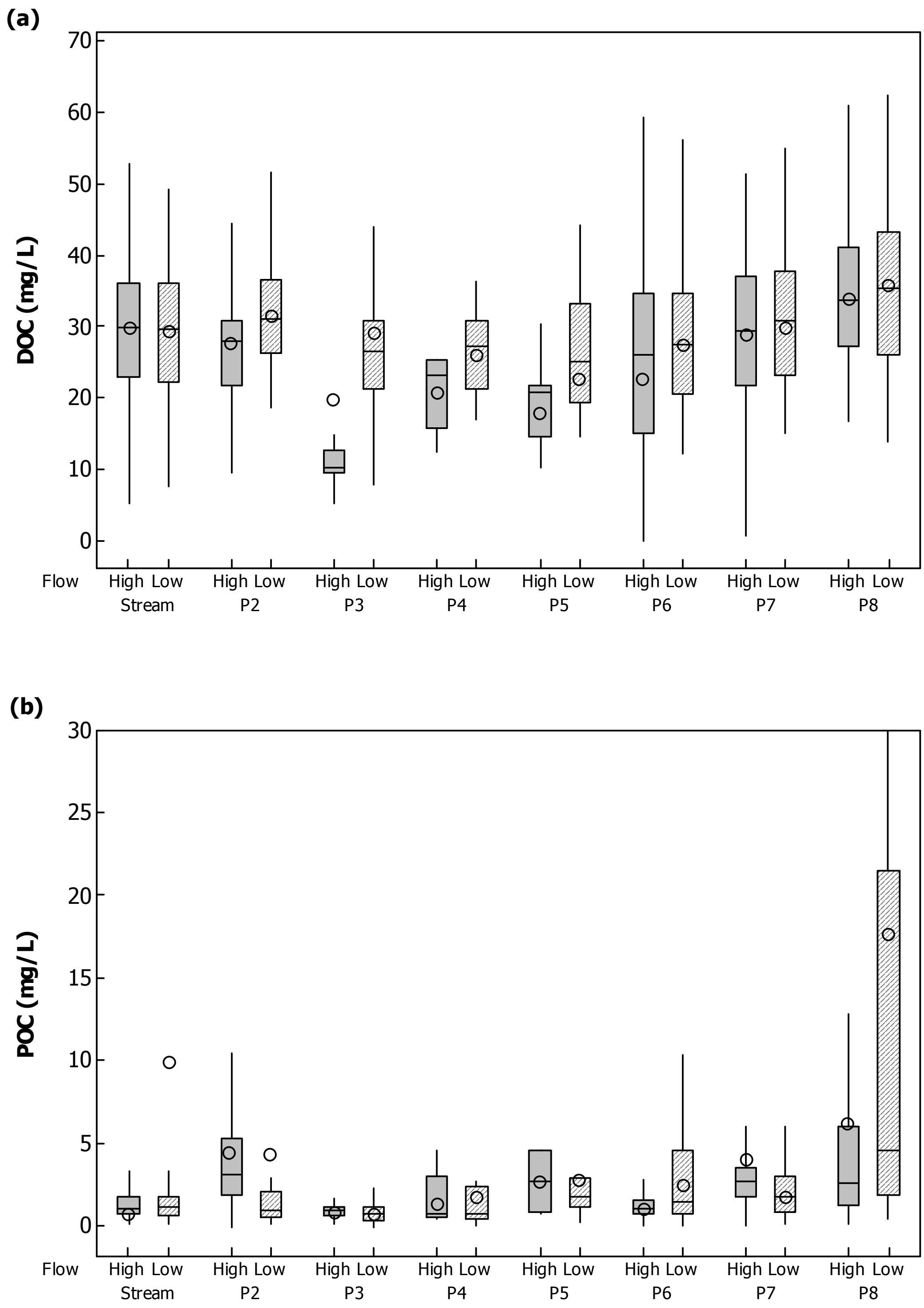
Figure 2. Box and whisker plots for a) DOC and b) POC concentrations for samples taken when flow was above mean (high) or below mean (low). P1 not shown because discharge data were only available for 54 % of the time. Shaded indicates high flow and hatched indicates low flow. The open circles indicate the volume-weighted mean in each case. The upper end point of the whiskers indicates Q3 + (1.5 × (Q3-Q1)). The lower end point of the whiskers indicates Q1 – (1.5 × (Q3-Q1)).

Figure 3. Stream discharge and stream and pipe DOC concentrations (a) compared with POC and concentrations (b) for P6 and P7 during a storm event in July 2008. Auto-samplers triggered at different times and so not all sampling is simultaneous for all points.

