Biogeosciences

Dissolved organic carbon dynamics in a UK podzolic moorland catchment: linking storm hydrochemistry, flow path analysis and sorption experiments

M. I. Stutter, S. M. Dunn, and D. G. Lumsdon

The James Hutton Institute, Craigiebuckler, Aberdeen, UK

Correspondence to: M. I. Stutter (marc.stutter@hutton.ac.uk)

Abstract. Better knowledge of spatial and temporal delivery of dissolved organic carbon (DOC) in small catchments is required to understand the mechanisms behind reported long-term changes in C fluxes from some peatlands. We monitored two storms with contrasting seasons and antecedent conditions in a small upland UK moorland catchment. We examined DOC concentrations and specific UV absorbance (SUVA at 285 nm), together with solute concentrations required to undertake end-member mixing analyses to define dominant flow paths contributing to streamflow. This was combined with laboratory soil-solution equilibrations. We aimed to resolve how seasonal biogeochemical processing of DOC and flowpath changes in organo-mineral soils combine to affect DOC exported via the stream. An August storm following a dry period gave maximum DOC concentration of $10\,\text{mg}\,\text{l}^{-1}$. Small DOC:DON ratios (16–28) and SUVA (2.7–$3.61\,\text{mg}^{-1}\,\text{m}^{-1}$) was attributed to filtration of aromatic compounds associated with up to 53 % B horizon flow contributions. This selective filtration of high SUVA DOC was reproduced in the experimental batch equilibration system. For a November storm, wetter antecedent soil conditions led to enhanced soil connectivity with the stream and seven times greater DOC stream-load (maximum concentration $16\,\text{mg}\,\text{l}^{-1}$). This storm had a 63 % O horizon flow contribution at its peak, limited B horizon buffering and consequently more aromatic DOC (SUVA 3.9–$4.51\,\text{mg}^{-1}\,\text{m}^{-1}$ and DOC:DON ratio 35–43). We suggest that simple mixing of waters from different flow paths cannot alone explain the differences in DOC compositions between August and November and biogeochemical processing of DOC is required to fully explain the observed stream DOC dynamics. This preliminary evidence is in contrast to other studies proposing hydrological controls on the nature of DOC delivered to streams. Although our study is based only on two storms of very different hydrological and biogeochemical periods, this should promote wider study of DOC biogeochemical alteration in headwaters so that this be better incorporated in modelling to predict the impacts of changes in DOC delivery to, and fate in, aquatic systems.

1 Introduction

The loss of dissolved organic carbon (DOC) from soils to waters is a critical process in C cycling within upland environments and influences geochemical and biological conditions in receiving aquatic ecosystems. There have been widespread and numerous reports of, and attempts to explain, increasing (and sometimes decreasing) DOC concentrations in surface waters in the US, Canada and Europe (Worrall et al., 2004; Skelkvåle et al., 2005; Monteith et al., 2007). In a recent paper Morel et al. (2009) give three main reasons why examining the delivery of DOC to streams from their catchments during storm events is a critical part of furthering these explanations: (i) that the majority of DOC is exported during storm events, (ii) that event-duration (i.e. hourly) changes in DOC concentrations gives insight into DOC delivery, and (iii) enables understanding and models of DOC sources and flow-paths to be developed. We briefly review the background to studying storm events in small peatland catchments. We also suggest that evaluating the composition as well as concentration of DOC is crucial to understanding the fates and impacts

of the DOC in the stream and may provide an additional parameter discriminating DOC sources and interactions during transport.

The presence of organo-mineral soils in moorland catchments contributes strongly to streamwater DOC variability in space and time (Stutter et al., 2006, 2009) and brings contrasting DOC dynamics to peat-dominated catchments (Clark et al., 2008). In deep peat systems large stream DOC concentrations at moderate flows may become diluted by direct rain inputs as flows increase (Clark et al., 2008). These event waters are rapidly transferred to streams due to the poor infiltration of the peat matrix, or from macropore flows, now recognised as including "peat pipes" (Holden, 2006). For organo-mineral soil landscapes increases in DOC concentrations with discharge are attributed to flushing of organic rich surface soils as they rewet. Conversely, between rain events, surface soils become isolated from active flow pathways and deeper, mineral flowpaths prevail. Subsoil flowpaths generally have reduced DOC concentrations due to sorption interactions with mineral surfaces (Ussiri and Johnson, 2004). These interactions result in changes in different properties to the DOC reaching the stream during inter-event and baseflow conditions.

The quantity and composition of DOC that is observed in soil solutions and runoff depends on the interactions of a range of biotic and abiotic mechanisms which govern its production and transport (Kalbitz et al., 2000). Biological decomposition of litter and humified soil organic matter is a fundamental process driving solubilization of macromolecular forms of DOC, such as fulvic and humic acids, as well as simpler molecules from microbes and vegetation. The production and subsequent transport of potentially soluble organic compounds show strong patterns of seasonality related to temperature, rainfall patterns and soil moisture cycles (Lumsdon et al., 2005). The DOC released from soils may be modified during transport to the stream, depending on flow path routing and residence times (Worrall et al., 2002). These flow paths in turn affect residence time, sorption interactions with soil surfaces and mixing with DOC from different water sources during transport and are strongly dependent on the spatial distribution of catchment soils in three dimensions (Aitkenhead et al., 1999; Dawson et al., 2004; Stutter et al., 2006). Catchment DOC sources are often studied through analysis of stream hydrochemical changes during storms, when the dominant exports of stream DOC occur (Hinton et al., 1997, 1998). However, it is less common to compare storm periods with contrasting antecedent conditions when certain biogeochemical and transport processes affecting DOC may combine to give contrasting delivery of DOC.

Our premise is that to improve understanding of the nature of DOC delivered to streams requires integrated knowledge of transport and biogeochemical factors taken together. Transport processes include DOC sources within different landscape units (McGlynn and McDonnell, 2003; Jensco and McGlynn, 2010) and the connectivity of these units with changing hydrology (Dunn et al., 2006; Laudon et al., 2011). Biogeochemical processes include a range of geochemical (sorption and alteration of DOC by contact with soil surfaces) as well as biological (for example, microbial processing and plant exudation) interactions. Such processes together give a changing signal of DOC amount and composition between source soils (Scott et al., 2001; Stutter et al., 2007a, b) and during transport to the stream (Kaiser and Guggenberger, 2005; Hagedorn et al., 2000; Hood et al., 2006). In this study we employ a combination of techniques, examining: (i) DOC concentrations and simple compositional indicators (C-normalised UV Analysis, DOC:DON ratios), (ii) storm concentration vs. discharge hysteresis, (iii) an end-member mixing model elucidating flow pathway contributions to stream flow, and (iv) laboratory sorption equilibrations to characterise interactions between DOC-rich surface waters and subsoil taken from the catchment. We aimed to investigate how seasonal changes in biogeochemical processing of DOC and in changes in flow paths and catchment response to wetting combine to control concentrations and compositions of DOC exported over two storms at different times of year. Morel et al. (2009) concluded that DOC delivery in a small catchment was a product of hydrological processes alone. Instead we hypothesise that, between seasons, simple mixing of waters between flow paths is insufficient to explain variation in the DOC exported and biogeochemical processing must be considered.

2 Data and methods

2.1 Study site

Streamwaters and soil solutions were sampled in the $1 \, \text{km}^2$ headwater of the Cairn Burn draining the SE fringe of the Grampian Mountains (56°54′ N, 2°33′ W; Fig. 1), part of the Glensaugh UK Environmental Change Network (ECN) site (http://www.ecn.ac.uk/sites/glens). The Cairn Burn catchment (NE Scotland) has been the focus of a number of investigations into hydrological flowpaths (Dunn et al., 2006) and DOC properties in soil solutions (Lumsdon et al., 2005; Stutter et al., 2007a). Average annual precipitation is 1115 mm at 300 m altitude (2004–2006). The catchment lies north of the Highland Boundary fault on coarse Dalradian acid schist drifts over the altitude range 250–455 m. The soils (Table 1; Fig. 1b; Strichen Association; Glentworth and Muir, 1963) comprise hill peat (>50 cm) on upper, gentle slopes covered by *Sphagnum* sp. and *Eriophorum vaginatum* (hair's-tail cottongrass). Peaty podzols on intermediate slopes (average organic horizon depth 25 cm) have developed in thin glacial till vegetated by *Calluna vulgaris* (heather), *Vaccinium myrtillus* (blaeberry), *Deschampsia flexuosa* (wavy hair-grass) and *Nardus stricta* (mat-grass). Freely drained humus-iron podzols (average organic horizons depth 15 cm)

Table 1. Soil types in (a) the whole catchment and (b) channel margins (defined as 10 m strips adjacent to the stream channel).

		Soil type area coverage (%)				
	Area (km^2)	Peat	Mineral alluvium	Peaty Podzol	Peaty Gleysol	Humus iron Podzol
(a) Whole catchment	0.97	40	1	42	14	3
(b) Channel margins	0.03	<1	7	15	70	7
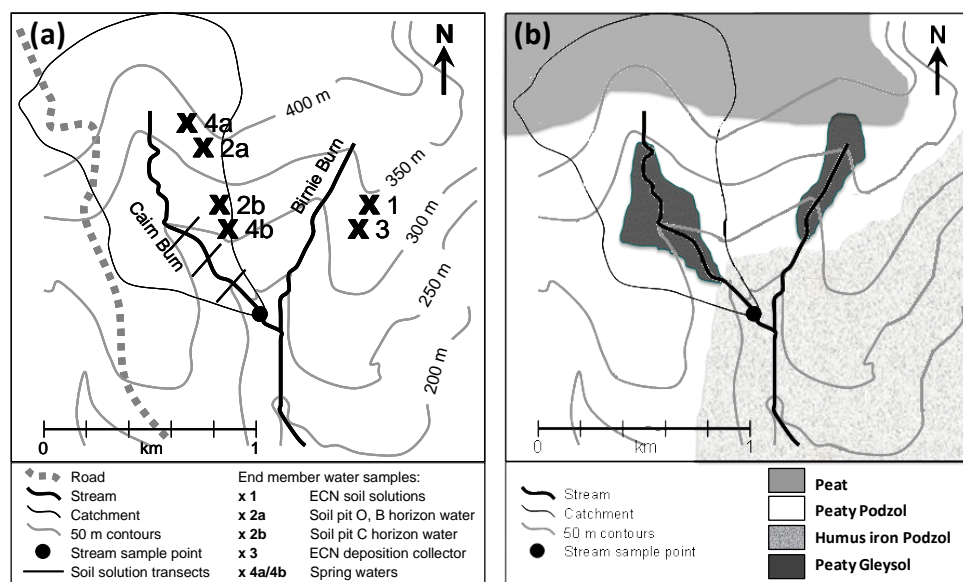
Fig. 1. (a) Catchment location, drainage network, stream and source water sample locations and **(b)** soil distribution.

occupy steeper slopes covered by *C. vulgaris* and *V. myrtillus*. Peaty gleys occupy flatter areas bordering the streams. Land use is limited to rough grazing for sheep (stocking density 100 sheep km^{-2}) and heather management, which includes rotational controlled burning (approximately a twelve year cycle of burning). Peaty podzols have deeper organic horizons (20–50 cm) than humus iron podzols (10–20 cm) and under the Scottish taxonomy system peats are organic material >50 cm. Typical C contents of organic surface horizons of peats, peaty- and humus iron podzols are 450, 300 and 190 mgC kg^{-1}, respectively.

