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Published article:

Holden, J, Smart, RP, Baird, AJ, Chapman, PJ, Dinsmore, KJ and Billett, MF (2012) *Natural pipes in blanket peatlands: Major point sources for the release of carbon to the aquatic system*. *Global Change Biology*, 18 (12). 3568 - 3580 .
ISSN 1354-1013

<http://dx.doi.org/10.1111/gcb.12004>

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

3

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

5

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14 Date revision submitted to Global Change Biology: 30 June 2012

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16

17 **Keywords:** Blanket peat, tunnel erosion, carbon export, dissolved organic carbon

18 (DOC), particulate organic carbon (POC), macropores, pipeflow, piping, throughflow

19

20 **Abstract**

21 Natural soil pipes, which have been widely reported in peatlands, have been shown to
22 contribute significantly to total stream flow. Here, using measurements from eight
23 pipe outlets, we consider the role of natural pipes in the transport of fluvial carbon
24 within a 17.4-ha blanket-peat-covered catchment. Concentrations of dissolved and
25 particulate organic carbon (DOC and POC) from pipe waters varied greatly between
26 pipes and over time, ranging between 5.3 and 180.6 mg L⁻¹ for DOC and 0.08 and 220
27 mg L⁻¹ for POC. Pipes were important pathways for peatland fluvial carbon export,
28 with fluxes varying between 0.6 and 67.8 kg yr⁻¹ (DOC) and 0.1 and 14.4 kg yr⁻¹
29 (POC) for individual pipes. Pipe DOC flux was equivalent to 20 % of the annual DOC
30 flux from the stream outlet while the POC flux from pipes was equivalent to 56 % of
31 the annual stream POC flux. The proportion of different forms of aquatic carbon to
32 total aquatic carbon flux varied between pipes, with DOC ranging between 80.0 and
33 91.2 %, POC from 3.6 to 17.1 %, dissolved CO₂-C from 2.4 to 11.1 % and dissolved
34 CH₄-C from 0.004 to 1.3 %. The total flux of dissolved CO₂-C and CH₄-C scaled up
35 to all pipe outlets in the study catchment was estimated to be 89.4 and 3.6 kg yr⁻¹
36 respectively. Overall, pipe outlets produced discharge equivalent to 14 % of the
37 discharge in the stream but delivered an amount of aquatic carbon equivalent to 22 %
38 of the aquatic carbon flux at the catchment outlet. Pipe densities in blanket peatlands
39 are known to increase when peat is affected by drainage or drying. Hence,
40 environmental change in many peatlands may lead to an increase in aquatic carbon
41 fluxes from natural pipes, thereby influencing the peatland carbon balance and
42 downstream ecological processes.

43

44 **Introduction**

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

60

61 Macropores are known to be common hydrological pathways in peatlands (Baird,
62 1997, Holden, 2009). Natural soil pipes are large macropores, often many centimetres
63 in diameter and several tens of metres in length, which may form branching networks.
64 Pipes have been reported in most types of peatland around the world (Dittrich, 1952,
65 Eggesmann, 1960, Glaser, 1998, Ingram, 1983, Rapson *et al.*, 2006, Rudolf & Firbas,
66 1927, Woo & DiCenzo, 1988), and have frequently been reported in blanket peatlands
67 (e.g. Gunn, 2000, Holden, 2006, Holden & Burt, 2002b, Holden *et al.*, 2004, Jones,

68 1981, Jones *et al.*, 1997, Markov & Khoroshev, 1988, McCaig, 1983, Norrstrom &
69 Jacks, 1996, Price, 1992, Rapson *et al.*, 2006, Thorp & Glanville, 2003).

70

71 Little is known about peatland pipe formation and enlargement processes, but it is
72 thought that peatlands are suitable environments for pipe development because of the
73 strong vertical and lateral gradients in hydraulic conductivity within peat and a
74 plentiful water supply (Holden, 2005a, Holden & Burt, 2003a, Rosa & Larocque,
75 2008). Drying of peat resulting in crack formation during desiccation has previously
76 been suggested as one mechanism for pipe initiation and pipe network expansion
77 (Gilman & Newson, 1980, Jones, 2004) but plentiful rainfall is likely to be required to
78 flow through the cracks to open them up and further erode them. Drainage of peat
79 through open ditch networks has also been found to be associated with enhanced
80 densities of soil pipes (Holden, 2005a, Holden, 2006). Therefore, it may be that
81 environmental change that encourages peat desiccation such as warmer summers with
82 more drought periods may encourage enhanced pipe development in these systems.

83

84 Pipes appear to be important sources of water for peatland streams. Maximum
85 discharges of 0.7 to 10 L s⁻¹ from single peat pipes have been reported (Chapman,
86 1994, Gilman & Newson, 1980, Holden & Burt, 2002b, Woo & DiCenzo, 1988). Pipe
87 responses to rainfall tend to be 'flashy' (rapid hydrological response), suggesting
88 good connectivity between pipes and surface and near-surface peat layers (Holden &
89 Burt, 2002b; Smart *et al.*, in press). Around 10 % of streamflow was derived from
90 pipe networks in Little Dodgen Pot Sike, a deep blanket peat catchment in the North
91 Pennines of England (Holden & Burt, 2002b), while Smart *et al.* (in press) found that
92 pipes contributed 13.7 % of the discharge in the nearby Cottage Hill Sike catchment,

93 the focus of the study described below. The relative contribution of pipeflow to
94 stream flow compared to other water sources varies with antecedent conditions
95 (Chapman, 1994, Holden & Burt, 2002b, Jones, 1990), and many pipes cease flowing
96 during dry conditions (ephemeral pipes). At Cottage Hill Sike, the relative
97 contribution of pipeflow to streamflow was found to be greatest at low flows when
98 some of the continuously-flowing (perennial) pipes became relatively more important
99 for maintaining streamflow (Smart et al., in press).

