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Release of aquatic carbon from two peatland catchments in E. Finland during the spring snowmelt period

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Abstract Spring snowmelt in the arctic and boreal regions represents the most significant event in the hydrological year. We measured concentrations and fluxes of different carbon species in 2 small contrasting (control v drained) forested peatland catchments in E. Finland between April and June 2008 and compared these to long-term annual fluxes. Measurements were made using a combination of continuous sensors (CO_2, temperature, pH, discharge) and routine spot sampling (DOC, POC, DIC, CO_2, CH_4, N_2O). The highest concentrations of CO_2 and CH_4 in streamwater were observed under low flow conditions before the spring flood event, reflecting accumulation and downstream release of gaseous C at the end of the winter period. Over the length of the study mean CH_4 concentrations were 10× higher in the drained site. The snowmelt event was associated with a dilution of DOC and CO_2, with the drained catchment showing a much flashier hydrological response compared to the control site, and post-event, a slower recovery in DOC and CO_2 concentrations. Fluxes of all carbon species during the snowmelt event were significant and represented 37–45% of the annual flux. This highlights the challenge of quantifying aquatic C fluxes in areas with large temporal variability and suggests that inability to "capture" the spring snowmelt event may lead to under-estimation of C fluxes in northern regions.

Keywords Carbon dioxide · DOC · Flux · Methane · Peatland · Snowmelt

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Introduction

The important role that aquatic systems play in carbon release from northern hemisphere peatlands is now widely recognised both in terms of lakes (Algesten et al. 2004; Kortelainen et al. 2006b; Benoy et al. 2007; Nilsson et al. 2008) and streams (Billett et al. 2004; Dinsmore et al. 2010; Rantakari et al. 2010). Concerns that changing climate and management practices will accelerate the fluxes of aquatic and atmospheric carbon released from peatlands, suggests that the sink strength of peatlands may change in the future. Several studies (Walvoord and Striegl 2007; Balcarczyl et al. 2009) highlight the

potential for dissolved organic carbon (DOC) release as permafrost melts, as well as the release of CO_2 and CH_4 (Walter et al. 2006; Mastepanov et al. 2008; Walter et al. 2008), which has remained stored within the peatland carbon repository for significant periods of time. In addition, the management of peatlands (extraction, drainage, afforestation) is known to disturb internal C cycling and lead to enhanced C export, either directly to the atmosphere, or indirectly to the drainage system (Holden 2005). The fate of this C after entering the aquatic system is a major area of uncertainty in the terrestrial C budget (Dinsmore et al. 2010). The ability of northern hemisphere peatlands to continue to sequester C and act as a long-term store is therefore an important natural feedback mechanism to rising global atmospheric CO_2 concentrations.

Peatlands exchange carbon in gaseous forms (CO_2 and CH_4) with the atmosphere, with most undisturbed systems acting as net annual sinks for C. In years when climatic conditions favour respiration over photosynthesis (short, cool, wet summer seasons), peatlands may act as a small source of C to the atmosphere. In addition, N_2O which has a global warming potential (GWP) 298 times that of CO_2 (IPCC 2007), may also be involved in land–atmosphere exchange. Carbon is also released from peatlands via the drainage system in particulate, dissolved (organic and inorganic) and gaseous forms. Hence a true peatland carbon budget needs to consider both the aquatic loss term as well as the land–atmosphere exchange term (Billett et al. 2004; Roulet et al. 2007; Nilsson et al. 2008; Dinsmore et al. 2010). In some terrestrial systems where either runoff or disturbance is high, C export through drainage can be a significant loss term (e.g. Evans et al. 2006), possibly resulting either in a C neutral system or a system which is a net annual C exporter. Lateral downstream transport of DOC, DIC (dissolved inorganic carbon) and particulate organic carbon (POC) is also associated with dissolved CO_2, CH_4 and N_2O. Since streams and pools associated with many northern hemisphere peatlands are supersaturated in CO_2 and CH_4 with respect to the atmosphere (e.g. Dinsmore et al. 2009), both gases can also be lost vertically by evasion (degassing) from the water surface. Whilst the evasion flux term in peatland C budgets is beginning to be quantified (Dinsmore et al. 2010) or estimated (Worrall et al. 2009), less is known about concentrations and fluxes of N_2O.

An important control on aquatic carbon fluxes from peatlands is the frequency of extreme hydrological events, including drought and storms; the quantification of C loss during these events is one of the main challenges in calculating catchment C budgets in temperate regions (e.g. Clark et al. 2007). In cooler northern peatlands, which experience lower precipitation and continental-type climates with less storm events, peatland C fluxes are highly seasonal and strongly related to the length of the winter ice cover period, the thickness of snow cover and the intensity of the spring snowmelt period. Snowmelt is the most extreme hydrological event in these regions and it has been estimated that between 52 and 66% of the annual runoff can occur during the spring period (Laudon et al. 2004). Kortelainen et al. (1997) calculated that half of the annual runoff and export in 22 headwater catchments occurred in spring, although the spring period represented only 10–15% of the year. Quantifying the concentrations, fluxes and forms of C exported at this time of year is therefore important in terms of understanding the processes that control C release. If climate change leads to changes in the duration and extent of the winter snow cover period in the northern boreal, subarctic and arctic regions, C release in peatland drainage is also likely to be affected. This has recently been highlighted with respect to changes in permafrost cover (Schuur et al. 2009).

It is estimated that Finnish peatlands cover ~30% of the land area and store ~5960 million tonnes of C (Turunen 2008). Approximately 35% of Finnish forests are located on peatlands and of these 54% are drained (Finnish Statistical Yearbook of Forestry 2009). Typically streams draining Finnish peatlands originate in mires or lakes and drain slowly across relatively flat land surfaces, the catchment boundaries often constrained by fluvioglacial moraines and terraces. The hydrological year is characterised by very low winter flows, a major spring snowmelt event, a summer low flow period and a number of autumn high flow events associated with storms.

The aim of this study was to investigate the hydrochemistry of 2 streams draining small catchments (Välipuro undrained/control; Suopuro partially drained) in the North Karelia Region of Eastern Finland during the 2008 spring snowmelt event, and

quantify the fluxes of various forms of carbon released (POC, DOC, DIC, CO_2, CH_4). In addition to dissolved concentrations of the greenhouse gases CO_2 and CH_4, we also measured N_2O. Carbon fluxes during this 2-month period were then compared to the long-term fluxes of TOC (total organic carbon) and TIC (total inorganic carbon) from both the undrained (control) and partially drained catchments. The study lasted ~60 days and was constructed around two methods of data collection; spot sampling approximately every 2 days and the deployment of continuous sensors, in particular the use of in-stream and in-soil CO_2 sensors, allowing small-scale temporal resolution of events. The study shows in detail the transition in peatland stream water chemistry at the end of the winter as temperatures rise and the soil–plant system begins to "reconnect" with the aquatic system.

Study site

The two study catchments were located in the north-eastern part of the Haapajärvi-Valtimojärvi catchment (63°52′N, 28°39′E), in North Karelia, Eastern Finland (Fig. 1). The two catchments, Välipuro (0.86 km^2) and Suopuro (1.13 km^2) are located next to each other in an area of managed forest; both contain large areas of peatland (Välipuro 56%, Suopuro 70%). The sites are closed hydro-geomorphological units, thus allowing complete water and nutrient budgets to be made (Finér et al. 1997). The soils are primarily humic podzols and histosols overlaying a layer of glacial till on a bedrock of granite gneiss (Table 1) (Ahtiainen et al. 1988). Peat depth in the area ranges from 2.5 m to 3.2 m (Ahtiainen et al. 1988; Latja and Kurimo 1988). The dominant tree species in both catchments are Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) with birch (*Betula pubescens*) and willow (Salix *sp*.) also present in smaller numbers (Ahtiainen et al. 1988). The understorey consists of dwarf shrubs (*Vaccinium myrtillus* and *Vaccinium Vitis-idaea*) and feather mosses (*Plearozium schreberi* and *Hylocomium splendens*).