2.2 Catchment hydrology

Stream flows were derived from 15 min stage height measurements over a pre-calibrated flume. The UK Environmental Change Network (ECN) operates a site comprising soil solution samplers, soil moisture, precipitation amount and bulk deposition collector on a broad ridge site 700 m east of the study catchment with peaty to humus iron podzols (sites 1, 3; Fig. 1). Although outside of the study catchment, this is on the same dominant podzol soil type and similar altitude. Soil moisture was measured every 30 min (Theta probes, Delta-T Devices, Cambridge, UK). Measure-

ments were made according to the ECN protocols (http://www.ecn.ac.uk/protocols/index.asp).

2.3 Streamwater sampling

Routine streamwater samples were collected approximately weekly ($n = 98$) during October 2004 to November 2006 from the Cairn Burn in pre-rinsed HDPE bottles. During selected storms, additional streamwater grab samples were taken. These events occurred during August 2005 and November 2006 (hereby termed August-2005 and November-2006) and had contrasting antecedent conditions (Fig. 2). Samples were collected at time intervals ranging from one hour (during rapid flow rate change) to four hours in August-2005 ($n = 15$) and November-2006 ($n = 12$) storms. The storm in August-2005 followed an extended period of baseflow, whilst the storm in November-2006 occurred when soil moisture in the catchment was already substantially recharged after the autumn rewetting. The maximum discharge for the August-2005 storm ($41 \, \mathrm{s}^{-1}$) and November-2006 storm ($162 \, \mathrm{l s}^{-1}$) equalled the 7 percentile and 1 percentile flows, respectively, during the study period of October-2004 to November-2006. The antecedent flow conditions prior to the storms in August-2005 ($4 \, \mathrm{l s}^{-1}$) and
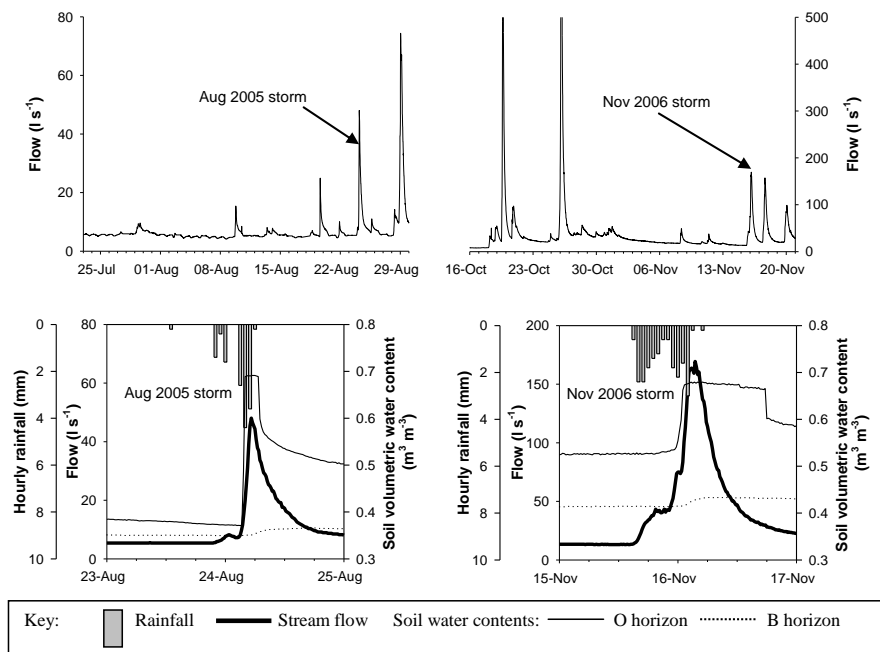
Fig. 2. Antecedent and storm event hydrological conditions.

November-2006 ($141 s^{-1}$) equalled the 86 percentile and 40 percentile flow conditions, respectively.

2.4 Characterisation of source waters contributing to stream flow

A number of catchment water sources (locations in Fig. 1) were sampled for comparison with streamwaters. (1) Soil waters were collected fortnightly (October-2004 to November-2006, at the site of soil moisture measurements) from O and B horizons of a podzol using tension lysimeters (Prenart Super Quartz, Frederiksberg, Denmark). To increase the spatial coverage of soil waters in the catchment, other soil waters were collected, as detailed below. (2) Gravity-draining soil waters were also collected from two podzol soil pits (2a and 2b) whenever flow occurred during monthly visits in 2007. Pits had open faces draining into bottles from gutters at the base of each horizon and were backfilled with inert plastic beads. Pit 2a gave samples from O ($n = 2$) and B horizons ($n = 3$) and pit 2b from the C horizon ($n = 12$). (3) Atmospheric inputs were characterised by chemical analysis of bulk deposition sampled weekly by the ECN (October-2004 to November-2006). (4) Two springs (denoted 4a, 4b) were sampled monthly through 2007 ($n = 13$ for each).

To investigate differences in DOC concentrations or compositions between riparian and hillslopes soils, surface solutions (0–10 cm depth) were collected using tension lysimeters (Rhizon Soil Moisture Sensors; Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands) during a one-off sampling in August-2005. Flat riparian areas (5–20 m width each

side of the stream) occur in the lower catchment and remain wet through summer periods. Three transects of soil solution samples were taken across the stream (Fig. 1a) with the following soil distributions: (i) hillslope peaty podzols and humus iron podzols ($n = 22$); and (ii) riparian peaty gleys ($n = 8$).

2.5 Hydrochemical analyses

pH was determined on unfiltered samples (Radiometer SAC90, Copenhagen, Denmark). Other analyses were conducted on samples filtered through 0.7 μm Whatman GF/F papers. Filtrates were analysed for UV absorbance (285 nm; Shimadzu UV240, Kyoto, Japan), major cations (ICP optical emission spectroscopy, Agilent 7500ce, Tokyo, Japan) and major anions (ion chromatography, Dionex DX600, Sunnyvale, California). Nutrient concentrations were determined by automated colorimetry (San++ analyser, Skalar, Breda, the Netherlands) for NO_3-N, NH_4-N, then for total dissolved N (TDN) and dissolved organic carbon (DOC) using an automated persulphate/UV digestion procedure, all according to the instrument manufacturer's standard methods. The colorimetric detection limits were 0.1, 0.01 and 0.001 mg l^{-1} for C, N and P, respectively. Dissolved organic nitrogen (DON) was calculated from the difference between TDN and (NO_3-N + NH_4-N). All sampling and analyses followed ECN protocols (http://www.ecn.ac.uk/protocols/index.asp).

Spectral absorbance of DOC is widely used to distinguish composition characteristics of DOM. Light absorbance by DOC is strongest in the UV region, approximately broad

and unstructured, and declines near-exponentially with increasing wavelength (Bricaud et al., 1981). A range of wavelengths have been related to compositional indicators by SUVA. These relationships include: 254 nm with percent aromaticity of DOC (Weishaar et al., 2003) and with biodegradability (Fellman et al., 2008), 260 nm with hydrophobicity (Dilling and Kaiser, 2002), 280 nm with binding constants (Chin et al., 1994), 285 nm with land use change (Kalbitz et al., 1999), 350 nm for discriminating soil and anthropogenic derived C (Spencer et al., 2007). Thacker et al. (2008) compared specific absorption values within this range, related to discharge variation in a peatland stream, and found that temporal variability in DOC was greater at 280 nm than 254 nm, but not as much as at 340 nm. SUVA values derived from the UV absorbance region have been directly related to aromatic contents associated with contributions of humic substances, as determined directly using ^{13}C-NMR (e.g. Weishaar et al., 2003). To discriminate DOC of differing compositions and link these to sources and flow paths, we used the measure of carbon normalized (specific) UV absorbance (SUVA) at 285 nm (hereby denoted as SUVA-285), as this has traditionally been used by our laboratory (Stutter et al., 2007a, b).

2.6 Analyses of water source contributions to streamflow by end-member mixing analysis

A three-component end-member mixing approach was used to distinguish the fractions of water contributing to streamflow by different flow pathways at different times. The analysis was based on a commonly applied method (see e.g. Sklash et al., 1986; Hooper et al., 1990; and see Jenkins et al., 1994 for presentation of the full equations), using two different hydrochemical tracers and encapsulated within a simple uncertainty framework. The equations for the mixing analysis are based on a mass balance of water and tracer and in this example were used to distinguish between waters sourced from the O horizon, B horizon and groundwater springs. The method requires that tracers are mass conservative and assumes that concentrations of the tracers are constant across the duration of the analysis. By graphical interpretation it was found that three end members adequately described streamwaters and hence two chemical tracers were required. Morel et al. (2009) show the benefits of using DOC as a tracer where it is the direct object of study. We also chose Si as being independent to DOC and defining a different set of flow paths. DOC is usually not considered ideal for analyses of this type as it is not a mass conservative tracer. However, over the duration of storm events biogeochemical processing is unlikely to cause any significant changes and DOC has been successfully used within mixing analyses in several studies (e.g. Ladouche et al., 2001; Katsuyama and Ohte, 2002; Morel et al., 2009). Over the longer 2-yr analysis the issue of mass conservation needs to be considered in interpretation of the results. Like the study of Morel et al. (2009) we incorporated variability in the DOC concentrations of the soil water end members by

(i) examining for differences between August and November concentrations of DOC in the source waters and using time-varying end members where differences were significant and (ii) by incorporating variation of the end members (via a Monte-Carlo approach) to define the 10 percentile and 90 percentile bounds of the end-member contributions. We also explored alternate use of SUVA-285 with either Ca, or Si as possible tracer pairs.