100

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

115

116 Dinsmore *et al.* (2011) have shown that pipes in the peat at Cottage Hill Sike act as
117 important sources to river water and the atmosphere of CO₂ and CH₄. The variability

118 in concentrations and fluxes of dissolved gases between pipes was large, with mean
119 concentrations in individual pipes ranging from 0.70 to 6.51 mg C L⁻¹ of CO₂ and
120 0.90 to 897 µg C L⁻¹ of CH₄. Total dissolved CO₂ and CH₄ fluxes from a subsample of
121 eight pipe outlets were estimated to represent 3% and 38% of downstream export of
122 the respective gases from the stream outlet whilst contributing only 2% of runoff.
123 There was also strong evidence of rapid degassing from pipe waters at their outlets
124 (Dinsmore *et al.*, 2011) suggesting that they act as point sources of greenhouse gas to
125 the atmosphere. It is not known whether the pipes deliver a similar proportion of DOC
126 and POC compared to their water contribution or, as with dissolved gases, whether the
127 relative roles of pipes in transporting organic carbon is more important than their
128 water contribution.

129

130 Holden *et al.* (2012) have shown that pipe outlets within the Cottage Hill Sike
131 catchment over a 33-month period varied in size and shape through time. The cross-
132 sectional area of 85 % of pipe outlets changed, 20 % of pipe outlet areas altered by
133 more than 50 cm² (equivalent to a median 207 % change in area, including both
134 increases and decreases, for this upper fifth of pipes) and one changed by 312 cm² (98
135 % reduction in size). Although pipe outlets may not be wholly representative of the
136 internal morphology of pipe networks, the evidence of rapid morphological change
137 does suggest that pipes may be important contributors of POC to blanket peatland
138 stream systems. The aim of the work reported herein was to quantify not only the
139 POC flux from the pipes but also to investigate the flux of DOC from pipes. As with
140 the studies of Dinsmore *et al.* (2011), Smart *et al.* (in press) and Billett *et al.* (2012),
141 we focused on the Cottage Hill Sike catchment in the North Pennines, England. We
142 investigated i) the relative contribution of pipe DOC and POC export to total

143 downstream losses, and, by using the dissolved gas flux data presented by Dinsmore
144 *et al.* (2011), ii) the role of pipes in total aquatic carbon loss from the Cottage Hill
145 Sike catchment.

146

147 **Study Site**

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

161

162 A high resolution topographic survey using real time kinematic GPS ground survey
163 (with a horizontal precision of +/-1 cm and a vertical precision of +/-3 cm) was
164 conducted on the catchment. This GPS survey focussed on the areas adjacent to the
165 catchment perimeter where the location of the catchment divide was most uncertain.
166 Using this technique the catchment area was found to be 17.4 ha which was lower
167 than the previous estimate of 20 ha which is quoted in earlier papers for the catchment

168 (e.g., Clark *et al.*, 2007). Figure 1 shows the catchment boundary determined by
169 ground survey.

170

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

186

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

192

193 Vegetation cover within Cottage Hill Sike is most commonly *Calluna vulgaris* (L.)
194 Hull., *Eriophorum vaginatum* L. with some *Empetrum nigrum* L. and *Sphagnum*
195 *capillifolium* (Ehrh.) Hedw.. Water-table measurements on a uniform slope in the
196 catchment show that the water table is within 5 cm of the surface for 83 % of the time
197 and rarely falls to depths greater than 20 cm (Evans et al., 1999). The peat is acidic,
198 with a pore-water pH of 3.6 to 4.3 (Adamson *et al.*, 2001). The mean pH for Cottage
199 Hill Sike streamwater was 4.34 between 1993 and 2007 (Tipping *et al.*, 2010), with
200 4.01 and 4.75 being the 5th and 95th percentiles. Low pH, associated with a low mean
201 Ca concentration of 1.1 mg L⁻¹ (Tipping *et al.* 2010), suggests that there is little
202 groundwater contribution from the mineral matter underlying the peat. Estimates of
203 the annual DOC flux from Cottage Hill Sike for 1993 to 2007 range from 14.3 g C m⁻²
204 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
205 (Billett *et al.*, 2010). These values were based on weekly sampling, but may be
206 underestimates because most DOC is likely to be transported during storms, which
207 requires more intensive sampling (Clark *et al.*, 2007).

208

209 **Materials and methods**

210 A detailed catchment survey to locate and measure pipe outlets occurred on three
211 occasions between August 2007 and April 2010 as described in Holden *et al.* (2012).
212 Additionally, each pipe outlet was visited 12 further times during storms and dry
213 periods between 2007 and 2010 to determine whether pipe discharge was continuous
214 or ephemeral. A mean of 84 pipe outlets was identified across the catchment, with a
215 mean of 24 pipes continuously-flowing and a mean of 60 ephemerally-flowing. The
216 distinction between continuous and ephemeral pipes is partly qualitative, because,
217 during the very driest conditions, flow from many of the continuously-flowing pipes