Both streams are at an altitude of ~200 m; sample sites were located at the catchment outlets, 1.5 km (Välipuro) and 0.75 km (Suopuro) downstream from the source (Table 1). The streams are typically between 0.5–1.5 m wide and 0.5–1.0 m deep; Suopuro originates in a small pool, Välipuro in a mire. Although the relief of the 2 catchments is similar, the shape of Suopuro (Fig. 1) suggests that flowpath travel times to the stream are likely to be longer. The catchments vary in terms of management practices; forestry operations at Suopuro include ditching (1983) and a 1.4 ha area of clear-cutting (1999). Välipuro is undrained with a small amount (7.7 ha, <10% of catchment area) of clear-cutting in the period 1999–2001. This took place close to the catchment boundary and is unlikely to affect water quality. The outlets of

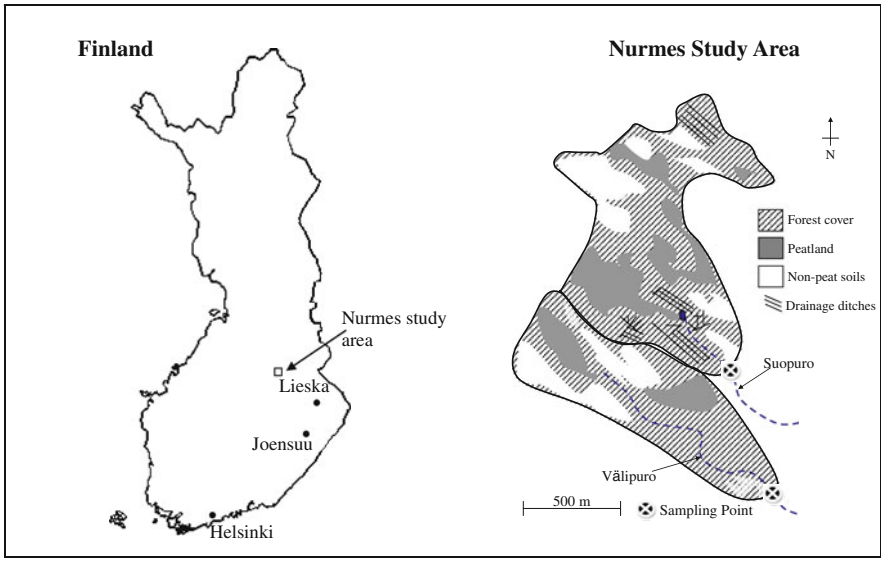

Fig. 1 Location map and underlying characteristics of the 2 study catchments in E Finland

Table 1 Site characteristics of the Välipuro and Suopuro catchments and underlying hydrochemical data for 2008. Stream chemistry data was provided by SYKE and represents an average monthly value ($n = 11$)

	Valipuro	Suopuro
Lat/long	N63°52′ E28°39′	N63°52′ E28°39′
Catchment area (km^2)	0.86	1.13
Peatland (% of area)	56%	70%
Altitude range (m)	185–200	188–202
Drained area (%)	0%	13%
Main stream length (m)	1500	750
Mean annual water temp. (°C)	4.4	5.7
Mean annual runoff (mm)[a]	354 (±63)	372 (±74)
Dominant tree species	Norway spruce and Scots pine	Norway spruce and Scots pine
Geology	Granite gneiss overlain by glacial till	Granite gneiss overlain by glacial till
Soil type	Peat and podzol	Peat and podzol
Streamwater pH	4.26	4.66
Streamwater Ca (mg l^{-1})	0.6	0.7
Streamwater Mg (mg l^{-1})	0.4	0.3
Streamwater Na (mg l^{-1})	0.9	0.6
Streamwater K (mg l^{-1})	0.2	0.12
Streamwater Al (mg l^{-1})	0.20	0.09
Streamwater Fe (mg l^{-1})	1.22	1.40
Streamwater TOC (mg l^{-1})	33	21
Streamwater TIC (mg l^{-1})	2.6	2.3
Streamwater Cl (mg l^{-1})	0.3	0.2
Streamwater $NO_2 + NO_3$ (μg l^{-1})	8.0	10.6
Streamwater NH_4 (μg l^{-1})	8.7	7.1

Peatland % area = area of bog + fen (Ahtiainen et al. 1988)

[a] 1978–2008 long-term mean

both catchments are monitored by the Finnish Environment Institute (SYKE) and Finnish Forest Research Institute (METLA), with a gauging weir continuously measuring flow. The streams are sampled once a month for TOC (collected since 1978), TIC (since 2007) and a range of other determinants (Table 1). Annual runoff for Välipuro and Suopuro in the study year (2008) was 515 and 461 mm, respectively, higher than the long-term (1978–2008) average of 354 (±63) and 372 (±74) mm. The long-term (1979–2006) average annual air temperature and precipitation at the sites are 1.5°C and 612 mm, respectively, with 241 mm falling as snow (5–6 months of annual snow cover).

The outflows of the catchments were intensively monitored between 7th April and 1st June 2008, to coincide with the main snowmelt runoff period. The main runoff event started on the 29th April and finished 8 days later on the 6th May. This agreed with SYKE's forecasting and allowed 23 days of pre-flood sampling and 25 days of post-flood sampling giving enough time for the stream to return to base flow.

Methods

The sites were instrumented at the start of the sampling period to make continuous measurements of a range of variables. The sites were then visited regularly (1–3 day intervals) to collect spot samples, measure CO_2 evasion and snow depth.

Continuous sampling

A Campbell Scientific datalogger (CR1000) system was established at the catchment outlets of both sites with seven sensors (air temperature, soil temperature (CS108), stream temperature (CS547A), pH (CSIM11), stage height (PDCR 1830 series pressure transducer), soil CO_2, stream CO_2) connected to each

logger. Data was averaged and stored every 10 min. The sensors were located in an area ~ 8 m upstream from the weir in an area of free flowing water; soil sensors were installed initially in the snow (5–10 cm above ground) and following snowmelt at 5 cm depth in the unfrozen soil. Measurements of CO_2 concentration in the stream and adjacent soil were made using Vaisala CARBOCAP® (transmitter series GMT220), single-beam dual-wavelength, non-dispersive infra-red absorption (NDIR) sensors. Sensor accuracy and preparation for use in wet environments is described in Johnson et al. (2010). The Vaisala CARBOCAP CO_2 sensors were originally adapted for use in soils by Tang et al. (2003) and Jassal et al. (2004) and have since been deployed in the aquatic environment by Johnson et al. (2006), Dinsmore and Billett (2008), Hari et al. (2008) and Dinsmore et al. (2009) to make direct and continuous measurements of aquatic CO_2 concentrations.

Manual 'spot' sampling and analysis

Stream water samples were collected in 500 ml glass bottles and filtered through pre-ashed and weighed 0.7 μm Whatman GF/F glass fibre filters (Wetzel and Likens 1991). The filtrate was stored at 4°C in the dark prior to transportation to the laboratory at CEH Edinburgh where it was analysed for DOC and DIC using a PPM LABTOC Analyser within 3 weeks of collection (detection range 0.1–4000 mg l^{-1}). The filters were air-dried and packed into plastic bags for transportation; particulate organic carbon (POC) concentrations were determined by loss on ignition (at 375°C for 16 h, as described in Ball 1964).

Manual 'spot' measurements of greenhouse gases (CO_2, CH_4 and N_2O) were made using the headspace technique (Kling et al. 1991; Hope et al. 2001; Billett et al. 2004; Billett and Moore 2008). Headspace samples were analysed using an HP5890 Series II gas chromatograph with flame ionisation and electron capture detectors (detection limits: $CO_2 < 199$ppmv, $CH_4 < 1.26$ ppmv, $N_2O < 0.2$ ppmv). Water temperature, atmospheric pressure and elevation were recorded and dissolved gas concentrations calculated using Henry's Law.

CO_2 evasion (degassing) measurements were achieved using a water tight floating chamber, an opaque injection-moulded polypropylene box, with external dimensions 610 mm × 300 mm × 150 mm, attached to an EGM-4 infra-red gas analyser (PP system version 4.13); accumulation of CO_2 within the closed system was recorded every minute for a 15 min period. The relationship between time, CO_2 concentration, chamber area and volume was used to determine evasion rates (Billett and Moore 2008).