For this study, uncertainty in end-member values was included in the analysis by adopting a procedure similar to that presented by Bazemore (1994). Genereux (1998) compared this method with one based on general uncertainty propagation techniques and found that both methods gave similar results. The uncertainty analysis involved application of a Monte Carlo method to solve the three-component mixing equations 10 000 times. Values for the end members were randomly sampled from a normal distribution based on the mean and standard deviation of monitored data. In this way, the uncertainty in the values of the end members, resulting from spatial and temporal variability and laboratory analytical error, could be included in the analysis. The analysis was applied separately to the two storm events as well as the 2-yr weekly data using different distributions of end-member values for each application. The Monte-Carlo simulations were used to produce time-series estimates of the flow proportions sourced from the different soil horizons at different probability levels.

2.7 Analyses of concentration discharge hysteresis during storms

Over the course of the two storms patterns of concentration-discharge (C-Q) hysteresis in concentrations of DOC, major solutes and SUVA-285 were examined to support the results of mixing diagrams and analyses. This hysteresis occurs due to the cyclical nature of concentrations and stream discharge, whereby concentrations differ on the rising and falling hydrograph limbs at a given discharge (Evans and Davies, 1998). We describe hysteresis forms using the 3 stage descriptive process proposed by Evans and Davies (1998), giving six classifications (C1-3, A1-3; Table 2) according to:

 i. Rotational pattern (Clockwise, or Anticlockwise) – clockwise and anticlockwise hysteresis refer to concentrations that are greater, or lesser respectively on the falling limb of the hydrograph than rising limb at a given discharge.

 ii. Curvature (Convex, or Concave) – convex denotes that the entire curve forms a loop, whereas concave is used where all or a significant part of one limb is concave.

 iii. Trend (Positive, or Negative) – where a loop is described as "Concave" then it has an associated trend assigned, either positive or negative, denoting increasing or decreasing concentration with increasing discharge, respectively.

Table 2. Classification of concentration-discharge hysteresis loops after Evans and Davies (1998).

Classification	Rotation	Curvature	Trend
C1	Clockwise	Convex	N/A
C2	Clockwise	Concave	Positive
C3	Clockwise	Concave	Negative
A1	Anticlockwise	Convex	N/A
A2	Anticlockwise	Concave	Positive
A3	Anticlockwise	Concave	Negative
E	Figure of eight shaped		

On the basis of complex hysteresis shapes we included an additional class of figure of eight shape (denoted by E).

2.8 Soil-solution equilibration experiment

The soil-solution batch equilibrations investigated the modifying effect of contact between DOC enriched soil solutions from organic surface soils and mineral soil surfaces. Soil solutions were O horizon ECN piezometer soil solutions (source waters 1) pooled to gain sufficient volume into periods of winter (January–March), or summer (May–July). These solutions were fresh from the field with no processing except filtration. The solutions of natural DOC were equilibrated with a podzol Bs horizon sampled from the study catchment. This soil is the dominant mineral subsoil in all the sub-catchments (Table 1) and is the soil at the site of the ECN piezometers. The Bs soil has a high sorption capacity for DOC as indicated by the large reactive component of Al and especially Fe hydrous oxides (Table 3). Soil solutions from ECN piezometers were equilibrated (at 5 °C to limit microbial degradation of DOC) with air-dried, <2 mm sieved Bs soil (1 g:30 ml ratio). Equilibrations were performed in triplicate for times of 10, 60, 180 min and 1 and 3 days to test the effect of time of exposure to soil surfaces. DOC concentrations and SUVA-285 were determined for sample filtrates, blanks of soil with 0.001 M NaCl and soil solutions with no soil (included for each time point in triplicate). Soils of high C contents that have previously been air-dried are known to release large amounts of DOC when rewet due to C release from lysed cells and phyico-chemical disturbance of the soil during drying (Kalbitz et al., 2000). However, in our case we were equilibrating natural waters of high DOC contents with strongly sorbing soils with the aim of assessing uptake, not release. However, the effect of soil drying and rewetting on the release of a certain type of DOC and implications for resulting changes in SUVA-285 might be more important than for net DOC uptake in terms of mass.

3 Results

3.1 Catchment hydrology

The August-2005 storm followed a prolonged dry period with pre-event stream flow of $4 \, \mathrm{l \, s^{-1}}$ (Fig. 2). A total of 67 mm rainfall fell in the preceding month (6 % of annual total) and evapotranspiration at this time would have been high. The August-2005 storm was preceded by a minor rise in flow, then a sharp rise in response to 3 h of rain (maximum intensity $4.8 \, \mathrm{mm \, h^{-1}}$). Pre-event soil moisture indicated that O and B horizons were dry (0.38 and $0.34 \, \mathrm{m^3 \, m^{-3}}$ respectively), but O horizon soil moisture rose sharply during the event and then remained saturated (at constant $0.68 \, \mathrm{m^3 \, m^{-3}}$) for 5 h before a sharp decline. Prior to the November-2006, event two large storms (20 and 26 October) had already ended the period of summer drought. These wetter antecedent conditions in November-2006 (138 mm rainfall in the preceding month) gave pre-event stream flow of $14 \, \mathrm{l \, s^{-1}}$. The catchment was already wetted up with recharged soil moisture in O and B horizons (pre-event values 0.53 and $0.43 \, \mathrm{m^3 \, m^{-3}}$) and during the storm the O horizon remained saturated ($\sim 0.68 \, \mathrm{m^3 \, m^{-3}}$) for 18 h. The November-2006 storm had two shoulders before the peak in flow following 12 h less intense but continuous rainfall. Discharge totals for the August-2005 and November-2006 events were 1.5 mm and 5.7 mm, respectively (with discharge totals calculated for the periods shown in the plots in Fig. 2). The total event rainfall was 15 mm (August-2005) and 22 mm (November-2006), indicating that runoff delivered approximately 10 % and 25 % of the rainfall, respectively.

3.2 Changes in DOC and major ion concentrations during the storms

Time-series of solute concentrations are given in Fig. 3a and b for the August-2005 and November-2006 storms, respectively, with selected C-Q hysteresis plots in Fig. 4. Maximum DOC concentrations were greater for the November-2006 ($16 \, \mathrm{mg \, l^{-1}}$) than August-2005 ($10 \, \mathrm{mg \, l^{-1}}$) storm event. For both storms stream DOC concentrations (Fig. 3) were similar before storms ($\sim 2.5 \, \mathrm{mg \, l^{-1}}$), reached maximum DOC concentrations after the peak discharge and showed anticlockwise C-Q hysteresis (Fig. 4a). Hysteresis curves for DOC were classified as A1 and A2 types for August-2005 and November-2006 storms, respectively, indicating a more open form for August-2005 and flattened curve in November-2006 with convex loop form. A sharp rate of increase in DOC concentrations in August-2005 related to an intense rainfall and rapid discharge increase.

Compositional indicators for DOC showed strong differences between the storms. Following an initial drop in DOC:DON ratio early in the August-2005 storm, DOC:DON ratios increased to plateau on the August-2005 flow recession, but values remained considerably smaller throughout
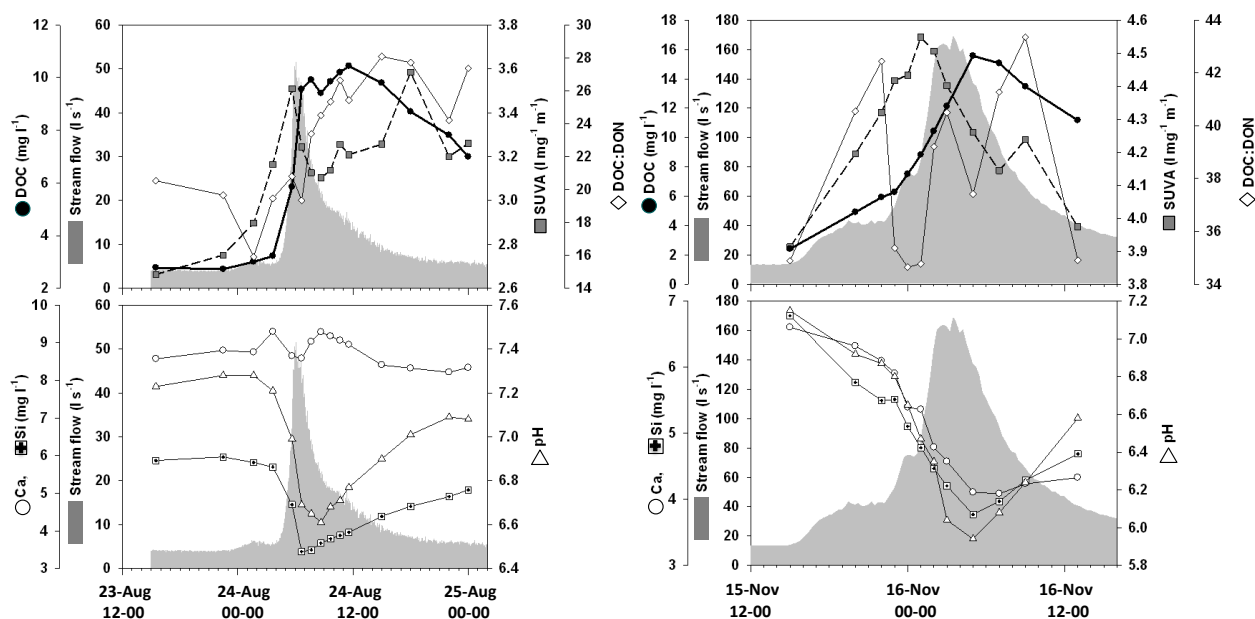
Fig. 3. Temporal change in flow and solute properties during storms in August-2005 **(a)** and November-2006 **(b)**.
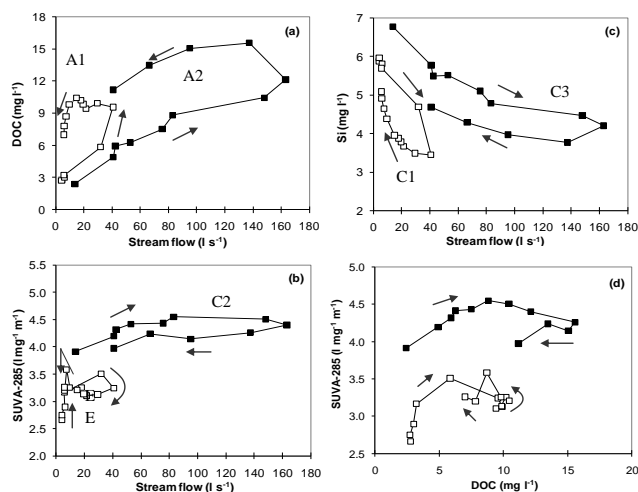

Fig. 4. Hysteresis in **(a–c)** solute properties against stream flow and **(d)** SUVA against DOC concentration for the August-2005 (white squares) and November-2006 storms (black squares). Arrows indicate the direction of hysteresis for storm data and curves are classified according to the scheme in Table 2.

the August-2005 storm (16–28) than during November-2006 storm (35–43). In November-2006 there were two periods of increased DOC:DON ratios: during the initial discharge rise and on the main discharge rise. C-Q hysteresis of DOC:DON was anticlockwise for both storms. The August-2005 storm had smaller SUVA-285 values (2.7–3.61 mg^{-1} m^{-1}) than the November-2006 storm (3.9–4.51 mg^{-1} m^{-1}). For both storms SUVA-285 increased from early in the storm and

peaked prior to maximum discharge. In November-2006 SUVA-285 declined rapidly during recession, whilst in August-2005 attained a second, greater peak when discharge had returned to near baseflow. This led to flattened C2 type hysteresis in November-2006, with a dominantly clockwise but figure of eight shape in August-2005. Hysteresis of SUVA-285 against DOC (Fig. 4f) showed that the maximum SUVA was attained much earlier relative to maximum DOC concentrations in November-2006 than August-2005.