218 was very low. Eight of the pipes (P1-P8; Figure 1) were chosen to provide a selection
219 of typical pipes within the catchment as a whole (based on size of outlet, depth of pipe
220 outlet relative to the peat surface and flow conditions) for continuous gauging. Pipe
221 nomenclature is consistent with Dinsmore *et al.* (2011), Smart *et al.* (in press) and
222 Billett *et al.* (2012). The outlets of these pipes ranged from 1 cm to 30 cm in diameter
223 (Table 1). Further details on pipe geomorphology for all of the pipes in Cottage Hill
224 Sike are given in Holden *et al.* (2012). The mean diameter of the pipe outlets in the
225 catchment was 9.8 cm (standard error = 0.7 cm) ranging from 0.8 to 45 cm in
226 diameter, the latter being the only case of a pipe outlet with a diameter larger than 30
227 cm. Flow from the pipes was gauged either using calibrated V-notch weirs and
228 pressure transducers, or tipping bucket flow gauges, the latter for pipes where flows
229 were thought to be lower (Holden & Burt, 2002b). Pipe discharge was monitored from
230 December 2007 to December 2009.

231

232 Samples of pipe water were collected from each of the pipe outlets every two weeks
233 except from those pipes that were not flowing at the time of sampling. Because
234 blanket peatland streams have very flashy hydrological regimes, most two-weekly
235 visits would coincide with low flow periods (Clark *et al.*, 2007). Therefore, five of the
236 pipes (P2, P3, P6, P7 and P8) were randomly chosen to be fitted with ISCO 6712C
237 auto-samplers. These operated during storm events, and collected water samples from
238 the pipe outlets at 15-60 minute intervals. For an eight-week period from 24 April
239 2008 the auto-sampler at P6 collected samples at 24-hour intervals.

240

241 Flow at the catchment outlet (Figure 1) was gauged using a glass-fiber reinforced
242 plastic flume, and weekly water samples from the flume were collected by staff from

243 the UK's Environmental Change Network (ECN) who operate a soil sampling plot
244 within the catchment (Figure 1). Additional stream water samples were collected
245 during storms using an ISCO 6712C auto-sampler.

246

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

257

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

264

265 During the early stages of the monitoring programme, very high and/or very low pipe
266 flows were not captured by some of the flow gauges. Subsequent adjustments to the
267 instrumentation had to be made to ensure that the full range of pipe flows was

268 recorded. During the latter stages of monitoring, some equipment failure occurred due
 269 to frost/ice damage. Hence, the flow records for different pipes are of different lengths
 270 (Table 1). However, the pipe-flow record is complete for all pipes (except P1 – see
 271 below) for the 12-month period starting on 24 April 2008. In order to avoid any
 272 seasonal bias we largely focus on the results for this 12-month period, and summary
 273 results for April 2008-9 are provided in Table 1. However, because previous results
 274 for annual fluxes from Cottage Hill Sike have been reported on a calendar-year basis
 275 (Billett *et al.*, 2010), we also present some of the summary results for calendar years
 276 where appropriate. Results from the full monitoring period for each pipe are also
 277 presented in Table 1. The logger for P1 frequently broke and only 54 % of its
 278 discharge record is complete. However, because the logger breakage occurred
 279 randomly across the discharge range (based on examination of rainfall and discharge
 280 at the stream and from other pipes), we were able to use its discharge record to
 281 produce an annual DOC and POC flux for the pipe.

282

283 Routine samples collected every two weeks in combination with storm samples were
 284 used to derive fluxes of carbon. Total and annual fluxes of DOC and POC for each
 285 pipe and for the stream were calculated using the following equation (Verhoff *et al.*,
 286 1980, Walling & Webb, 1985):

$$287 \quad \text{Flux} = \frac{K \cdot \sum_{i=1}^n (Q_i \cdot C_i)}{\sum_{i=1}^n Q_i} \cdot Q_r$$

288

[equation 1]

289 where K is a conversion factor to scale units to annual catchment values, C_i is the
 290 instantaneous concentration associated with Q_i the instantaneous discharge, Q_r is the
 291 mean discharge for the full study period, and n is the number of instantaneous samples

292 analysed. Dinsmore *et al.* (2011) used equation 1 to calculate CO₂ and CH₄ fluxes
293 from the pipes. These data were combined with data on DOC and POC fluxes to
294 produce the overall aquatic carbon export for each of the monitored pipes.

295

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

304

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

312

313 **Results**

314 *Meteorological conditions*

315 For the 12 months from 24 April 2008 precipitation at Cottage Hill Sike was 2105
316 mm, some 5 % higher than the long-term average. Stream runoff was 1758 mm

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

328

329 *DOC and POC concentrations*

330 Over the period December 2007 to December 2009 the concentration of DOC in pipe
331 water collected during storm sampling and regular fortnightly sampling ranged from
332 5.3 to 180.6 mg L⁻¹, while for POC the range was very similar at 0.08 to 220 mg L⁻¹.
333 The range of concentrations for the stream was 5.3 to 89.9 mg L⁻¹ for DOC and 0.1 to
334 25.5 mg L⁻¹ for POC. These data show that, while the maximum stream-water DOC
335 concentration was around half that observed in pipe water, the maximum stream-
336 water POC concentration was eight times lower than that observed in pipe water
337 samples suggesting that pipe-stream transfer of carbon is more effective for DOC than
338 for POC.