Long-term site data

Long-term hydrochemical data for the sites was provided by SYKE (Finnish Environment Institute) and meteorological data by METLA (Finnish Forest Research Institute). Total organic carbon has been measured on a monthly basis since 1978 and more recently (2007) DIC has been determined as part of the routine analysis. Flow has been measured continuously using a 'V' notch gauging weir for the past 30 years. We use the SKYE and METLA long-term datasets in two ways; (1) to compare our 2-month snowmelt dataset with annual 2008 values, and (2) to contrast our study year (2008) with the period 1978–2008.

Data analysis

Carbon fluxes during the snowmelt period were calculated using algorithms outlined by Walling and Webb (1985). 'Method 2' was used for the continuous measurements and 'Method 5' for the spot sampling data, and to estimate annual export using the long-term flow data from SYKE (Hope et al. 1997).

$$\text{'Method 2' Load} = K \sum_{n}^{i=1} [CiQi/n]$$

$$\text{'Method 5' Load} = K.Qr \sum_{n}^{i=1} [CiQi] / \sum_{n}^{i=1} Qi$$

K refers to a conversion factor to take account of the period of record, Ci is the instantaneous concentration associated with individual samples, Qi is the instantaneous discharge at the time of sampling, Qr is the mean discharge for the period of record and n is the number of samples.

Discharge was calculated using our water pressure readings taken at the time of sampling and the weir stage-discharge relationship produced by SYKE (Välipuro: $Q = 0.2827x^2 - 2.4813x - 20.238$; Suopuro: $Q = 0.2823x^2 - 2.56x - 19.396$; $R^2 > 0.99$

in both cases); continuous discharge was calculated using this method with the additional step of relating our water pressure measurements to weir stage height (Valipuro $R^2 = 0.96$; Suopuro $R^2 = 0.98$).

Due to significant potential for autocorrelation in continuous datasets, statistical correlation analyses were only carried out on 'spot' sample data. The continuous data was used to describe patterns in temporal variability. Datasets were tested for normality and transformed using a natural log where necessary; autocorrelation in spot samples was removed using first order residuals where appropriate. Significant relationships between variables were examined using linear regression on the transformed datasets. Paired T or Mann–Whitney *U* tests were used to examine differences between catchments. Standard error is represented by ± unless otherwise stated; all analyses were carried out on Minitab® statistical software.

Results

Inter-Catchment Differences in Concentration

Mean pH in both catchments was low, with Välipuro (pH 4.25) exhibiting a small, but statistically significant higher pH than Suopuro (pH 4.13) (Table 2). Mean conductivity in Välipuro was also significantly higher (Välipuro 31.8 µS; Suopuro 17.5 µS). In contrast, water temperature was significantly lower in Välipuro (mean 0.9°C) compared to Suopuro (mean 3.2°C). For greenhouse gas concentrations during the snowmelt period, only CH_4 was significantly higher in Suopuro (14.3 µg l^{-1}) compared to Välipuro (1.42 µg l^{-1}). Concentrations of DOC, DIC and POC were higher in Välipuro, although the differences were only significant for DOC and DIC (Table 2).

Table 2 Mean streamwater hydrochemical data (minimum and maximum values are in parentheses) during the spring 2008 snowmelt period

	Välipuro	Suopuro
Continuous sampling		
Discharge (l s^{-1})	44.3 (4.45–304)	51.0 (2.15–796)
Discharge (l ha^{-1} s^{-1})	0.51 (0.05–3.53)	0.45 (0.02–7.04)
CO_2–C (mg l^{-1})	2.70 (1.25–4.20)	2.18 (1.31–3.70)
Air temp (°C)	3.70 (−10.9–23.7)	4.24 (−10.2–24.8)
Water temp (°C)**	0.92 (−0.32–5.38)	3.15 (−0.02–10.1)
Soil temp (°C)	5.24 (−0.26–15.1)	3.80 (−0.2–11.5)
pH**	4.25 (4.09–4.39)	4.13 (3.91–4.48)
Spot sampling		
CO_2–C (mg l^{-1})	2.97 (1.61–5.26)	2.70 (1.55–6.48)
CH_4–C (µg l^{-1})**	1.42 (0.07–35.7)	14.3 (2.99–70.5)
N_2O–N (µg l^{-1})	0.63 (0.18–1.41)	0.56 (0.34–1.06)
DOC (mg l^{-1})**	26.2 (17.6–33.0)	17.5 (9.78–23.9)
POC (mg l^{-1})	0.88 (0.38–1.71)	0.82 (0.30–1.07)
DIC (mg l^{-1})**	3.07 (0.72–5.35)	1.22 (0.24–3.06)
Conductivity (µS)**	31.8 (21.5–40.8)	17.5 (13.8–40.8)

Spot sampling ($n = 40$) began on 7/04/08; continuous sampling on 11/04/08

Mean variables are significantly different at * $P < 0.01$ and ** $P < 0.05$

Temporal changes in flow, temperature and concentration

The complete 2008 hydrological record showed a typical 12-month cycle for boreal regions (Fig. 2). The highest flows occurred during the spring snowmelt period following a 3–4-month period of base and low flows. The post-snowmelt period was characterised by relatively low flows, with late summer and autumn high discharge events occurring between August and November 2008.

Although mean discharge during the snowmelt study period was not statistically different between the 2 catchments (Table 2), it was higher in the larger catchment (Suopuro). Mean discharge over the 2-month period in the 2 study catchments was 3.3 and 5.3 times higher than the average annual (1978–2008) values for Välipuro (13.3 l s^{-1}) and Suopuro (9.6 l s^{-1}). Compared to the winter baseflow values on 01/03/2008, the maximum flows in Välipuro (02/05/2008) and Suopuro (01/05/2008) were 138 and 318 times higher, respectively. Temporal changes in the hydrograph of both catchments showed that flows in Suopuro were greater during the snowmelt period, with much stronger day-night variation in flow rates (Fig. 3a, b).

The main snowmelt period lasted ~8 days and began on the 29th April 2008 coinciding with a rapid rise in mean daily air temperature from 3.4 to 10.9°C from 27th April to 4th May (data not shown). Diurnal changes in water temperature became stronger as