We depict concentration changes of selected inorganic solutes (Figs. 3 and 4) to help infer changes in flow paths in support of the DOC analyses. The pH, initially similar prior to both storms (Fig. 3; pH 7.2), declined to smaller values and with greater tailing in November-2006 (pH 5.9) than in August-2005 (pH 6.6). Change in pH could show the greater contribution of organic acids from humic substances of hillslope O horizon flushing in November-2006, although we do not have charge balance nor modelling data to support this. Si and Ca concentrations are subsequently used to define endmember compositions. Si showed clockwise C-Q hysteresis patterns for both storms. For Ca (C-Q shapes not depicted), hysteresis was an indiscriminate figure of eight shape (E) in August-2005, but clockwise (C3) for November-2006.

3.3 Characteristics of catchment source waters

Table 4 compares compositions of source waters with those of the streamwaters during the two storms and regular weekly monitoring. Four classes of potential source waters were identified with the following solute characteristics:

Table 3. Selected analytical properties of the Strichen Bs soil used in the equilibration experiments (taken from Filius et al., 2000). Fe_{ox} and Al_{ox} relates to amorphous hydrous oxide concentrations determined by acid ammonium oxalate extraction.

Organic Carbon (gC kg^{-1})	Humic acid (g kg^{-1})	Fulvic acid (g kg^{-1})	Fe_{ox} (g kg^{-1})	Al_{ox} (g kg^{-1})	$Al_{0.1MHCl}$ (mg kg^{-1})	Ca (mmol kg^{-1})	pH
34.3	4.8	52.6	27.5	9.5	1836	0.8	4.68

Particle size	Sand (%)	Silt (%)	Clay (%)
	58	34	8

Table 4. Ranges of values for flow (Q) and solute concentrations during the two storms compared with the background stream hydrochemistry (2 yr weekly data, $n = 98$) and (b) catchment source waters 1–4 (mean ± 1 standard deviation). Two values for soil solutions 1a and 1b denote August and November concentrations from 2004–2006 ($n = 7$ for each) with significant differences (denoted as * $p < 0.05$; t-test).

	Q $1s^{-1}$	DOC mg l^{-1}	SUVA-285 $1 mg^{-1} m^{-1}$	DOC:DON	pH mg l^{-1}	Ca mg l^{-1}	Si
Streamwater							
August-2005 storm	4–41	2.7–10.4	2.7–3.6	16–28	6.6–7.3	8.2–9.3	3.5–6.0
November-2006 storm	14–163	2.4–15.6	3.9–4.5	35–43	5.9–7.2	4.1–6.6	3.8–6.8
Background stream	5–178	4.6 ± 4.0	3.8 ± 0.6	32 ± 15	6.6	5.5 ± 2.0	4.9 ± 0.8
Source waters							
(1a) O horizon soil solution	Aug	38.0 ± 6.9*	4.0 ± 0.7	56 ± 4	3.9	0.5 ± 0.2	
	Nov	23.3 ± 3.6	5.0 ± 0.2	49 ± 1	4.2	0.2 ± 0.1	
(1b) B horizon soil solution	Aug	3.3 ± 0.4*	2.9 ± 1.1	53 ± 28	4.7*	0.2 ± 0.1*	
	Nov	3.9 ± 0.5	3.0 ± 0.2	39 ± 25	4.9	0.1 ± 0.1	
(2a) O horizon pit waters		19.8 ± 0.5	3.5 ± 0.1		4.5	1.4 ± 0.4	1.5 ± 0.2
(2a) B horizon pit waters		31.0 ± 5.5	2.1 ± 0.5		5.1	1.3 ± 0.2	1.6 ± 0.3
(2b) C horizon pit waters		5.3 ± 5.4	1.0 ± 0.4		6.5	3.7 ± 0.9	6.9 ± 3.0
(3) Deposition		2.1 ± 2.3	0.5 ± 0.5	14 ± 10	4.7	0.3 ± 0.2	0.02 ± 0.02
(4a) Spring 1		3.4 ± 0.6	1.4 ± 0.3		5.4	18.2 ± 5.6	5.2 ± 1.4
(4b) Spring 2		3.1 ± 3.7	0.6 ± 0.3		6.4	4.1 ± 0.7	7.9 ± 2.8

1. O horizon soil waters (sources 1a, 2a) – had small concentrations of Si (1.5 mg l^{-1}) and Ca (0.2–1.4 mg l^{-1}), low pH (3.9–4.5), but large DOC concentrations (20–38 mg l^{-1}) and high SUVA (3.5–5.01 mg^{-1} m^{-1}).

2. B horizon soil waters (sources 1, 2b) – had small concentrations of Si (1.6 mg l^{-1}) and Ca (0.1–1.3 mg l^{-1}), moderate pH (4.7–5.1) and low SUVA (2.1–3.01 mg^{-1} m^{-1}). DOC concentrations were small for piezometers (3–4 mg l^{-1}) although the soil pit B horizon had 31 mgC l^{-1}.

3. Deep soil-, ground-waters (C horizon 2c, springs 4a, b) – had large concentrations of Si (5.2–7.9 mg l^{-1}), a considerable range in Ca (4–18 mg l^{-1}), small DOC concentrations (3–5 mg l^{-1}) and SUVA (0.6–1.41 mg^{-1} m^{-1}).

4. Bulk deposition – characterised by small concentrations of Si (0.02 mg l^{-1}), Ca (0.3 mg l^{-1}), DOC (2 mg l^{-1}) and with low SUVA-285 (0.51 mg^{-1} m^{-1}).

O horizon piezometer waters had significantly greater DOC concentrations in August than November samples (Table 4). Conversely, B horizon piezometer waters had significantly smaller DOC and pH values and larger Ca and conductivity in August than November samples. As Si concentrations are not part of routine ECN analyses, we used 1.5 and 1.6 mg l^{-1}, respectively, for the O and B horizons of the piezometers based on the analyses of the soil pit waters for those horizons. The erroneously high DOC concentration for the soil pit B horizon was likely due to preferential flowpath transfer of O horizon runoff into the B horizon just upslope of the gravity draining runoff water collection face. However, this composition was not used as an end member in the EMMA approach.

On a single date we also undertook multiple transects comparing hillslope soils (peaty podzols and humus iron podzols) and riparian soils (dominated by gleyed podzols) in terms of DOC concentration, or SUVA-285, and found no significant difference between the soil groups (Fig. 5; t-tests $p = 0.5$ and 0.6, respectively). Organic horizon surface soil solutions
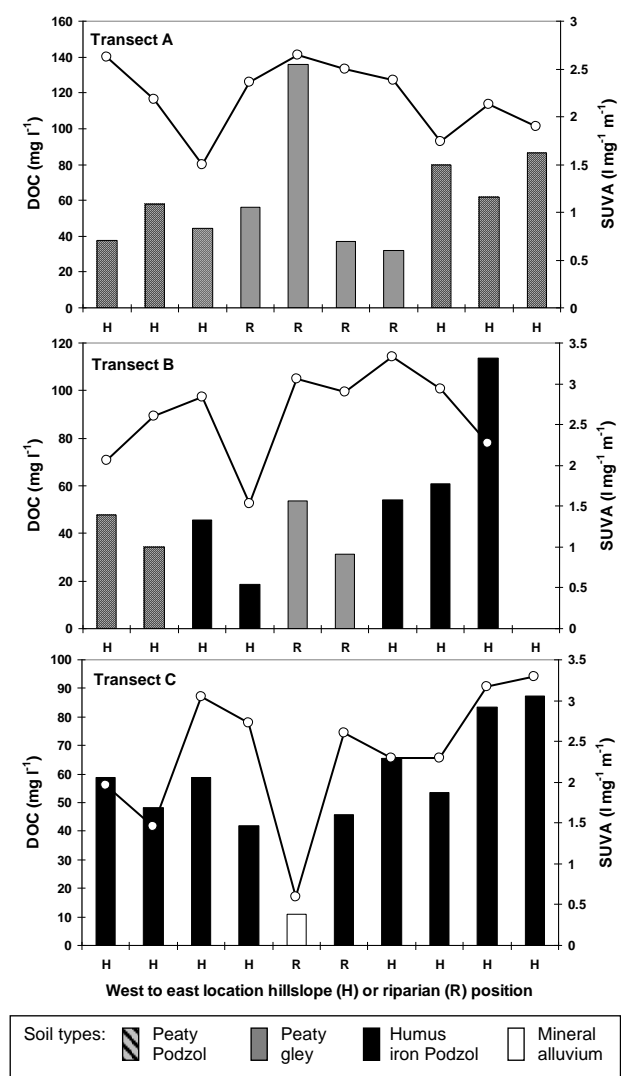
Fig. 5. Spatial changes in surface soil solution DOC concentration (bars) and SUVA (line) over three 300 m transects (A upstream, B middle, C downstream) perpendicular to the stream channel spanning hillslope to riparian (shaded area of graphs) locations. Different soil types are denoted by the fill pattern of the graph bars.

showed limited differences between hillslope and riparian areas in terms of DOC and SUVA characteristics. Hillslope soils were either peaty podzols or humus iron podzols on steeper slopes. The uppermost transect (A) was sampled across a band of peaty gleysols which provide a potentially large store of soil water to feed the catchment stream. The only indication of difference between riparian and hillslope zones was in the slightly larger SUVA values for the gleysols than hillslope podzols in transect A. Concentrations of DOC on the hillslopes ranged from 20–110 mg C l^{-1} (greatest for humus iron podzols) and from 10–130 mg C l^{-1} in the riparian soils (mineral alluvium to peaty gleysols). However, given the wetter conditions in riparian gleysols, the storage

of DOC for flushing may be considerably larger than on hillslopes (circumstantial evidence for this greater riparian soil water store is based on soil type and the fact that soil water samplers filled much more quickly than on hillslopes during the summer sampling).