339

340 Using Spearman's Rank correlation there were no significant associations between
341 discharge and DOC or POC concentrations or between POC and DOC concentrations

342 for any of the sampling points including the stream (all $p > 0.05$). Water samples were
343 separated into two groups: those taken when discharge was above mean flow and
344 those taken when discharge was below mean flow. We found that median DOC
345 concentrations were greater for all pipes when discharge was above mean flow
346 (Figure 2). Volume-weighted mean DOC concentrations were also greater for all
347 pipes for discharges above the mean when compared to discharges below the mean
348 (Figure 2, open circles). For POC, the median concentrations in pipe waters were
349 significantly greater at high flows compared to low flows in all but two cases.
350 Volume-weighted mean POC concentration was greater at high flow for four pipes
351 (P4, P5, P6, P8) than when discharge was below the mean value (Figure 2).
352
353 Concentrations of DOC and POC were highest from pipe P8 (Figure 2). Pooling data
354 from the ephemeral and perennial pipes showed that mean DOC concentrations were
355 similar between the two pipe types (30.5 and 27.9 mg L⁻¹ respectively, with standard
356 errors of 0.6 and 0.4 mg L⁻¹). However, the mean POC concentration of the ephemeral
357 pipe water was more than twice that of the perennial pipes (5.4 and 2.2 mg L⁻¹
358 respectively, with standard errors of 0.6 and 0.1 mg L⁻¹).
359
360 The interquartile range of DOC concentration was larger for six of the eight pipes
361 compared to the stream. DOC concentrations in pipe water fluctuated widely during
362 storms (Figures 3 and 4), and apparent exhaustion of DOC supply was rarely evident.
363 Temporal variability in pipe water DOC concentrations was also present during low-
364 flow periods. For example, in P6, DOC concentrations changed from 25 mg L⁻¹ to 87
365 mg L⁻¹ and then to 45 mg L⁻¹ on three consecutive days during low flow in late May
366 2008 (Figure 5).

367

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

378

379 *Aquatic carbon fluxes*

380 Using equation 1 and the two-weekly stream water data, we estimated the total DOC
381 and POC flux for Cottage Hill Sike in calendar year 2008 (enabling comparisons to be
382 made with other calendar years for the site) to be 36.5 and 2.4 g C m⁻² yr⁻¹,
383 respectively. In 2009, which was a drier year, the values were 29.7 and 1.9 g m⁻² yr⁻¹,
384 respectively. However, these values were much lower than the fluxes determined
385 when values of DOC and POC from storm events were also included in the analysis.
386 Combining the regular and storm water samples, DOC and POC fluxes for the stream
387 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
388 2.4 g m⁻² yr⁻¹ POC (2009).

389

390 The DOC and POC fluxes were highly variable between pipes (Table 1). DOC fluxes
391 varied by more than a factor of 100, and POC fluxes by more than a factor of 140. For

392 the 12 months from 24 April 2008, the total DOC yield from individual pipes ranged
393 from 0.6 kg to 67.8 kg, while the POC flux varied from 0.1 kg to 14.4 kg. The total
394 DOC flux from the eight monitored pipes was equivalent to 2.1 % of the DOC flux
395 from the catchment outlet. These results suggest that, when scaled to the 84 pipe
396 outlets across the Cottage Hill Sike catchment, the pipes could be responsible for an
397 estimated 20 % of DOC leaving the catchment via the stream, provided there is no
398 storage of DOC in the stream bed and banks or loss to the atmosphere. The total POC
399 flux from the monitored pipes alone was equivalent to 5.2 % of the POC leaving the
400 catchment in the stream. The POC flux from all pipes in the catchment was estimated
401 to be equivalent to 56 % of that leaving the catchment in stream flow.

402

403 Table 1 includes dissolved gas fluxes for the pipes based on data collected by
404 Dinsmore *et al.* (2011) but recalculated for the 12 months from 24 April 2008. The
405 aquatic carbon fluxes from the pipes are dominated by DOC, which represents 84.7 %
406 of the total carbon flux. However, DOC is even more important within the stream,
407 representing 92.5 % of the total downstream aquatic carbon flux. The relative
408 importance of different forms of aquatic carbon to the total flux from individual pipes
409 varied from 80.0 to 91.2 % (DOC), 3.6 to 17.1 % (POC), 2.4 to 11.1 % (dissolved
410 CO₂-C) and 0.004 to 1.3 % (dissolved CH₄-C). The flux values for gaseous forms of
411 carbon do not, however, include the evasion flux from the water surface to the
412 atmosphere, which is known to be significant from individual pipes (Dinsmore *et al.*,
413 2011). Overall, pipes in Cottage Hill Sike were estimated to provide about 22 % of the
414 aquatic downstream carbon flux that is eventually lost from the catchment at the
415 stream outlet.

416

417 The maximum dynamic contributing area was estimated for each pipe by Smart et al.
418 (in press). These estimates enable an approximation of the area-weighted carbon flux
419 from each pipe outlet. The values for pipes P1 to P8 were 7, 12, 12, 8, 9, 12, 19 and
420 $26 \text{ g C m}^{-2} \text{ yr}^{-1}$ respectively. All of the pipes therefore have lower area-weighted
421 aquatic carbon fluxes than the stream ($57 \text{ g C m}^{-2} \text{ yr}^{-1}$) for the 12 months from 24
422 April 2008 although, because the pipe area-weighted fluxes are based on maximum
423 dynamic contributing area, they represent minimum area weighted fluxes.