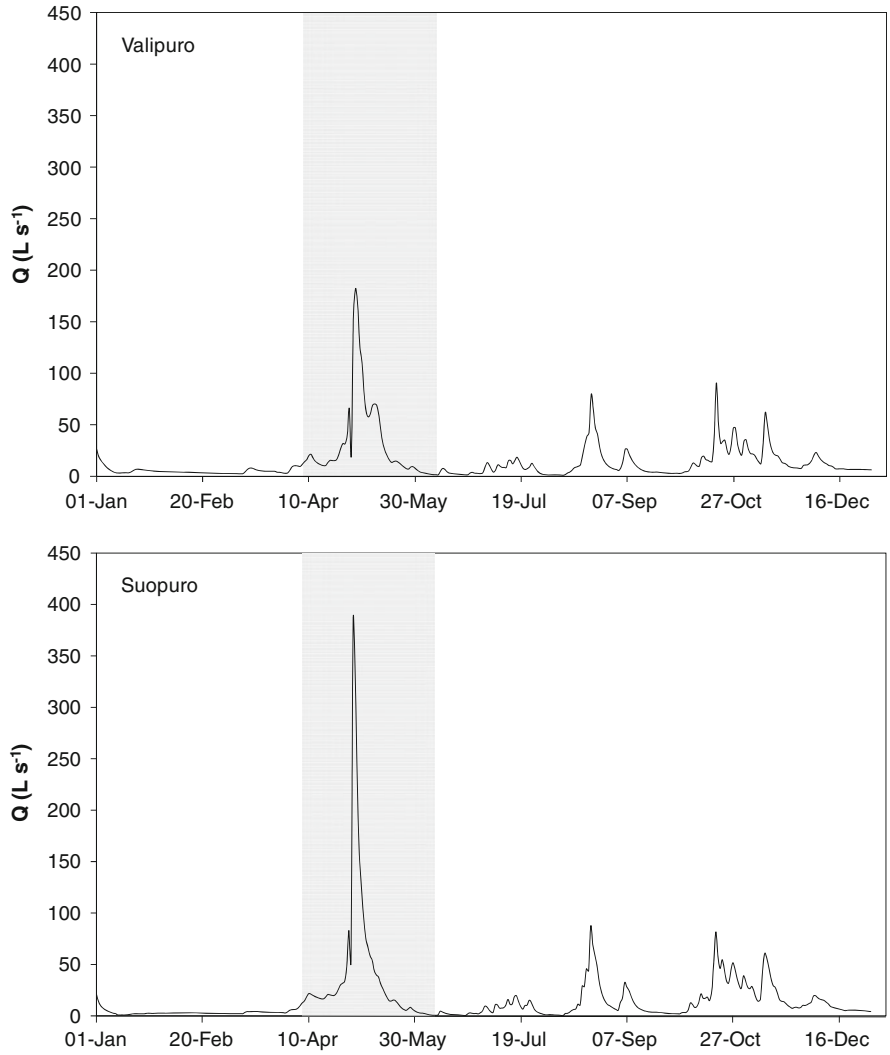

Fig. 2 Annual 2008 hydrograph of the Välipuro and Suopuro catchments. The shaded area in both graphs shows the period of intensive measurements (7th April–1st June) during the spring snowmelt period

catchment runoff became increasingly influenced by rising and more variable daily air temperatures. Averaged daily flow rates were within the long-term range recorded by SYKE for the preceding 29 years (1979 to 2007). In both catchments strong diurnal cycles were exhibited by flow, water and soil temperature (Fig. 3); statistically these cycles were not significantly correlated. In Suopuro, water and soil temperatures increased at approximately the same rate over the study period (correlation $P < 0.01$), as they did in Välipuro in the early part of the study while the ground was still frozen. However, in Välipuro after the main snowmelt period ended soil temperature had increased to $\sim 6°C$ higher (both day and night) compared to water temperature, which remained low for the rest of the sampling period. The precise time at which soil and water temperatures diverged in Välipuro was not captured since the sensor was flooded and could not be placed below ground until the soil had thawed.

The first spot measurements of dissolved gas concentrations in both streams took place over 4 days (7–10 April) before the continuous monitoring system was fully operational. During this time we measured very high concentrations of CO_2 and CH_4 in the outflows of both catchments (Välipuro $\leq$ 5.26 mg CO_2–C l^{-1} and $\leq$ 0.87 µg CH_4–C l^{-1}; Suopuro $\leq$ 6.48 mg CO_2–C l^{-1} and $\leq$ 70.49 µg CH_4–C l^{-1}), equivalent to e*p*CO_2 and e*p*CH_4 values of 15 and 19 and 13 and 1072, respectively (*ep* is defined as excess

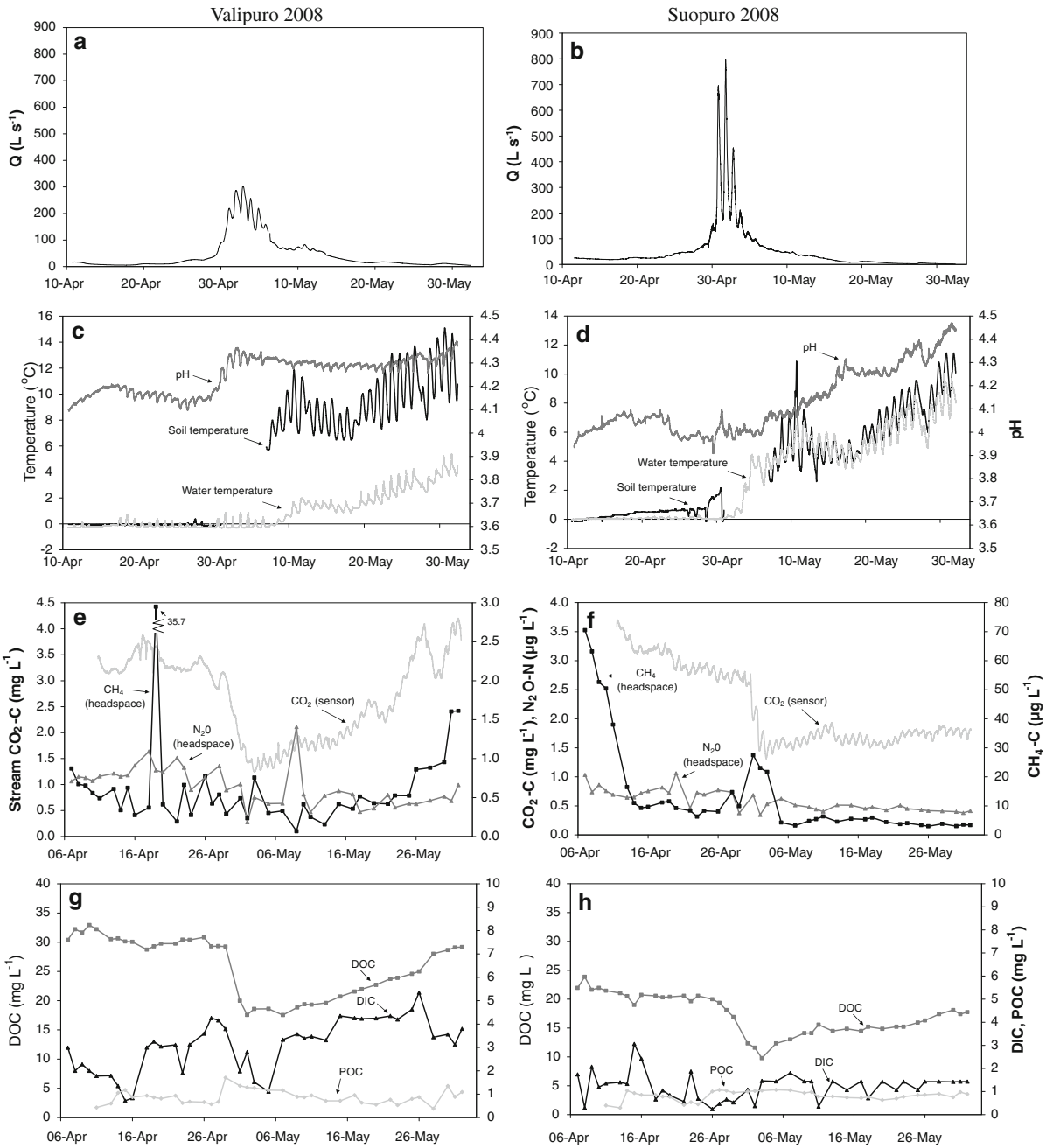

Fig. 3 Temporal changes in discharge (**a**, **b**), pH, soil and water temperature (**c**, **d**), dissolved CO_2, CH_4 and N_2O concentrations (**e**, **f**) and DOC, POC and DOC concentrations (**g**, **h**) during the 2008 spring snowmelt event in Välipuro and Suopuro

partial pressure e.g. pCO_2 water/pCO_2 atmosphere). On each consecutive day after 7th April concentrations in the stream water decreased as CO_2 and CH_4, presumably trapped beneath the ice, was lost. We do not have the benefit of earlier samples to know how much higher the concentration of both gases were beneath the snow pack, but Välipuro and Suopuro clearly exhibit evidence of a CO_2 and CH_4 "burst" at the beginning of the spring snowmelt period. Continuous measurement of CO_2 concentrations initially beneath the snow and then beneath the soil, showed that CO_2 accumulated within the snow pack and then

as air temperatures began to rise, soil concentrations increased and began to exhibit diurnal variation (Fig. 4). This was also seen in the streamwater CO_2 sensors after snowmelt and also reflected diurnal variation in the aquatic system; this has also been observed in other studies (e.g. Dawson et al. 2001).