3.4 End member mixing analyses of flow path contributions to stream water

The solute compositions of the four source water classes outlined above formed the basis of the selection of end members for flow path analyses. Figure 6 shows the ranges of stream water chemistry for August-2005, November-2006 storms and regular weekly monitoring compared against the source water compositions for solute tracer pairs: (a) DOC-Si, (b) SUVA-Si, and (c) SUVA-Ca. Direct atmospheric deposition inputs appeared to make little contribution to stream water chemistry, confirming the three source waters contributing to stream water chemistry as the O horizon, B horizon and groundwater springs. Tracer pairs of SUVA-Ca and SUVA-Si were unsuccessful at bounding the range of observed stream chemistries. There appears to be an undefined composition of large Si and SUVA values affecting stream concentrations. The DOC-Si tracer pair was therefore chosen for the end-member mixing analysis and it was most successful at defining the majority of stream water compositions within the bounds of these three source compositions.

Values for the mean and standard deviation of end members were calculated from piezometer soil waters for the O and B horizon compositions and from spring 4b for the spring water composition. On the basis of significantly different August and November DOC concentrations in both O and B horizon piezometer waters, different distributions were used for the O and B horizon end members, for the three different analyses of (i) August-2005 storm, (ii) November-2006 storm, and (iii) 2-yr simulation as follows:

1. O horizon 38.0 ± 6.9 mg C l^{-1}, B horizon 3.3 ±0.4 mgC l^{-1}

2. O horizon 23.3 ± 3.6 mg C l^{-1}, B horizon 3.9 ±0.5 mgC l^{-1}

3. O horizon 24.1 ± 9.3 mg C l^{-1}, B horizon 3.5 ±0.8 mgC l^{-1} (calculated across the whole sampling period 2004–2006).

DOC compositions for spring water were observed not to have any pattern of seasonality which necessitated setting separate August and November values. The concentration of 3.1 ± 3.7 mg C l^{-1} was used, according to the composition of spring 2 which bounded the stream compositions (Fig. 6; Table 4). Si concentrations for all end members were noted not to have seasonally-related variation and set as 1.5 ± 0.2 mg l^{-1} for the O horizon, 1.6 ± 0.3 mg l^{-1} for the B horizon and 7.9 ± 2.8 mg l^{-1} for the spring water.
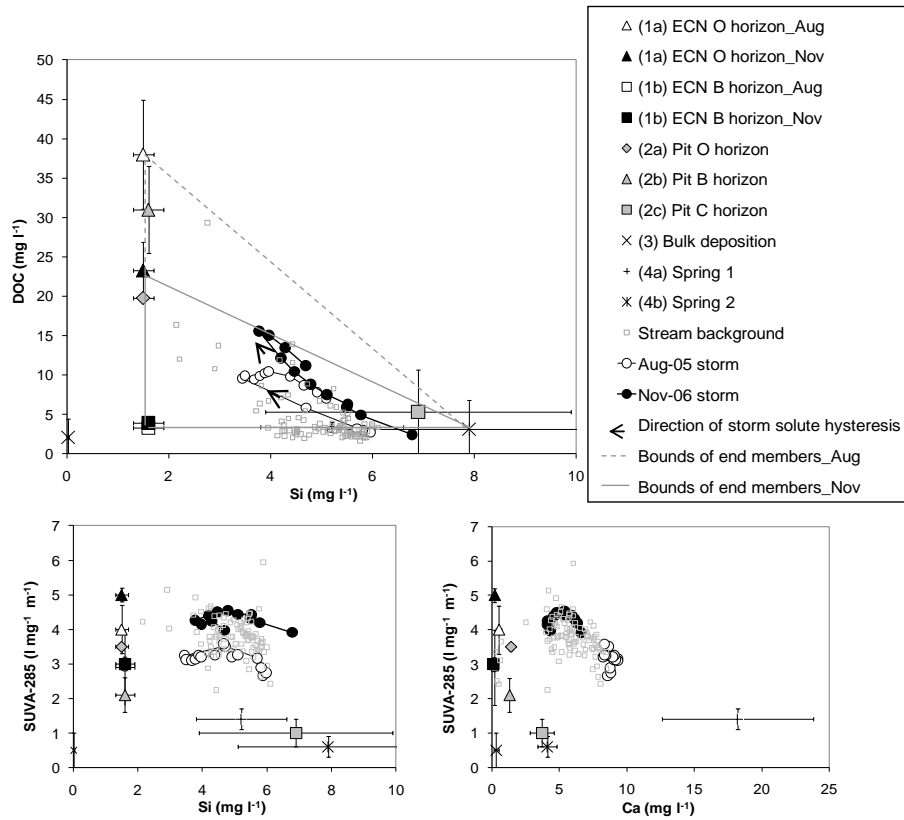
Fig. 6. End-member mixing diagrams comparing streamwaters during storms and during background weekly stream monitoring with compositions of catchment source waters using solute tracer pairs: **(a)** DOC vs Si, **(b)** SUVA-285 vs Si, and **(c)** SUVA-285 vs. Ca.
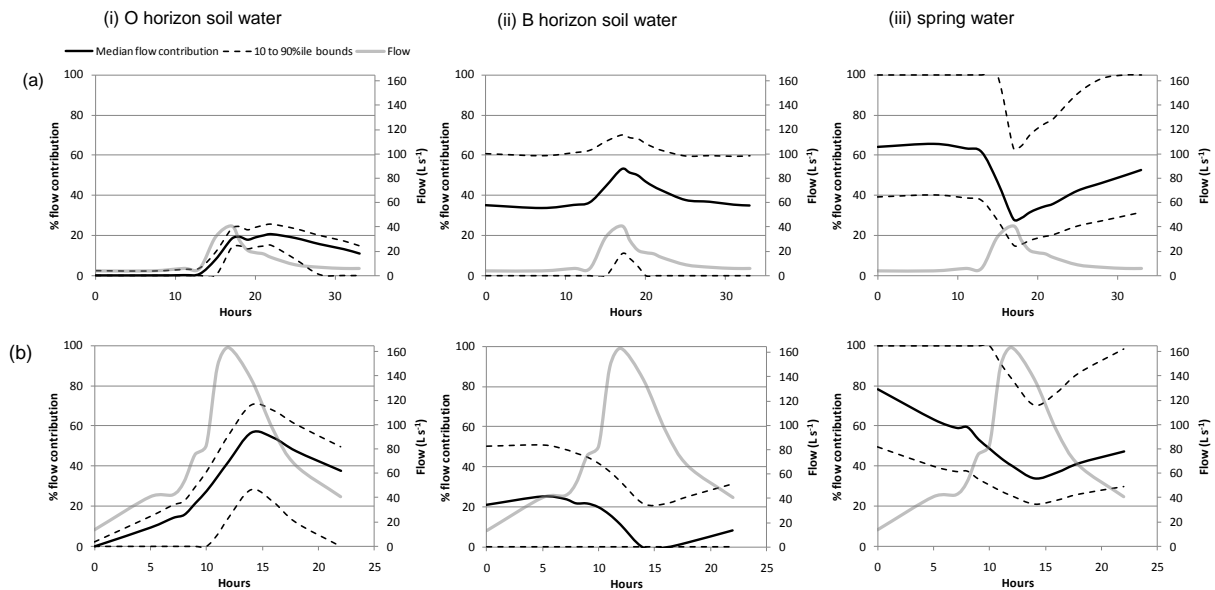

Fig. 7. End-member mixing analysis derived contributions of water flow paths to stream flow for storms in **(a)** August-2005 and **(b)** November-2006. Percentage flow contributions are given for **(i)** O and **(ii)** B horizon soil waters, and **(iii)** spring water. Estimations of uncertainty are given as 10 and 90 percentile bounds.

The hydrograph separations based on the end-member analysis are presented in Fig. 7. For each case the median runoff components were plotted together with the 10 and 90-percentile values. The bounds for the O horizon runoff contribution were quite well constrained in each case due to the distinct DOC characteristics of the O horizon compared with the B horizon and springs. Differentiation between the B horizon and spring contributions was less clear cut, with larger uncertainty bounds on the flow contributions. However, some characteristics could still be identified such as a decrease in spring flow contribution compared to the B horizon during hydrograph peaks.

The DOC-Si tracer analysis (Fig. 6a) shows that streamwater compositions during regular fortnightly monitoring were dominated by mixing of spring waters and B horizon soil waters (reflecting the dominance of baseflow conditions), with increasing influence of O horizon waters at higher flows. Stream compositions for the two storms are described against two triangles (dotted line for August, solid line for November; Fig. 6a) drawn to account for the seasonality in the O horizon end member. Both storm compositions originate along the line between the B horizon and spring water end members, then move toward the O horizon end member, turn anticlockwise, to decline back towards spring water compositions but closer to the line connecting O horizon and spring water end members. Stream water compositions in November-2006 curve towards, and reach, the line between O horizon and spring water end members before DOC concentrations decline, but during August-2005 remain well below this line.

Pre-event stream flow had contributions spring > B horizon > O horizon similarly for both storms. Both storms had similar ranges (based on the uncertainty in the end members) in the contributions of spring waters (28–66 % August-2005 and 34–78 % November-2006), but there were major differences in the relative contributions of soil waters between the storms. The August-2005 storm was dominated by B horizon waters (flow-weighted average (FWA) 45 %, range 34–53 %) with limited O horizon contributions (FWA 13 %, range 1–22 %). Conversely, the November-2006 storm was dominated by O horizon waters (FWA 41 %, range 0–63 %) with limited B horizon contributions (FWA 14 %, range 2–25 %). These contrasting storm types can be compared to the long-term FWA flow contributions (2-yr of weekly data) of 56 %, 13 % and 31 % for spring, O and B horizon waters, respectively, and suggest a limited time that O horizon flow paths contribute in this catchment. Interestingly, in absolute terms (Fig. 7) B horizon waters attained similar maximum contributions during the two storms (22 and $271 \, \mathrm{s}^{-1}$ in August-2005 and November-2006, respectively). The major difference was the greater rate at which flow was routed through the O horizon and the longer recession to this O horizon flow in November-2006 compared to August-2005. SUVA-285 correlated positively ($r = 0.80$; $p \leq 0.001$) with B horizon flow ($l \, \mathrm{s}^{-1}$) over the November-2006 storm but did not correlate significantly with any other flow components (absolute or %) at any time.