424

425 **Discussion**

426 The concentration of DOC from pipe outlets varied widely during storm events (see
427 also Chapman 1994), fluctuating through time even when discharge was falling
428 steadily (e.g. Figure 4). However, a general dilution effect was observed during higher
429 flow periods indicative of source limitation or dilution by rainwater and/or overland
430 flow. Even between storms, DOC concentrations were highly variable in individual
431 pipes (Figure 5). Clark *et al.* (2008) measured DOC concentrations from pore waters
432 in the upper 50 cm of the peat profile within the study catchment at daily intervals
433 during October 2002, and found little daily variability at any measured depth for
434 periods between storms. Our observation of more dynamic DOC concentrations in
435 pipe water may suggest that there are frequent changes to source waters for pipes and
436 that the pipes do not obtain their source waters from one depth alone within the peat.
437 The carbon source may change through time as discharge varies and as preferential
438 flow networks connect to or disconnect from the pipe. Interestingly, this suggestion is
439 not supported by isotopic ($\delta^{13}\text{C}$ and ^{14}C) analysis of DOC from the pipe system at
440 Cottage Hill Sike, which shows that both the source and age of DOC is relatively
441 consistent between pipes and changes little during individual storm events (Billett *et*

442 *al.* 2012). Therefore, alternative mechanisms may be responsible for the wide
443 fluctuations in DOC from pipe waters which may be related to variability in
444 production as well as transport. It may be possible that for the same depth, different
445 sources of DOC or parts of the upper peat are being accessed (e.g., sedge root
446 exudates, decomposition products from *Sphagnum*, decomposition products from
447 *Calluna*). This idea is consistent with the isotopic data because these sources would
448 be of similar isotopic ages. Such mechanisms require further investigation.

449

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

459

460 The fluctuations in pipe DOC concentrations during storms may be explained by pipe
461 networks containing many small U-shaped bends or “sumps” (Holden, 2004). Some
462 of the sumps within the pipe network may contain water, which over longer low-flow
463 periods has attained high concentrations of DOC produced by oxidation of pipe wall
464 material or from drainage water percolating from the surrounding peat. As the pipe
465 network becomes hydrologically-connected during the storm event different parts of
466 the network may contribute more or less DOC to runoff. It may also be that there are

467 different water sources contributing to the pipe flows at different points in time.
468 However, it should be noted that Billett *et al.* (2012) found that most DOC produced
469 by peat pipes within the catchment was isotopically modern, and further work is
470 required to explain the temporal variability in DOC produced by pipe outlets.
471
472 Stream fluxes of DOC at Cottage Hill Sike estimated in our study for 2008 (63.4 g C
473 m⁻² yr⁻¹) and 2009 (51.5 g C m⁻² yr⁻¹) were larger than those previously reported for
474 the site for any year since the start of the long-term record in 1993 (Billett *et al.*, 2010,
475 Clark *et al.*, 2007). There are three possible reasons for these larger flux values. First,
476 the earlier (lower) flux values were based on a slightly larger catchment area for
477 Cottage Hill Sike (20 ha) compared to our more accurate value of 17.4 ha based on
478 the GPS survey. Correcting for catchment size increases the earlier published values
479 by 13 %. However, that alone still places 2008 and 2009 as the two highest flux years
480 in the record. Secondly, in combination, 2008 and 2009 produced the wettest two-year
481 period in the long-term DOC flux record. Rainfall exerts a dominant control on DOC
482 fluxes within the catchment (Clark *et al.*, 2007). Thirdly, and most importantly, the
483 use of auto-samplers allowed high flow events to be routinely sampled. Incorporating
484 high-flow measurements resulted in the estimated annual flux of DOC and POC from
485 Cottage Hill Sike increasing by 73 % and 26 %, respectively, compared to the use of
486 weekly routine samples alone. Our results strongly suggest that reliance on weekly or
487 fortnightly sampling results in a major underestimate of DOC and POC flux from
488 blanket peatlands. The published DOC flux estimates from Cottage Hill Sike of 14 to
489 33 g C m⁻² yr⁻¹ have previously been thought of as normal for peatlands (Billett *et al.*,
490 2004). It may be that storm sampling across a wider range of peatlands will result in
491 consistently higher flux estimates. If we did not use the revised catchment area and

492 did not include storm samples in our flux calculation, then DOC fluxes for 2008 and
493 2009 would be 31.8 and 27.7 g C m⁻² yr⁻¹ which is within the range of values
494 previously reported for the catchment. It should also be noted that, because we did not
495 have auto-samplers installed on P1, P4 and P5, it is also very likely that the DOC and
496 POC fluxes for these pipes are underestimates.

497

498 At 3.0 and 2.4 g C m⁻² yr⁻¹, the POC flux from the stream at Cottage Hill Sike was not
499 especially high, and is fairly typical of relatively undisturbed peatlands (e.g. Dinsmore
500 *et al.*, 2010), but is lower than actively-eroding systems (Pawson *et al.*, 2008). The
501 relative contribution of DOC and POC to total peatland aquatic carbon flux appears to
502 be similar to estimates for other sites (Dawson *et al.*, 2002, Hope *et al.*, 1997).