As the main snowmelt period started CO_2–C concentrations decreased in response to increased discharge; at Välipuro concentrations recovered during the study period ($P < 0.01$), but this was not seen at Suopuro during the time frame of the study. Additionally, at the time of the main snowmelt event and thereafter, CO_2 concentrations began to show strong diurnal fluctuations superimposed on the underlying (more longer term) hydrologically driven changes (Fig. 3e, f). At Suopuro, CH_4–C concentration exhibited a linear relationship with flow ($P < 0.01$), which was not seen in Välipuro. DOC concentration behaved in a similar way to CO_2, with a decrease at both sites (dilution), and a marked recovery at Välipuro ($P < 0.01$), but not Suopuro. Although DIC concentrations increased in Välipuro during the study period, there was no apparent relationship with flow; POC concentrations remained low (≤ 1 mg l^{-1}) throughout the spring snowmelt period and showed no temporal trends. The pH of runoff in both catchments increased during the snowmelt period, the increase in Välipuro being more rapid than in Suopuro (Fig. 3c, d).

We used 2 methods to monitor streamwater CO_2 concentrations during the study; continuous measurement using Vaisala CO_2 sensors, and discontinuous spot sampling using headspace analysis; both methods are known to produce comparable results (Johnson et al. 2010). However, in this study we found that in both catchments CO_2–C concentrations measured using the two different methods diverged near the peak of the snowmelt hydrograph (Fig. 5). In both cases headspace CO_2 concentrations were consistently higher for a period of 13 days, after which comparability in the 2 monitoring methods returned. The headspace method sampled water approximately 10 cm below the stream surface, whereas the CO_2 sensors were fixed 10 cm above the streambed throughout the study (sensor concentrations are adjusted to account for changes in water pressure as depth changes). At the start of the study period we assumed that the water column was initially well mixed, however as the divergence in calculated concentrations occurred during peak flow when the vertical separation between sampling points (headspace v sensor) was greatest, we conclude that CO_2 concentrations within the water column became stratified for a period of time until water levels dropped.

Hysteresis

Hysteresis in streamwater concentration/discharge relationships was examined with respect to all the different carbon species in both study catchments (Fig. 6). A linear response whereby solute concentrations increase/decrease on the rising limb, and decrease/increase at the same rate on the falling limb, are rare in peatland catchments (Evans and Davies 1998). Carbon dioxide concentrations measured using

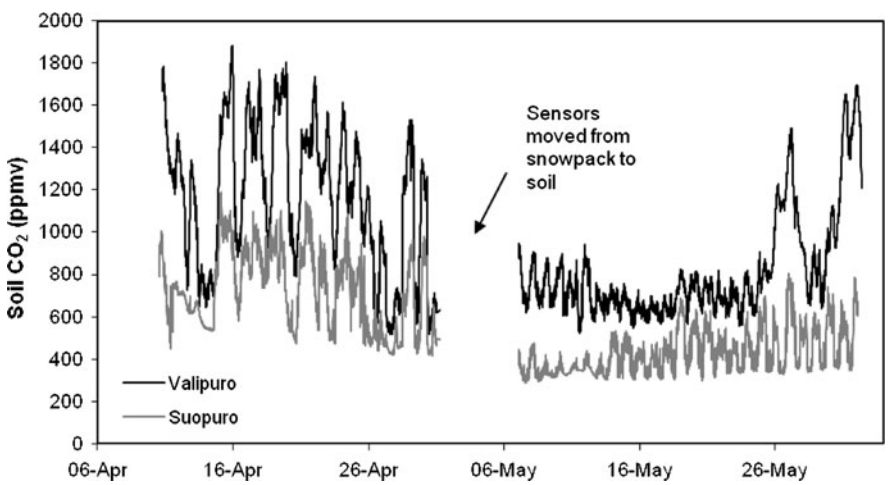

Fig. 4 Temporal changes in snow and soil CO_2 concentrations during the 2008 spring snowmelt event. Sensors were moved from the snow to soil (5 cm depth) after the snow pack disappeared

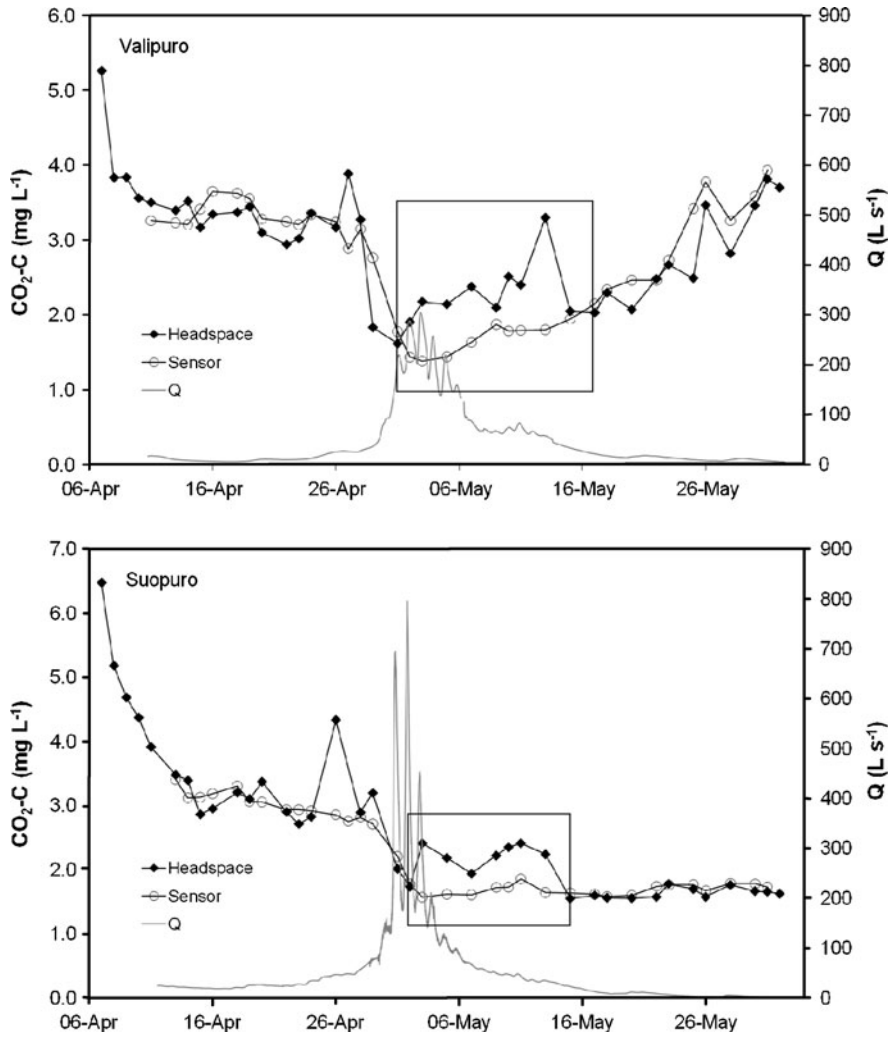

Fig. 5 Comparison of the two methods (headspace v continuous sensor) used to measure CO_2 concentrations in Välipuro and Suopuro; the inset highlights the period of time in which concentrations diverged during and after peak snowmelt

both methods (continuous sensor and headspace) exhibited hysteresis, with the sensor characterised by a clear clockwise loop and the headspace a more complex 'figure-of-8' loop (Fig. 6a–d). The starting and finishing shape and direction of the headspace 'figure-of-8' loop were consistent with the sensor plot, however the CO_2 concentrations rose late in the hydrograph coinciding approximately with peak flow. The hysteresis plots of DOC for the 2 catchments (Fig. 6e, f) were the same shape as those shown by the CO_2 sensors. In Välipuro the start and finish of the loop almost coincide; this is not repeated in Suopuro as DOC concentrations do not return after the snowmelt event to the original concentrations, but remain low. For CH_4 (Fig. 5g, h) and POC (data not shown) there was no clear pattern in either catchment.