3.5 Sorption experiment

Laboratory batch isotherms (Fig. 8) were used to show how DOC compositions available for transport to the stream may be affected by sorption interactions when waters enriched in DOC having passed through surface O horizons contact strongly sorbing Bs soil material in the catchment. Equilibration of O horizon soil solutions, sampled during winter and summer (initial concentrations 15 and 25 mg DOC l^{-1}, respectively), with Bs soil resulted in decreasing SUVA over time, indicating that DOC fractions that were more highly UV absorbing were preferentially sorbed to the Bs soil surface. Furthermore, both the selective uptake of the more UV absorbing fraction and the overall uptake of DOC mass (for summer O horizon solutions only) increased over time. This is evidence that the Bs mineral subsoil selectively filters strongly UV absorbing C forms during transport to the stream where flow paths allow contact with this material. These time-series equilibration results also show that this alteration of DOC mass and composition by Bs surfaces increases with contact time between percolating solutions and the subsoil. Hence, Bs horizons are reactive in terms of filtering the DOC from surface soils on route to some streams, the strength of this effect increasing with reaction time. There was no net change in the amount of winter DOC sorbed over time, indicating that the sorption of highly UV absorbing compounds displaced those less UV absorbing. Conversely, the reaction of summer DOC (having initially greater SUVA than winter DOC) with Bs soil material caused increasing net uptake of solution DOC onto the soil surface over time, with overall loss of strongly UV absorbing forms from solution. There was no apparent "first flush" effect of DOC release that is sometimes observed when a previously dried soil is initially rewet.

4 Discussion

In this discussion we focus on the evidence presented of concentration change over the events, concentration – discharge (C-Q) hysteresis form, hydrograph separation by EMMA and laboratory experimentation of soil – DOC interactions to answer three questions:

1. Do the contrasting antecedent hydrological conditions between the two storms bring differences in the sources and timing of DOC delivery from this small catchment to its stream?

2. Do the contrasting conditions bring differences in the nature of the DOC delivered as assessed by simple compositional indicators?
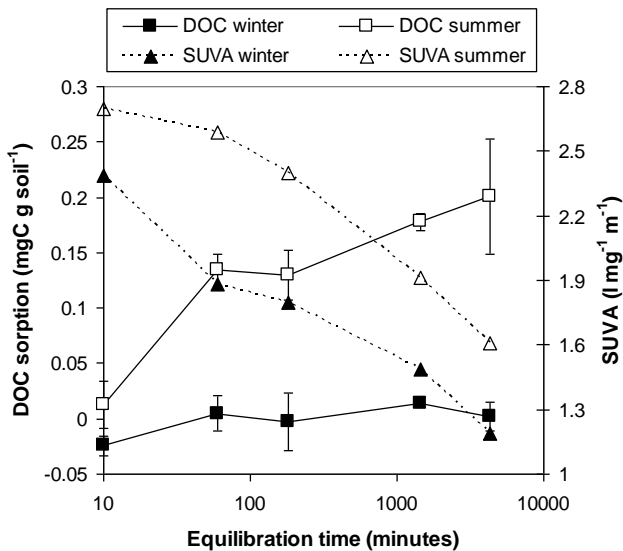
Fig. 8. Time-dependent isotherm equilibration results for the sorption of O horizon soil solution DOC (collected in winter and summer) onto podzol Bs horizon subsoil. The net uptake of DOC and the composition (in terms of SUVA) for the final solutions are given for each time point.

3. Are seasonal differences in biogeochemical processing of the DOC required to explain the quantity and nature of the DOC delivered, beyond hydrological processes alone?

4.1 Delivery of DOC to the stream during the two storms

Anticlockwise C-Q hysteresis patterns for DOC during both storms (Fig. 4) arose as peak concentrations were retarded in relation to water volume. Hence, the prolonged elevated DOC concentrations during flow recessions ("tailing") for both storms indicated slower, and/or distant soil water DOC sources from a mixture of soils and flow path depths. This is the concept of "landscape discretization" introduced by McGlynn and McDonnell (2003) where different parts of the catchment have different (i) DOC concentrations, (ii) response to precipitation and (iii) travel times for the water to reach the stream. We show that there is a further aspect to this, namely the antecedent conditions of soil moisture, rainfall and biogeochemical processing in the catchment.

The hydrological response of small catchments has been described by either 2 component models comprising (i) event water (precipitation) and (ii) pre-event water (stored soil- or ground-water); or alternatively by 3 component models of (i) groundwater, (ii) soil-water and (iii) surface runoff similar in composition to rainfall or throughflow (e.g. Evans and Davies, 1998). These authors show that anticlockwise C-Q hysteresis of open form (type A1), as displayed for DOC in August-2005, results from concentrations in the order

soil water > groundwater > event water. However, the concave positive trending C-Q form showed by the November-2006 would, by the scheme of Evans and Davies (1998), result from the concentration order soil water > event water > groundwater. Instead, using the end-member mixing approach (EMMA), we identified three dominant flow contributions which, when seasonal differences were accounted for, explained stream chemistry for both storms, namely: (i) O and (ii) B horizon soil waters and (iii) groundwaters. There was no evidence for a direct precipitation input during either storm. This observation for this organo-mineral catchment is somewhat different to other studied headwaters in which the storm DOC response is dominated by (i) flushing of riparian wetland soils, with maximum contribution at peak stream discharge and maintained during recession; (ii) simultaneous maximum contribution in shallow and deep groundwater prior to peak discharge; and (iii) event (rainwater, or surface runoff) increasing after the discharge peak. This response is now well documented for forested and alpine headwaters (Boyer et al., 1996; Hagedorn et al., 2000; McGlynn and McDonell, 2003) and recently for an agricultural headwater by Morel et al. (2009). Instead our EMMA suggested that DOC delivery was dominated by a switch from groundwater to soil water from the hillslopes and that this was altered from a dominantly subsoil to surface soil source as the catchment wet up through autumn.

The greater overall DOC concentrations of the November-2006 storm were characteristic of more distant, numerous and larger source areas reacting together. During autumn, wetter soil conditions persist between storms compared with the summer (Fig. 2), hence O horizons over extensive catchment hillslope areas can remain connected to the stream. This greater contribution of O horizon soil water (63 % of stream flow for the November-2006 storm) across large connected areas of the catchment is the reason why autumn storms dominate annual loads of DOC from many catchments (Mullholland and Hill, 1997). The November-2006 storm load was 65 kg DOC in 22 h, compared to 9 kg DOC in 33 h for the August-2005 storm. Autumn storms continue to mobilise large loads of DOC until the reserves of soil DOC solubilized by summer biotic processing become depleted later in winter.

Where catchments contain organo-mineral soils, then changes in water flow paths between surface organic and deeper mineral horizons are recognised as an important control on the amount and timing of DOC flushing to the stream. For peat soils, where flow is restricted to a shallow surface layer, DOC concentrations can decrease with increasing storm event discharge as precipitation inputs dilute soil water DOC inputs (Hinton et al., 1997; Clark et al., 2008). However, even with only small contributions of organo-mineral soils in catchments, DOC concentrations strongly increase with increasing flow (as in the present study). Many studies have investigated the influence of changing from surface to deeper soil flow-path changes on DOC compositions (for
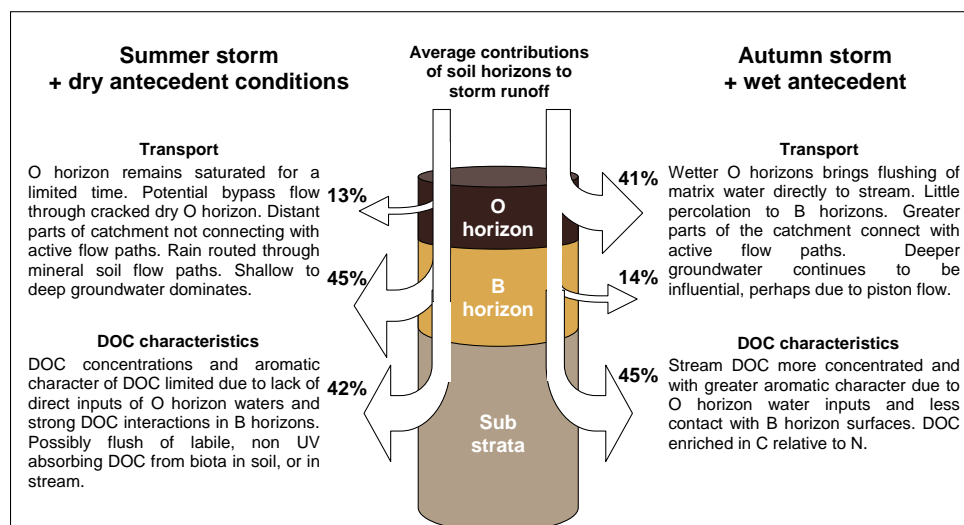
Fig. 9. Conceptual model of the contrasting conditions of summer (on the left) and autumn (on the right) in terms of DOC transport dynamics to the stream. The average flow contributions from horizons are those determined by the EMMA. While a podzol profile is shown the contributions of the O horizon waters may also come from a peat soil.

example Hinton et al., 1998; Meier et al., 2004), although most document forested ecosystems. It is generally recognised that surface organic horizons contribute large amounts of DOC as a by-product of microbial decomposition. Conversely, deeper flow paths between storm events are associated with less DOC reaching the stream as the surface layers become isolated and flow is restricted to subsoils. Hongve et al. (2004) proposed that increasing surface horizon flushing via increased rainfall intensity could be responsible for increasing DOC concentrations observed in surface waters. However, this simplistic view of DOC flushing from surface horizons underplays the importance of DOC-subsoil interactions in organo-mineral landscapes on the concentrations and compositions of DOC reaching the stream.

McGlynn and McDonnell (2003) showed the importance of riparian wet soils for DOC leaching during drier periods in headwaters. A lack of hydrochemical difference between riparian and hillslope topsoil waters (Fig. 5) made the EMMA approach difficult to use in order to support or refute the role of contributing waters from riparian areas. Despite similar compositions, riparian soils may have contributed rapidly connecting waters to stream flow and this may have been a strong influence in August-2005 when the hilslopes were comparably drier. Such processes could be investigated in future by soil hydraulic monitoring and modelling.