503 However, it should be recognised that, because our study included storm sampling,
504 the results may not be strictly comparable to many earlier studies which excluded
505 storm sampling. POC concentrations in the ephemeral pipes were more than twice
506 those of the perennial pipes (5.4 and 2.2 mg L⁻¹ respectively) indicating that, during
507 dry periods, POC builds up and is released during storms, or that these pipes erode
508 more during the storms themselves. POC build up does not appear to occur in
509 continuously-flowing pipes. Nevertheless, at low flows some continuously-flowing
510 pipes provided a regular supply of POC and at higher concentrations than found in the
511 stream. It is also important to note that the relative contribution of pipe-water
512 discharge to streamflow was greatest at low flows in the catchment (Smart *et al.*, in
513 press). POC delivery to streams in peatlands has traditionally been thought to occur
514 only via overland flow, stream erosion or deposition from wind-blown sources (Crisp
515 & Robson, 1979). We have, through direct measurement, shown that pipes are an
516 additional source of POC that may be important under both high and low flow

517 conditions. The discharge of POC at pipe outlets was equivalent to a large proportion
518 of the POC being lost by the stream. However, it is likely that some of the sediment
519 leaving pipes does not initially reach the stream but is deposited close to the pipe
520 outlet. This sediment-trapping results in the familiar sediment yield problem (Walling,
521 1983) whereby deposition and reworking of sediment means that the volume of
522 sediment transported towards river banks at any given time may not equal the volume
523 of sediment being removed by the river. POC discharged from a pipe outlet may be
524 subject to more rapid oxidation and decomposition than if it had remained within the
525 peat itself, although this will depend on the nature (recalcitrance or quality) of the
526 POC. The fluxes of POC from the pipe outlets also suggest that these systems are not
527 benign and that active erosion is taking place within the peat mass. This hypothesis is
528 supported by observations of changes in pipe outlet morphology in the study
529 catchment over time (Holden *et al.*, 2012).

530

531 P8 produced the largest annual carbon flux of any of the pipes. Its large carbon yield
532 is despite it being an ephemeral pipe. P3 was a continuously-flowing pipe and
533 provided an aquatic carbon flux very similar to that of P8. Thus, despite having
534 different flow regimes, these two pipes were both potentially important point sources
535 of aquatic carbon. P3 and P6 also produced significant quantities of dissolved gaseous
536 carbon. However, there was no association between dissolved gas concentration and
537 DOC or POC concentration (data not shown), nor any association between DOC and
538 POC concentration within pipe waters. The lack of associations between DOC, POC
539 and dissolved gas concentrations suggests the sources for each form of carbon
540 delivered by these pipes were different. This difference in source was confirmed by
541 $\delta^{13}\text{C}$ and ^{14}C analysis which showed that sources of dissolved gases (CO_2 and CH_4)

542 were more variable than DOC and POC both between pipes and within pipes (Billett
543 *et al.*, 2012). Natural pipes in the Cottage Hill Sike catchment released CO₂ and POC
544 of a range of ages (modern – 996 year BP), whereas DOC was consistently modern in
545 age. This suggests that carbon transport and delivery through peatland pipe networks
546 to the surface is highly dynamic and differs for individual carbon species.

547

548 At a catchment scale we estimated that pipe outlets produced a water discharge
549 equivalent to 14 % of the discharge in the stream system (Smart *et al.*, in press). If
550 pipes acted as a benign pathway for carbon, in that they are not different to other
551 features in the catchment in terms of erosion, peat decomposition and so on, we would
552 expect them to produce an equivalent of around 14 % of the aquatic carbon that is
553 exported by the stream system. However, the pipes produced aquatic carbon
554 equivalent to 22 % of that which leaves the catchment outlet as well as an unknown
555 amount of gaseous carbon which is lost to the atmosphere by evasion (Dinsmore *et al.*
556 2011). In addition, the high yields of POC from pipe outlets point to active erosion on
557 pipe walls or adjacent macropores demonstrating that pipes are not benign features of
558 peatlands.

559

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

567

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

575

576 This study has provided the first comprehensive set of observations on the role of
577 natural pipes in the transport of carbon in peatlands. At the 17.4-ha blanket peatland
578 study site in the North Pennines of England, pipes were found to be important
579 components of the peatland carbon system. It is estimated that pipes transport organic
580 carbon (DOC and POC) equivalent to 20 % of that exported by the stream. Including
581 gaseous inorganic species, pipes contributed 22 % of the total carbon exported by the
582 stream. The two-layered acrotelm-catotelm model of peatlands (Ingram, 1978, Ivanov,
583 1981) is often used by peatland scientists to describe hydrological and ecological
584 conditions within peatlands. However, many of the pipes we studied were deep within
585 the peat and their role in preferentially exporting water and carbon further highlights
586 the inadequacy of the acrotelm-catotelm concept to describe the hydrological
587 functioning of peatlands (Holden, 2005b, Morris *et al.*, 2011). Anthropogenic,
588 environmental and climatic processes that encourage pipe development in peatlands
589 are likely to have a disproportionately large impact on carbon fluxes and losses to the
590 aquatic system.

591

592 **Acknowledgements**

593 The research was funded by UK Natural Environment Research Council (NERC)
594 grant NE/E003168/1. Cottage Hill Sike is a NERC Centre for Ecology and Hydrology
595 Carbon Catchment and is part of the Moor House Environmental Change Network
596 site. We are grateful to ECN for background data from the catchment and to Natural
597 England for granting site access. We gratefully acknowledge the technical assistance
598 of David Ashley, Richard Grayson and Kirstie Dyson. We thank the four anonymous
599 reviewers of our manuscript and the subject editor for their insightful and constructive
600 comments.

601

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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

^aEphemeral or continuously-flowing pipe. ^bBased on the full period of flow measurement for each pipe. ^cCorrected for season by calculating for 24 April 2008 to 23 April 2009 (the 'study year'). ^dTaken from data collected by Dinsmore *et al.* (2011).