Carbon Fluxes

We calculated the export of each carbon species during snowmelt using Walling and Webb (1985) Method 5; this method uses concentration data from spot samples alongside the continuous flow record to obtain an export value from each catchment within the 2-month sampling period (Table 3). The long-term average TOC (1978–2008) and TIC (2007–2008) fluxes were calculated from mean monthly export values provided by SYKE. In both catchments measurement of POC concentration over the spring snowmelt period showed that it comprised 3.6% of TOC; we used this value to estimate DOC and POC concentrations and fluxes from the SYKE long-term TOC data. TIC is assumed to equal DIC. Dissolved

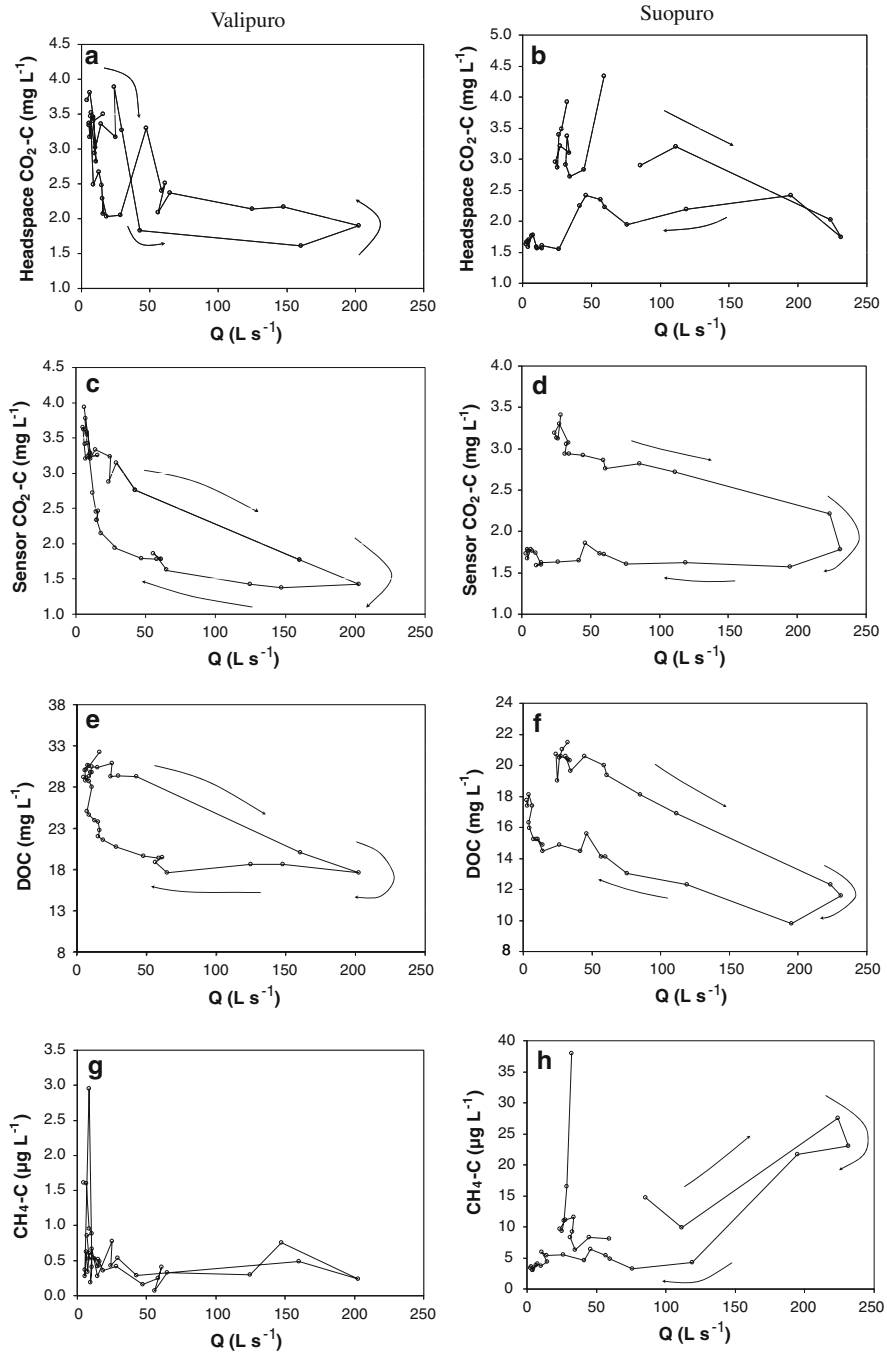

Fig. 6 Concentration (*Y* axis) discharge (*X* axis) relationships showing hysteresis in headspace CO_2 (**a**, **b**), sensor CO_2 (**c**, **d**), DOC (**e**, **f**) and CH_4 (**g**, **h**) concentrations during the 2008 spring snowmelt period in Välipuro and Suopuro

CO_2, CH_4 and N_2O concentration data were not collected by SYKE.

The long-term (1978–2008) annual export rates of DOC, POC and DIC from Välipuro were 10.5 ± 0.68, 0.39 ± 0.03 and 1.30 ± 0.28 g C m^{-2} yr^{-1}, respectively; in Suopuro the equivalent values were 7.02 ± 0.48, 0.28 ± 0.02 and 1.28 ± 0.9 g C m^{-2} yr^{-1}. Carbon fluxes were therefore higher from Välipuro compared to Suopuro for DOC and POC. Downstream export of C during the 2-month snowmelt study was dominated by DOC; mean export in both catchments during the 2-month snowmelt period was more than

Table 3 Mean monthly export of carbon and greenhouse gases during the 2008 snowmelt period and annual 2008 values ($n = 11$, monthly concentration data supplied by SYKE)

Export (g m^{-2} $month^{-1}$)	Välipuro		Suopuro	
	Snowmelt	2008	Snowmelt	2008
CO_2–C[a]	0.25 (±0.14)		0.24 (±0.26)	
CO_2–C[b]	0.31 (±0.03)		0.28 (±0.01)	
CH_4–C[b]	0.00009 ($\pm 0.2 \times 10^{-6}$)		0.0016 ($\pm 3.8 \times 10^{-8}$)	
DOC	2.87 (±1.91)	1.29 (±2.12)	1.78 (±0.94)	0.66 (±0.41)
DIC	0.37 (±0.02)	0.07 (±0.32)	0.12 (±0.01)	0.06 (±0.04)
POC	0.15 (±0.002)	0.05 (±0.03)	0.11 (±0.002)	0.02 (±0.01)
N_2O–N[b]	0.00007 ($\pm 1.0 \times 10^{-9}$)		0.0001 ($\pm 1.0 \times 10^{-9}$)	

Walling and Webb (1985) Method 2 was used to calculate export fluxes for the continuous sensor CO_2–C data, Method 5 for all other variables

[a] Refers to values derived from sensor CO_2–C concentrations

[b] Refers to values derived from headspace concentrations, ± is the standard error

3× the long-term (1978–2008) average and more than double the monthly average for 2008 as a whole (Table 3; Fig. 7). Likewise POC and DIC export was significantly higher during snowmelt (<5×) than either the long-term or 2008 annual monthly averages. Lateral downstream fluxes of CO_2 during the snowmelt period were comparable using both methods (sensor and headspace) and equivalent to an annual export of 3.1–3.8 and 2.9–3.4 g C m^{-2} yr^{-1} for Välipuro and Suopuro depending on the method used. Downstream fluxes of CH_4 and N_2O were insignificant. Mean CO_2 evasion fluxes calculated from spot measurements ($n = 36$) using chambers during the 2-month spring snowmelt event for Välipuro and Suopuro, were 69.2 ± 6.21 (range: 5.64–173) and 68.6 ± 8.05 (9.44–216) μg C m^{-2} s^{-1}, respectively.