Our conceptual diagram (in Fig. 9) summarises the processes affecting surface soil, B horizon and groundwater delivery to the stream. It is not surprising that the two storms in different seasons and at times of distinct antecedent soil water conditions differed considerably in the hydrological delivery of DOC. The extent and connectivity of the landscape units contributing DOC has already been discussed

here and is the pivotal process in the literature deemed to control the amount and nature of DOC entering the stream (McGlynn and McDonnell, 2003; Morel et al., 2009; Laudon et al., 2011). The flushing of organic-rich soil sites of DOC production includes organic rich surface horizons of podzols (Worrall et al., 2002), peats, or riparian wetlands (Hinton et al., 1998), all with high soil solution DOC concentrations (Fig. 5). It is proposed that these comprise finite, rapidly depleted stores of DOC, the magnitude dependent on both temperature-driven microbial DOC production and time since last flushing (Stutter et al., 2007b). Peat is recognised as having a complex pore structure, giving rise to interactions between micro- and macro-pore regions which retard solute transport in the matrix (Stutter et al., 2007b). Hence, DOC release in organic horizons is controlled by diffusion over intra-storm timescales, with production controls more important for inter-event timescales (Worrall et al., 2008).

The novelty of our study is in the preliminary evidence of the strength of interaction of biogeochemical processing with the hydrological transport signal of DOC. The alteration of DOC due to flow through B horizons is a key process affecting delivery in organo-mineral landscapes. The EMMA showed much greater B horizon flow contributions in August-2005 than November-2006 (maxima 53 % and 23 % of storm flow, respectively). The sorption interactions of DOC on hydrous ferric oxides (characteristic of podzol Bs horizons) are recognised as displacement of fast-adsorbing, low molecular weight compounds by slower-adsorbing, higher molecular weight DOC forms (e.g. Ochs et al., 1994). Podzol mineral subsoils therefore have a strong retention capacity for lignin-derived hydrophobic organic acids (Ussiri and Johnson, 2004). This concept is consistent

with our laboratory batch results (Fig. 8), but contrasts with field observations such as that of Qualls et al. (2000) who noted a near complete removal of DOC on contact with subsoils in a forested catchment. The laboratory sorption experiments showed the potential for podzol subsoils to dramatically change the composition, but not necessarily the concentration, of DOC transported from the site of production in organic surface soils to streams under conditions in situations where waters contact subsoils. Since the Bs horizon acts to exchange DOC between different forms (filtration and buffering capacity), then the "recharge" of DOC of different compositions to this moorland subsoil is important to the nature of the DOC available for displacement at different times of the year. This DOC-subsoil interaction principally involves freely draining hillslope podzols. Reductive dissolution of soil Fe and Al minimises DOC sorption in the wetter Gleysols and gleyed podzols (Hagedorn et al., 2000). Consequently, these soil types bordering the stream (Table 1) are expected to have little filtration and DOC buffering capacity (Fig. 5).

Groundwater was also a dominant water source (65–78 %) during both storms. Groundwater should be most depleted in DOC, especially aromatic and high molecular weight forms due to extended contact times with sorbing subsoils (Meier et al., 2004). However, groundwaters may mix with DOC-enriched waters when passing through riparian soils that act as DOC stores (Hagedorn et al., 2000). Although we did not measure borehole groundwaters, we considered spring water in this deeply weathered geology to be best representative of deeper groundwaters. We make the distinction between this surrogate for "deeper" groundwaters and the O and B horizon waters which were used as other sources distinct from groundwaters (although may be conceptualised as shallow ground-soil-waters).

4.2 The nature of DOC delivered to the stream and implications for water quality

We used SUVA-285 in combination with DOC:DON ratios as simple indicators of changes in DOC compositions between and during storm events. SUVA-285 appears a useful parameter to discriminate between source waters originating in and directly transported from surface organic horizons (high SUVA) and those originating from, or having long contact times with, deep sources or B horizons (low SUVA). These parameters supported the inferences that contributing source areas with different DOC composition signatures contribute variably in amount and timing between flow rise and recession of the contrasting storms.

In August-2005, a small initial rise in flow prior to the hillslope soil moisture increase probably flushed a near, or within, channel source of DON, resulting in lowered DOC:DON. The peak in SUVA-285 just prior to maximum discharge in August-2005 occurred just as the hillslope O horizons reached saturation. Such rapid runoff re-

sponse could either be initial contributions of hillslope surface throughflow or a piston effect of slope water displacing stored riparian waters. In August-2005, larger SUVA values were maintained throughout the recession, compared with rapidly decreasing SUVA values on the November-2006 recession. The November-2006 storm started from conditions of recharged soil moisture in hillslope soils and was preceded by large autumn storms four weeks previously. Larger overall SUVA and DOC:DON values, when compared to the August storm, suggested either: (i) the occurrence of greater terrestrial humic and fulvic acid contributions, or (ii) that remnants of lower molecular weight DOC components produced by summer biological activity had been removed by previous autumn storms, or mineralised in the soil, or (iii) different interactions with podzol subsoils. However, the SUVA peaked earlier than the O horizon waters, suggesting that O horizons contributed large amounts of DOC mixed with low SUVA components such as exudates from senescing vegetation.

A change in the distribution and intensity of rain storm events favouring intense storms in summer periods may lead to significant carbon impacts on aquatic ecosystems. This may have important implications in the context of predicted future climate change, envisaged to lead to wetter summers with intense summer storms (UKCIP, 2009). The low SUVA values indicating generally different DOC forms more dominant in summer than autumn may have implications for stream biota. The DOC associated with summer storms has the potential to greatly modify downstream energy availability to heterotrophs during the summer period of biological activity, with an associated effect on primary productivity (Arvola et al., 1996). Other studies have suggested that less UV absorbing forms of C (using wavelengths similar to that used in this study) are less aromatic (Weishaar et al., 2003) and more biodegradable (Fellman et al., 2008). Conversely, higher SUVA forms in autumn may be less biodegradable and more likely to reach the oceans without being returned to the atmosphere as CO_2, co-transport toxic metals and organic contaminants (Chin et al., 1994), posing challenges for drinking water treatment since SUVA has strong positive relationships with formation of carcinogenic treatment disinfection by-products and disruption of water treatment flocculants (Kitis et al., 2002).

4.3 Biogeochemical processing of DOC

We hypothesise that biogeochemical processing of the DOC is responsible for changes in the DOC delivered to the stream between the contrasting storms, beyond which can be entirely explained by hydrological delivery processes. Temporal variability in the end-member compositions of DOC for the surface soils is one indicator that this biogeochemical processing occurs in the catchment soils. There are unlikely to be a significant reservoir of autochthonous DOC produced and stored in the stream channel itself to influence greatly the signal of the allochthonous soil-derived DOC.

A number of aspects of seasonality affect the DOC in November relative to August. Reduced biological processing in autumn leads to decreased supply of soluble material (Lumsdon et al., 2005). Stream DOC compositions during two storms bracket the range of SUVA observed during the 2-yr of fortnightly data (eg Fig. 4b), indicating that the storms showed extremes in combined biogeochemical/hydrological processing of DOC. Pre-event stream DOC in August-2005 had small DOC:DON ratios and aromatic contents (low SUVA) but there was a large range in SUVA during the storm (2.7–$3.61\,\mathrm{mg^{-1}\,m^{-1}}$; Fig. 3). Conversely, in November-2006 greater DOC:DON and SUVA values in pre-event stream waters were more characteristic of soil fulvic and humic acid contributions (Weishaar et al., 2003), but the range in SUVA change was narrower through the event (3.9–$4.51\,\mathrm{mg^{-1}\,m^{-1}}$). Yet the EMMA predicted similar flow contributions before these storms in terms of a dominance of spring and B horizon waters with <1 % O horizon flow. In addition, counter-intuitively, SUVA was positively related to absolute flow routed through the B horizon during the November-2006 storm, where no relationships with flow path changes occurred during August-2005. There was no evidence of differences in SUVA-285 between August and November for the B horizon soil solutions at the ECN site (Table 4), although O horizons had greater SUVA-285 in November.

For the two storms presented, simple mixing of waters from different flow paths could not by itself explain the differences in DOC compositions between August and November, and biogeochemical processing of DOC is required to fully explain the observed stream DOC dynamics. This is in contrast to the much wider body of literature (McGlynn and McDonnell, 2003; Morel et al., 2009; Jensco and McGlynn, 2010; Laudon et al., 2011) which supports the dominant control of hydrology via the variation in connectivity of discrete landscape units delivering different amounts of DOC. Part of the influence of such discrete units is the signal from areas of organo-mineral soils where the subsoil influences the DOC passage. Yet our data suggest that these interactions are not purely hydrologically-controlled or consistent between seasons, and the plausible explanations given below should be investigated by further detailed studies. The Bs horizons showed an annual autumn period when their sorption potential for higher molecular weight, aromatic DOC components becomes impaired. This was not apparent from the laboratory soil-DOC equilibration experiment, as a standard Bs soil was used rather than the in-situ soil experiencing seasonality in the nature and amount of antecedent DOC exposure. Sorption of DOC onto Fe and Al complexes is highly pH- and ionic strength-dependent (Oste et al., 2002); and this would lead to impaired sorption, particularly of more aromatic forms at higher pH or lower concentrations of complexing cations. However, there may be a biological explanation. The impaired filtration may result from saturation of Bs reactive surfaces with DOC solubilized during summer.

During winter conditions when less metabolically-favourable DOC forms are available, biota may decompose Bs horizon stored organic matter, leading to an annual cycle of "regeneration" of these Bs surfaces. However, no other data to support or refute this process could be found in the literature.

5 Conclusions

We combined hydrochemical observation, hydrological modelling, DOC compositional indicators and soil – DOC batch experiments to resolve how the interactions between seasonal biogeochemical processing of DOC and flowpath changes in organo-mineral soils affect stream DOC. The studied small mixed organo-mineral soil catchment showed a very different response in the delivery of DOC to the stream between two contrasting storms. Since these storms differed in antecedent soil moisture, season and the induced runoff, this was unsurprising. However, looking in detail at the concentrations and simple compositional indicators of DOC has enabled us to suggest that biogeochemical processing of DOC is superimposed on the hydrologically-derined variation and necessary to fully explain the extent of the DOC difference between storm periods. Summer storms transfer appreciable concentrations of DOC to streams, likely strongly influencing downstream aquatic ecosystem energy balances. A strong filtration effect of podzolic subsoils means this DOC is low in UV absorbing compounds and likely to be more bioavailable. When the catchment is rewetted in autumn, large areas of organic soils connect to the drainage network, leading to large loads of DOC enriched in highly UV absorbing compounds. The novelty of the present study has been to demonstrate that variation in flow paths can produce such different concentrations and compositions of stream water DOC during periods of contrasting soil moisture/seasonality. Accordingly, it will be important to include an appropriate range of biological and geochemical interactions into catchment DOC modelling to predict both exports of headwater DOC and the fate and impact of this DOC in downstream ecosystems. Whilst only two storms were studied in detail, they frame very different periods of hydrological and potential biogeochemical processing of DOC in the catchment and provide preliminary evidence for further study of DOC biogeochemistry relative to (and in interaction with) hydrological factors. Future work should better investigate the temporal dynamics of DOC biogeochemistry in key landscape units of riparian wetland soils, and changes between units occurring over "transition" periods such as soil rewetting in late summer/autumn.