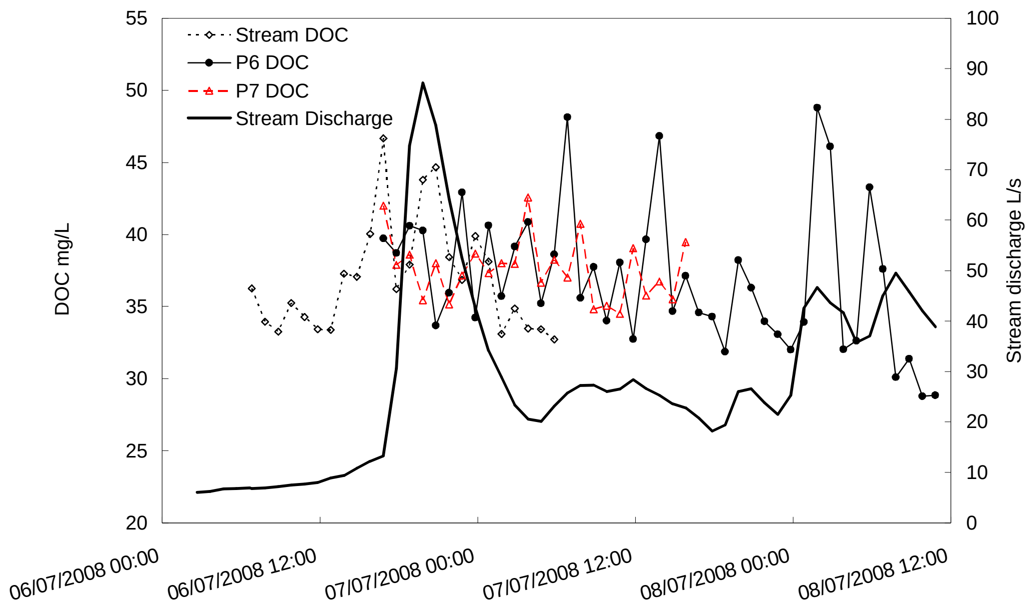
Figure 4. Discharge, DOC and POC concentrations for P3 during a storm on 13-14 March 2008. The auto-sampler triggered at 16:30 GMT on 13 March 2008 with rising flow.

Figure 5. Time-series of POC, DOC and instantaneous discharge at the time of aquatic carbon sampling based on sampling once per day using an auto-sampler on the outlet of P6 between over an eight week period in late spring and early summer 2008.

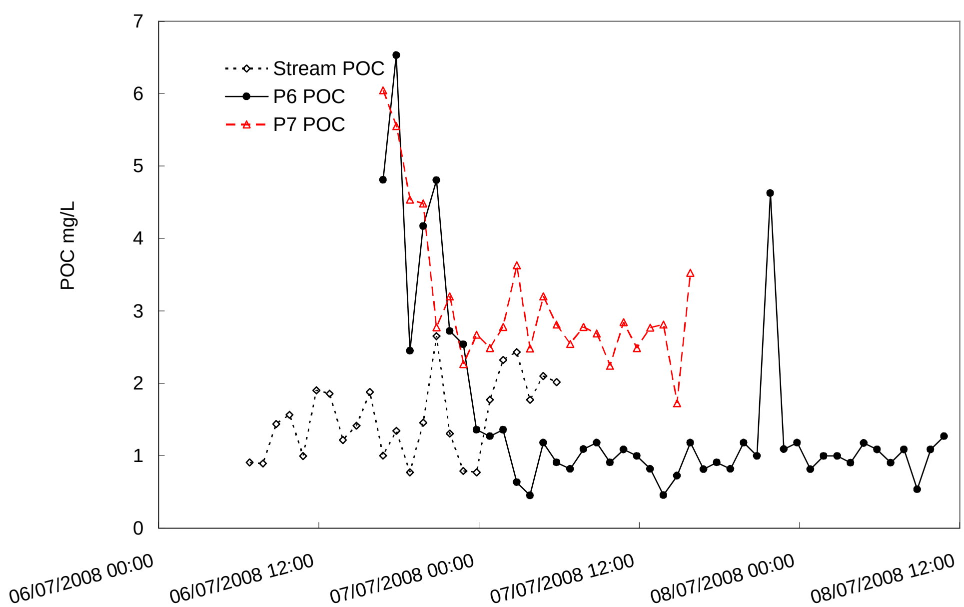

Cottage
Hill Sike
Cottage
Hill Sike
P3
P2
P5
P4
P1
P8
P7
P6
Trout Beck
N
0 30 60 120 180 240
m
Legend
Pipe outlet sampling point
Stream gauging station
ECN monitoring site
Surface water courses
Catchment
Surface elevation (m)
High : 579
Low : 538