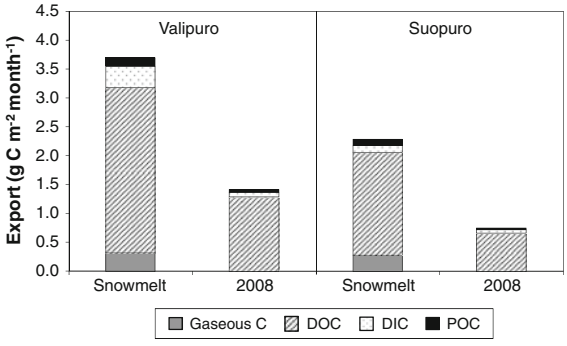

Fig. 7 Comparison of spring snowmelt C fluxes with annual 2008 values for Välipuro and Suopuro (units are g C m^{-2} $month^{-1}$). Dissolved gas concentrations are only available from the spring 2008 snowmelt period. Errors associated with individual fluxes are shown in Table 3

Discussion

Concentration changes during the snowmelt period

We recorded the highest concentrations of gaseous C at the beginning of the study which we interpret as evidence for release of CO_2 and CH_4 which had accumulated beneath the ice and snow pack within the stream system. Whilst CO_2 and CH_4 build up and release have been recorded from frozen lakes (Striegl and Michmerhuize 1998; Striegl et al. 2001; Kortelainen et al. 2006b; Juutinen et al. 2009) and pCO_2 has been observed to decrease after ice melt in lakes (Anderson et al., 1999), this to our knowledge is the first time that it has been seen in peatland streams. Our snow CO_2 sensor measurements imply that CO_2 storage occurs within the snow pack (reduced diffusivity and higher tortuosity), with the stream network providing a pathway for release.

The 2008 spring snowmelt event in Välipuro and Suopuro resulted in a significant dilution in DOC and dissolved CO_2 concentrations, which during May recovered in Välipuro, but not Suopuro. This suggests that initially relatively DOC- and CO_2-poor source water (probably snowmelt) was diluting the streamwater, and that recovery was much slower in Suopuro

because of source limitation. Other studies in arctic and boreal regions have also found significant changes in DOC concentrations during spring snowmelt. In northern Sweden Laudon et al. (2004), Cory et al. (2006) and Buffam et al. (2008) all observed that concentrations increased with increased flow, although Hruška et al. (2001) observed both de/increase in concentration depending on location within the catchment. High DOC concentrations have also been observed during the spring snowmelt period in the Yukon River Basin in NW Canada and Alaska (Striegl et al. 2005; Striegl et al. 2007), consistent with flushing of watershed DOC unaffected by microbial degradation. A positive relationship between DOC/TOC concentration and flow during the spring snowmelt event has been explained by a shift in hydrological pathway from deeper (mineral-rich) to shallower (organic-rich) horizons (Buffam et al. 2008) and this may also be linked to preferential flow through organic-rich riparian soils in forested catchments (Laudon et al. 2004). These hydrological changes are very similar to those occurring in unfrozen peats and organic mineral soils during storm flow, when increased DOC concentrations result from the transport of mobile DOC by near surface throughflow (e.g. Koehler et al. 2009). In Välipuro and Suopuro surface horizons were still frozen so no interaction with organic-rich soils occurred until after the soil had thawed. Decreases in DOC/TOC concentration with flow have been explained by dilution with snowmelt, which may be more common in unforested wetlands where surface flow occurs over ice and frozen soil (Schiff et al. 1998; Laudon et al. 2004). In contrast (to DOC), POC, DIC and CH_4 concentrations exhibited no clear response to the snowmelt event.

Dilution of CO_2 in response to high rainfall events has also been observed in a peatland stream (Dinsmore and Billett 2008). These authors showed that by removing the effect of dilution and estimating additions and losses of CO_2, that both surface peat CO_2 inputs into the stream and evasion loss during stormflow were important. In Välipuro and Suopuro we found that during and just after the main spring flow event the outflows of both catchments became stratified with an upper layer of faster flowing, CO_2 enriched water (Fig. 5). This would suggest an additional input of water containing high concentrations of CO_2 (relative to streamwater) from either overland flow or through-flow near the soil surface. The shape of the channel during the high snowmelt peak, when water rises beyond the natural channel and spreads over the riparian zone (overbank flow), appears to result in incomplete mixing within the water column.

The different concentration/discharge (C/Q) hysteresis plots observed from the sensor and headspace CO_2 concentrations (Fig. 6), also point towards an additional input to the surface water layer. Clockwise loops, such as those seen in the deep water sensor concentrations, have been produced theoretically using a model based on 2 source water components, where the concentration of the pre-event water is greater than the concentration of the event water (i.e. the initial snowmelt water) (Evans and Davies 1998). The 'figure-of-8' shape, also observed in storm flow water by Dinsmore and Billett (2008), is the result of an increase in CO_2 concentration late on the rising limb of the hydrograph; in Dinsmore and Billett (2008) this was attributed to variable source areas within the catchment and the arrival of a third component of CO_2-rich water from a deep peat source. Given that the additional input occurred only in the surface water, it is likely to be either tapping water from near the soil surface or result from high concentrations of dissolved CO_2 trapped within the packed snow associated with a higher snow pack $epCO_2$ value.

The C/Q hysteresis loops produced from the DOC concentrations (collected from the water surface) followed a similar pattern to deep water CO_2. Considering DOC alone, we would predict a 2 component model of source water, however, from the CO_2 concentration data we know that 3 separate water sources are contributing to surface stream water concentrations. Hence the third component, the water which appears to arrive late on the rising hydrograph limb, appears to contain high concentrations of CO_2 and relatively low DOC. Near-surface throughflow should contain significant amounts of DOC hence the water is most likely originating from the snow pack itself. Here we suggest that the snow pack contains 2 distinct layers, a loose packed surface layer, the first to melt as temperatures increase which contains very little C, and a deeper packed layer which melts later and appears to contain little DOC but high concentrations of trapped CO_2.

Carbon fluxes during the snowmelt period

Annual export values of DOC from northern peatlands are of the order of 20 g C m^{-2} yr^{-1} (Billett et al. 2004); this compared to a long-term (1978–2008) mean annual export of 10.5 and 7.02 g C m^{-2} yr^{-1} and an export in 2008 of 15.5 and 7.9 g C m^{-2} yr^{-1} for Välipuro and Suopuro, respectively. TOC export values from Suopuro are close to other Finnish catchments, whereas Välipuro values are among the highest recorded in Finnish catchments (Kortelainen et al. 1997; Kortelainen et al. 2006a). Monthly carbon export from the catchments during the snowmelt period was considerably higher than the average annual monthly values (Table 3) and in 2008 was 37% and 45% of the annual DOC load. These high spring export values are consistent with other studies which found that the 4 week spring snowmelt period in northern Sweden contributed 50–68% of annual TOC export (Laudon et al. 2004); at 5 gauging stations in the Yukon River Basin the 2-month spring flood accounted for 35–63% of the annual downstream DOC flux (Striegl et al. 2007). Half of the annual runoff and export of TOC in 22 headwater Finnish catchments located from the south to the Arctic Circle occurred in spring, although this period represented only 10–15% of the whole year; interannual variation among peatland catchments was significantly higher compared to forest catchments (Kortelainen et al. 1997).

The 8 days (29th April to 7th May) of extremely high flows when air temperature increased rapidly from daily highs of 12 to 25°C, accounted for 61% and 63% of the spring snowmelt runoff in the 2 catchments, respectively. During this 8 day period 16% of the annual DOC export in Välipuro occurred; 18% in Suopuro. Combining DOC, POC and DIC (CO_2 and CH_4 data not available for full year), we estimate that at least 17% and 19% of the total annual aquatic C export occurred during this 8 day period in Välipuro and Suopuro, respectively. Hence, studies that consider only the growing season, and fail to accurately measure snowmelt export are likely to significantly underestimate annual aquatic C losses.

Evasion of CO_2 from the stream surface is also likely to be an important loss term during the snowmelt period, although estimating the magnitude of the flux in this case is difficult because of the variability in the measurements. This is partly due to the difficulty in applying the chamber method to small, fast-flowing streams, and also to the extreme variability in flow rates. Given the known problems associated with applying the chamber method to small streams (Billett and Moore 2008), calculated evasion rates are likely to significantly underestimate actual evasion fluxes. However, our data from Välipuro and Suopuro are comparable or higher than other chamber measurements from flowing water (Hlaváčová et al. 2006; Billett and Moore 2008). Since CO_2 concentrations in both catchments are high (Fig. 5) it is likely that evasion to the atmosphere is a significant flux term, which becomes increasingly more important as the stream system is progressively exposed during the melting event.