Figure captions

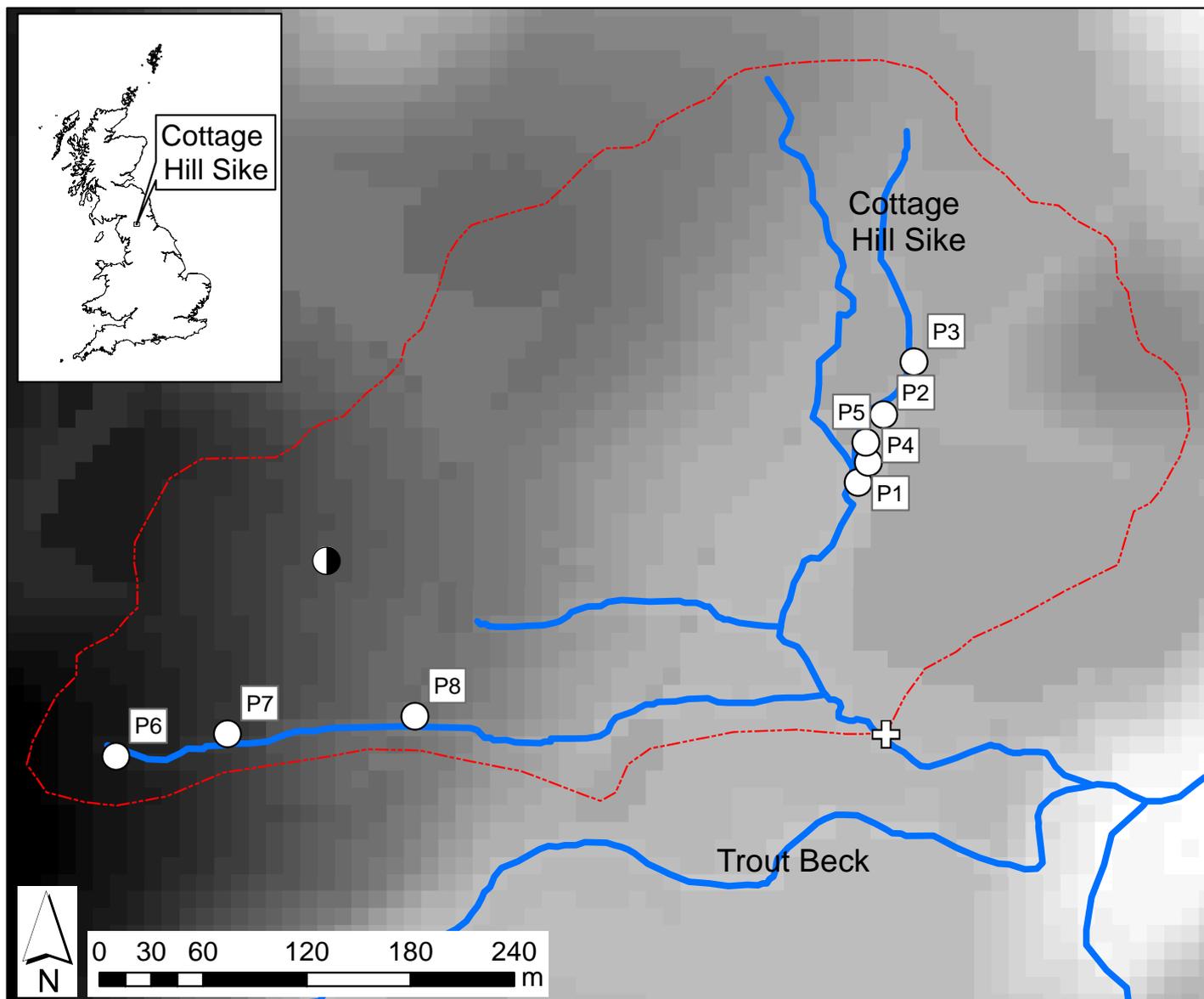
Figure 1. Map showing the location of Cottage Hill Sike and location of sampled pipes within the catchment.

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 $Q3 + (1.5 \times (Q3-Q1))$. The lower end point of the whiskers indicates $Q1 - (1.5 \times (Q3-Q1))$.

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.