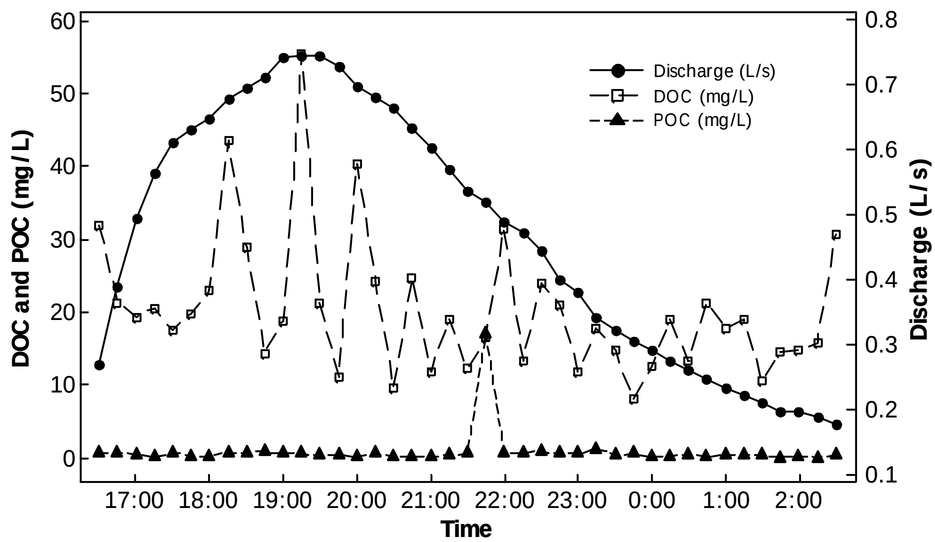

(a)
DOC (mg/L)
70
60
50
40
30
20
10
0
Flow
High Low
Stream
High Low
P2
High Low
P3
High Low
P4
High Low
P5
High Low
P6
High Low
P7
High Low
P8
(b)
POC (mg/L)
30
25
20
15
10
5
0
Flow
High Low
Stream
High Low
P2
High Low
P3
High Low
P4
High Low
P5
High Low
P6
High Low
P7
High Low
P8

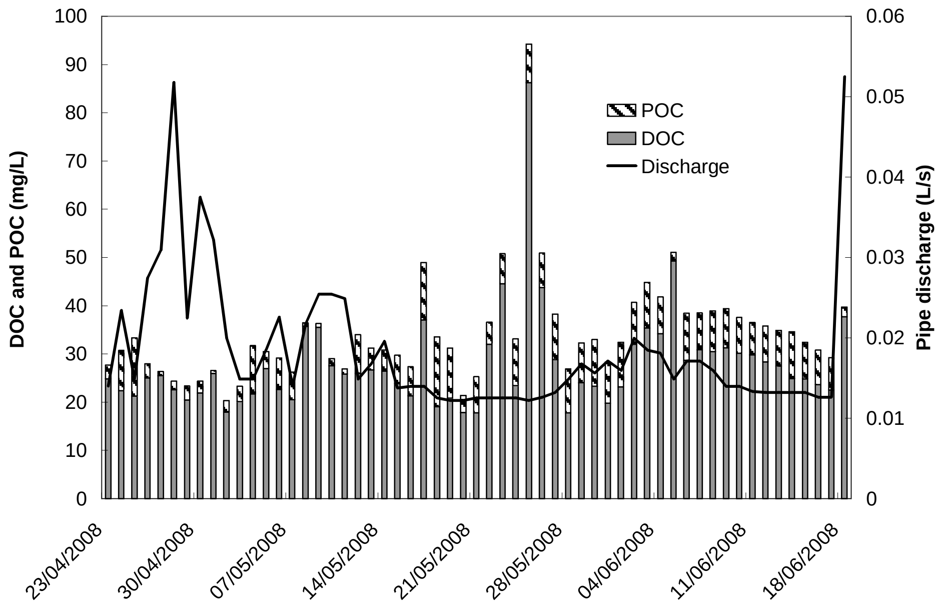
a)


Stream DOC
P6 DOC
P7 DOC
Stream Discharge
DOC mg/L
Stream discharge L/s
55
50
45
40
35
30
25
20
100
90
80
70
60
50
40
30
20
10
0
06/07/2008 00:00
06/07/2008 12:00
07/07/2008 00:00
07/07/2008 12:00
08/07/2008 00:00
08/07/2008 12:00

b)


Stream POC
P6 POC
P7 POC
POC mg/L
7
6
5
4
3
2
1
0
06/07/2008 00:00
06/07/2008 12:00
07/07/2008 00:00
07/07/2008 12:00
08/07/2008 00:00
08/07/2008 12:00


60
50
40
30
20
10
0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
DOC and POC (mg/L)
Discharge (L/s)
Discharge (L/s)
DOC (mg/L)
POC (mg/L)
17:00
18:00
19:00
20:00
21:00
22:00
23:00
0:00
1:00
2:00
Time


100
90
80
70
60
50
40
30
20
10
0
DOC and POC (mg/L)
0.06
0.05
0.04
0.03
0.02
0.01
0
Pipe discharge (L/s)
POC
DOC
Discharge
23/04/2008
30/04/2008
07/05/2008
14/05/2008
21/05/2008
28/05/2008
04/06/2008
11/06/2008
18/06/2008