Effect of drainage and forest management on peatlands

The Välipuro and Suopuro study catchments are part of a much larger, long-term study of the affects of afforestation on water quantity in the North Karelia region of E Finland (Ahtiainen et al. 1988; Ahtiainen and Huttunen 1999; Kortelainen et al. 2006a; Sarkkola et al. 2009; Rantakari et al. 2010). The study has shown that forestry operations increase runoff and leaching of dissolved N and P and especially solids, but the effects can be diminished by using water protection methods like vegetated buffer zones and sedimentation ponds (Ahtiainen and Huttunen 1999; Mattsson et al. 2006). Lepistö et al. (1995) and Kortelainen and Saukkonen (1998) have shown that clear differences in spatial variability in stream water chemistry are only shown by large scale differences in forestry operations.

There is a significant literature on peatland drainage (reviewed by Holden et al. 2004) showing that lowering the water table increases DOC production and losses from catchments. High drainage density is often associated with the largest sources of DOC (Mitchell and McDonald 1995). Models of the long-term effect of drainage suggest that it initially increases DOC export by 10–33% (Worrall et al. 2007). Our study showed that although a similar amount of water (per unit area) was released from both catchments, the drained site (Suopuro) showed a much flashier hydrological response with peak flows in early May almost three times greater than Välipuro. Concentrations and fluxes of all carbon species,

with the exception of CH_4, were consistently higher from Välipuro (control catchment) compared to Suopuro (drained catchment). The differences in snowmelt fluxes were also reflected in the long-term data and in individual years. In 2007 for example, Rantakari et al. (2010) estimated TOC fluxes for Välipuro and Suopuro of 13.6 and 10.1 g C m^{-2} yr^{-1}, respectively. Välipuro was also characterised by colder water temperatures (after the spring snowmelt event), higher pH and conductivity. In terms of streamwater DOC and CO_2, concentrations return much quicker to their higher pre-event levels in Välipuro compared to Suopuro. We therefore observed clear differences between the control and drained sites in terms of hydrological response to the 2008 spring snowmelt event. In addition, there were significant differences in carbon concentrations and fluxes between the 2 catchments which are discussed below.

The differences in runoff response and temperature between the 2 catchments can only partly be explained by ditching, which in the lower parts of the Suopuro catchment results in rapid flushing of the system leading to a depletion in mobile DOC and CO_2 pools and a greater lag time in terms of recovery in concentration. The importance of groundwater in the undrained Välipuro catchment is clearly demonstrated by colder water temperatures post-flood event and groundwater would appear to play an important role in not only "buffering" the snowmelt hydrograph in Välipuro, but also maintaining higher pH and conductivity values. The comparability of streamwater and soil temperatures at Suopuro throughout the 2-month study suggests that (compared to Välipuro) streamwater temperature is more influenced by snow cover and atmospheric temperature changes, suggesting that shallow, near-surface water is the dominant hydrological pathway.

The occurrence of higher concentrations and fluxes of DOC, POC, DIC and CO_2 from the control catchment compared to the drained forested peatland catchment (Fig. 7) disagrees with much of the literature, which shows that disturbance accelerates carbon loss from peatlands. Whilst ditching has been found to result in a short-term increase in organic carbon concentrations, in the long-term ditching lowers the groundwater level and can result in decreased TOC export (Hovi 1988). However, Sallantaus (1994) found no difference in TOC export between natural fen, natural bog, drained fen and drained bog several years after drainage.

In the case of Välipuro and Suopuro it appears that the differences are caused by intrinsic differences in catchment characteristics such as source areas or flow paths from soil to stream. A previous study (Hovi 1988) considering the effect of drainage on DOC, showed that concentrations in Suopuro rose from 27.8 to 35.7 mg l^{-1} between 1983 and 1984 when the drainage ditches were first cut. Over the same period, concentrations in Välipuro remained stable, dropping only slightly from 38.9 to 38.1 mg l^{-1} (Hovi 1988). In 2008 base flow DOC concentrations in Suopuro were less than in the pre-drainage year at $\sim$20 mg l^{-1}, however at Välipuro DOC concentrations were also lower at $\sim$30 mg l^{-1}. The Välipuro catchment therefore has naturally higher DOC concentrations and it was only during the drain cutting years that DOC concentrations at Suopuro increased above those at Välipuro; 24 years later the runoff at Suopuro has much lower DOC concentrations compared to 1983. The average annual mean TOC export from Välipuro and Suopuro (before ditching) has been estimated to be 12 g and 7.3 C m^{-2} yr^{-1}, respectively (Kortelainen et al. 2006a). Thus ditching is not the major driver of differences in DOC export between Välipuro and Suopuro. Clearly peatland disturbance in now much less of an issue in Suopuro than it was in the past and it appears that Välipuro has always been a groundwater fed peatland stream characterised by high DOC and CO_2 concentrations and fluxes. This is consistent with the presence of CO_2-rich groundwater in other peatland catchments (Billett et al. 2007; Dinsmore and Billett 2008).

In contrast to other C species streamwater CH_4 concentrations were 10× higher in Suopuro compared to Välipuro. The most likely reasons for this are (1) Suopuro originates in a small pool and has a higher area of peatland compared to Välipuro, and (2) the drainage of the peats in Suopuro provides connectivity between a large CH_4 store and the drainage network; this is absent from the undrained catchment.

Conclusions

Our results confirm that in northern boreal and arctic regions snowmelt is the most important period of C export from peatland catchments. Accurate

quantification of fluxes requires a flexible approach to monitoring and, because of the difficulty of making measurements during the spring period, it is likely that many export values from northern regions underestimate the true C flux.

We found that whilst catchment management did not affect water yield during the 2008 flood event, it did affect the hydrological response. In addition we found that DOC and CO_2 returned to their pre-event (higher) concentrations much faster in the undrained compared to the drained catchment.

Over the period 1979–2006 a rise in streamwater TOC concentrations (but not flux) has been observed in peatland catchments (including Välipuro and Suopuro) in E Finland and this change has been attributed to a rise in water temperature (Sarkkola et al. 2009). Since one of the main affects of warming in the cold regions of N Europe is likely to be a shift in the timing or magnitude of the spring flood event, it is interesting to speculate on what effect this might have on annual C export. Our flux calculations and those of others (Laudon et al. 2004; Striegl et al. 2007) suggest that 35–70% of DOC export occurs during the snowmelt period; hence reducing or removing the snow cover period might therefore appear to cause significant changes in annual DOC fluxes. In Välipuro and Suopuro 37–45% of the annual DOC flux was estimated to have been lost during the 2008 snowmelt event. Interestingly 40% of the annual precipitation in the region falls as snow, suggesting that the amount of water, stored in and then released from the snow pack, generates the equivalent DOC flux to rainfall derived runoff. We therefore conclude that a change in the magnitude of the spring flood event is unlikely to affect annual DOC export from these peatland catchments.

Here we present some of the first stream CO_2 data from forested peatland catchments. Concentrations and downstream fluxes are high compared to unforested peatland streams (Billett et al. 2004; Dawson et al. 2004; Dinsmore et al. 2010); even during the highest periods of flow minimum concentrations are still $\sim$1.5–2.0 mg C l^{-1}. This could be a consequence of conifer root respiration indicated by high subsurface snow pack and soil CO_2 concentrations measured at the 2 sites during the study period. The extremely high CO_2 (and CH_4) concentrations measured at the catchment outlets prior to snowmelt, show that the spring flood is not only a major DOC export event, but also a major period of aquatic gaseous C release. Whilst quantifying downstream DOC fluxes is relatively straightforward with the appropriate sampling frequency and methods, quantifying the fluxes (including the evasion term) of CO_2 and CH_4 released from these peatland systems during the spring snowmelt event still represents a significant research challenge.

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