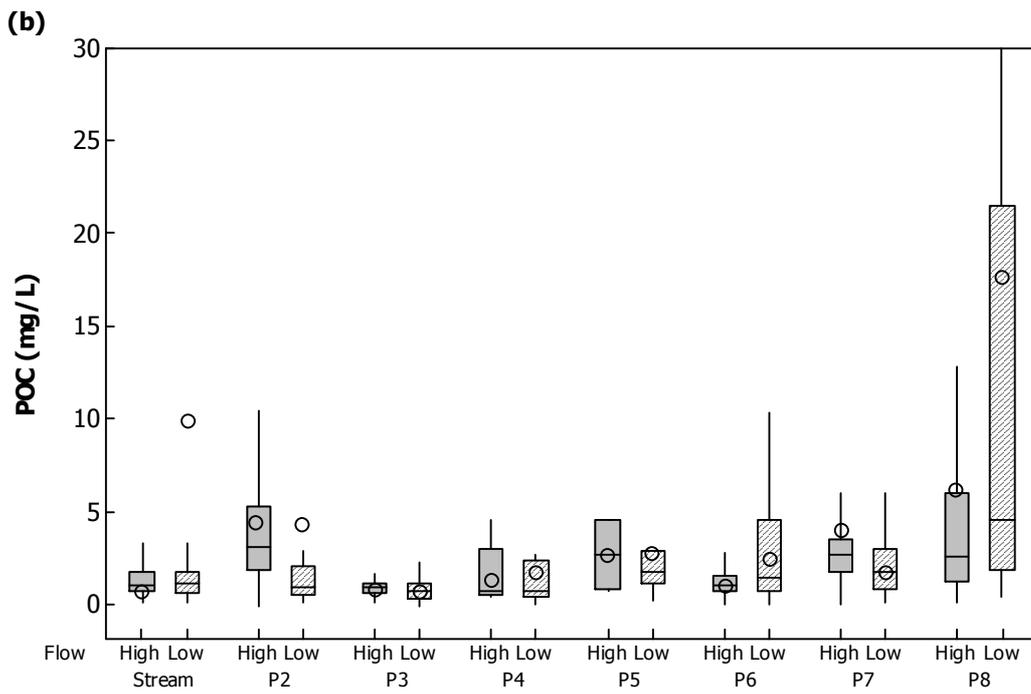
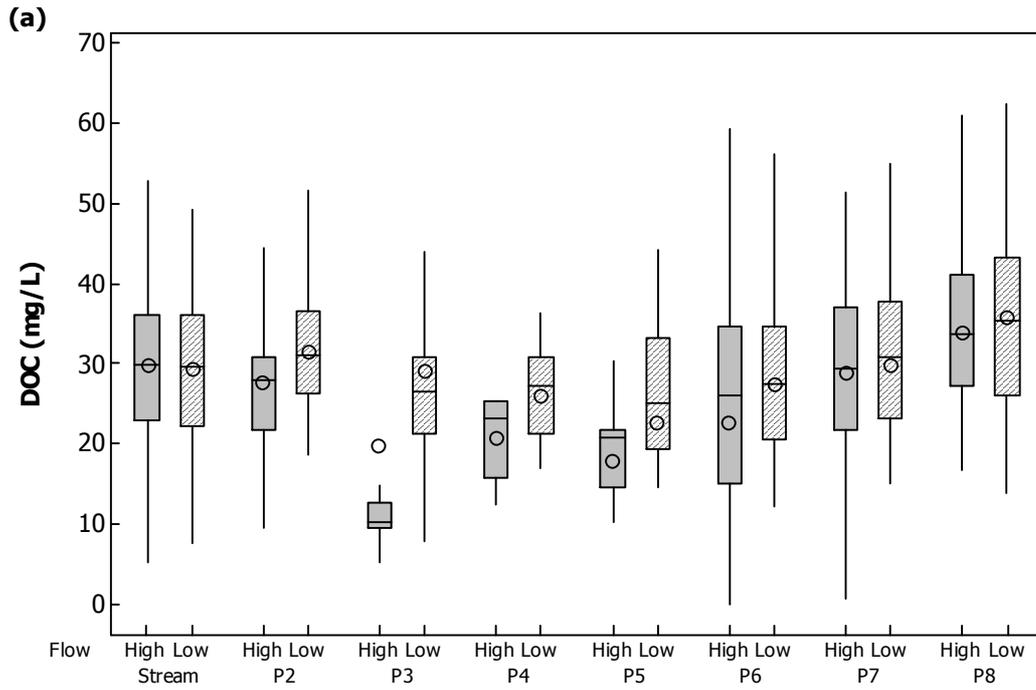
Figure 4. Discharge, DOC and POC concentrations for P3 during a storm on 13-14 March 2008. The auto-sampler triggered at 16:30 GMT on 13 March 2008 with rising flow.

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.

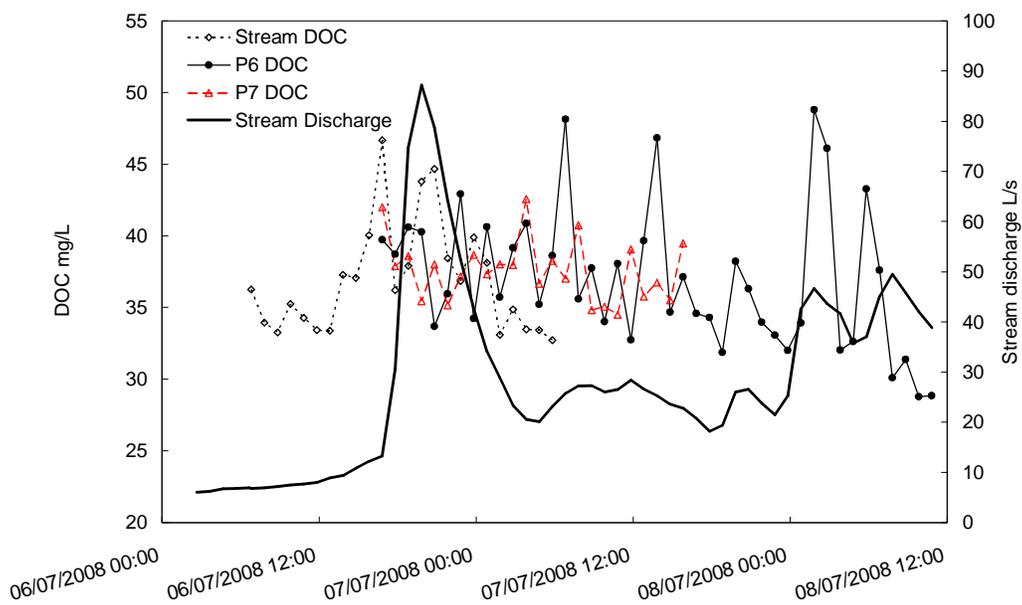


Legend

- Pipe outlet sampling point
- ⊕ Stream gauging station
- ◐ ECN monitoring site
- Surface water courses
- - - Catchment
- Surface elevation (m)
 High : 579
 Low : 538



a)



b)