Fred Worrall and another anonymous reviewer who contributed significantly to the arguments and presentation of the manuscript through their reviews.

Edited by: S. Bouillon

References

Aitkenhead, J. A., Hope, D., and Billett, M. F.: The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales, Hydrol Process., 13, 1289–1302, 1999.

Arvola, L., Kankaala, P., Tulonen, T., and Ojala, A.: Effects of phosphorus and allochthonous humic matter enrichment on the metabolic processes and community structure of plankton in a boreal lake (Lake Pääjärvi), Can. J. Fish Aquat. Sci., 53, 1646–1662, 1996.

Bazemore, D. E., Eshleman, K. N., and Hollenbeck, K. J.: The role of soil water in stormflow generation in a forested headwater catchment: synthesis of natural tracer and hydrometric evidence, J. Hydrol., 162, 47–75, 1994.

Boyer, E. W., Hornberger, G. M., Bencala, G. M., and McKnight D. M.: Response characteristics of DOC flushing in an alpine catchment, Hydrol. Process., 11, 1635–1641, 1996.

Bricaud, A., Morel, A., and Prieur, L.: Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains, Limnol. Oceanogr., 26, 43–53, 1981.

Chin, Y.-P., Aiken, G., and O'Loughlin, E.: Molecular weight polydispersity and spectroscopic properties of aquatic humic substances, Environ. Sci. Technol., 28, 1853–1858, 1994.

Clark, M., Lane, S. N., Chapman, P. J., and Adamson, J. K.: Link between DOC in near surface peat and stream water in an upland catchment, Sci. Total Environ., 404, 308–315, 2008.

Dawson, J. J. C., Billett, M. F., Hope, D., Palmer, S. M., and Deacon, C. M.: Sources and sinks of aquatic carbon in a peatland stream continuum, Biogeochemistry, 70, 71–79, 2004.

Dilling, J. and Kaiser, K.: Estimation of the hydrophobic fraction of dissolved organic matter in water samples using UV photometry, Water Res., 36, 5037–5044, 2002.

Dunn, S. M., Vinogradoff, S. I., Thornton, G. J. P., Bacon, J. R., Graham, M. C., and Farmer, J. G.: Quantifying hydrological budgets and pathways in a small upland catchment using a combined modelling and tracer approach, Hydrol. Process., 20, 3049–3068, 2006.

Environmental Change Network: available at: http://www.ecn.ac.uk/sites/glens, Glensaugh site, last access: November 2009.

Environmental Change Network: available at: http://www.ecn.ac.uk/protocols/index.asp, Protocols, last access: November 2009.

Evans, C. and Davies, T. D.: Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry, Water Resour. Res., 34, 129–137, 1998.

Fellman, J. B., D'Amore, D. V., Hood, E., and Boone, R. D.: Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, Biogeochemistry, 88, 169–184, 2008.

Filius, J. D., Lumsdon, D. G., Meeussen, J. C. L., Hiemstra, T., and van Riemsdijk, W. H.: Adsorption of fulvic acid on goethite, Geochim. Cosmochim. Ac., 64, 51–60, 2000.

Genereux, D.: Quantifying uncertainty in tracer-based hydrograph separations Water Resour. Res., 34, 915–919, 1998.

Glentworth, R. and Muir, J. W.: The Soils of the Country Round Aberdeen, Inverurie and Fraserbrugh, Her Majesty's Stationary Office, Edinburgh, 1963.

Hagedorn, F., Schleppi, P., Waldner, P., and Flühler, H.: Export of dissolved organic carbon and nitrogen from Gleysolsol dominated catchments – the significance of water flow paths, Biogeochemistry, 50, 137–161, 2000.

Hinton, M., Schiff, S. L., and English, M. C.: The significance of runoff events on the concentrations and exports of dissolved organic carbon from two Precambrian shield watersheds, Biogeochemistry, 36, 67–88, 1997.

Hinton, M. J., Schiff, S. L., and English, M. C.: Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian shield, Biogeochemistry, 41, 175–197, 1998.

Holden, J.: Sediment and particulate carbon removal by pipe erosion increase over time in blanket peatlands as a consequence of land drainage, J. Geophys. Res.-Earth Surf., 111, F02010, doi:10.1029/2005JF000386, 2006.

Hongve, D., Riise, G., and Kristiansen, J. F.: Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation?, Aquat. Sci., 84, 301–324, 2004.

Hood, E., Gooseff, M. N., and Johnson, S. L.: Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds Oregon, J. Geophys. Res., 111 G01007 doi:101029/2005JG000082, 2006.

Hooper, R. P., Christophersen, N., and Peters, N. E.: Modelling streamwater chemistry as a mixture of soil water end members: An application to the Panola Mountain catchment, Georgia, USA, J. Hydrol., 116, 321–343, 1990.

Jencso, K. G. and McGlynn, B. L.: Variable flushing mechanisms and landscape structure control stream DOC export during snowmelt in a set of nested catchments, Biogeochemistry, 99, 193–211, 2010.

Jenkins, A., Ferrier, R. C., Harriman, R., and Ogunkoya, Y. O.: A case-study in catchment hydrochemistry - conflicting interpretations from hydrological and chemical observations, Hydrol. Process., 8, 335–349, 1994.

Kaiser, K. and Guggenberger, G.: Storm flow flushing in a structured soil changes the composition of dissolved organic matter into the subsoil, Geoderma, 127, 177–187, 2005.

Kalbitz, K., Geyer, W., and Geyer, S.: Spectroscopic properties of dissolved humic substances – a reflection of land use history in a fen area, Biogeochemistry, 47, 219–238, 1999.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., and Matzner, E.: Controls on the dynamics of dissolved organic matter in soils: a review, Soil Sci., 165, 277–304, 2000.

Katsuyama, M. and Ohte, N.: Determining sources of stormflow from the fluorescence properties of dissolved organic carbon in a forested headwater catchment, J. Hydrol., 268, 192–202, 2002.

Kitis, M., Karanfil, T., Wigton, A., and Kilduff, J. E.: Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration, Water Res., 36, 3834–3848, 2002.

Ladouche, B., Probst, A., Viville, D., Idir, S., Baque, D., Loubet, M., Probst, J. L., and Bariac, T.: Hydrograph separation using iso-

topic, chemical and hydrological approaches (Strengbach catchment, France), J. Hydrol., 242, 255–274, 2001.

Laudon, H., Berggren, M., Agren, A., Buffam, I., Bishop, K., Grabs, T., Kansson, M., and Kohler, S.: Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: The role of processes, connectivity and scaling, Ecosyst., 14, 880–893, 2011.

Lumsdon, D. G., Stutter, M. I., Cooper, R. J., and Manson, R.: Model assessment of biogeochemical controls on dissolved organic carbon partitioning in an acid organic soil, Environ. Sci. Technol., 39, 8057–8063, 2005.

McGlynn, B. L. and McDonnell, J. J.: Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, Water Resour. Res., 39, 1090, doi:10.1029/2002WR001525, 2003.

Meier, M., Chin, Y.-P., and Maurice, P.: Variations in the composition and adsorption behaviour of dissolved organic matter at a small forested watershed, Biogeochemistry, 67, 39–56, 2004.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., and Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, Nature, 450, 537–540, 2007.

Morel, B., Durand, P., Jaffrezic, A., Gruau, G., and Molenat, J.: Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment, Hydrol. Process., 23, 2888–2901, 2009.

Mullholland, P. J. and Hill, W. R.: Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects, Water Resour. Res., 33, 1297–1306, 1997.

Ochs, M., Cosovic, B., and Stumm, W.: Coordinative and hydrophobic interaction of humic substances with hydrophilic Al_2O_3 and hydrophobic mercury surfaces, Geochim. Cosmochim. Ac., 58, 639–650, 1994.

Oste, L. A., Temminghoff, E. J. M., and van Riemsdijk, W. H.: Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration, Environ. Sci. Technol., 36, 208–214, 2002.

Qualls, R. G., Haines, B. L., Swank, W. T., and Tyler, S. W.: Soluble organic and inorganic nutrient fluxes in clearcut and mature deciduous forests, Soil Sci. Soc. Am. J., 64, 1068–1077, 2000.

Scott, M. J., Jones, M. N., Woof, C., Simon, B., and Tipping, E.: The molecular properties of humic substances isolated from a UK upland peat system A temporal investigation, Environ. Int., 27, 449–462, 2001.

Skjelkvåle, B. L., Stoddard, J. L., Jeffries, D. S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D. T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., and Worsztynowicz, A.: Regional scale improvements in surface water chemistry 1990–2001, Environ. Pollut., 137, 165–176 2005.

Sklash, M. G., Stewart, M. K., and Pearce, A. J.: Storm runoff generation in humid headwater catchments 2. A case study of hillslope and low-order stream response, Wat. Resour. Res. 22, 1273–1282, 1986.

Spencer, R. G. M., Baker, A., Ahad, J. M. E., Cowie, G. L., Ganeshram, R., Upstill-Goddard, R. C., and Uher, G.: Discriminatory classification of natural and anthropogenic waters in two UK estuaries, Sci. Total Environ., 373, 305–323 2007.

Stutter, M. I., Deeks, L. K., Low, D., and Billett, M. F.: Impact of soil and groundwater heterogeneity on surface water chemistry in an upland catchment, J. Hydrol., 318, 103–120, 2006.

Stutter, M. I., Lumsdon, D. G., and Cooper, R. J.: Seasonality of dissolved organic matter release from upland peat soils: a laboratory leaching study, Eur. J. Soil Sci., 58, 1007–1016, 2007a.

Stutter, M. I., Lumsdon, D. G., and Thoss, V.: Physico-chemical and biological controls on dissolved organic matter in peat aggregate soil columns, Eur. J. Soil Sci., 58, 646–657, 2007b.

Stutter, M. I., Lumsdon, D. G., Billett, M. F., Low, D., and Deeks, L. K.: Spatial variability in soil properties affecting organic horizon carbon storage in upland soils, Soil Sci. Soc. Am. J., 73, 1724–1732, 2009.

Thacker, S. A., Tipping, E., Gondar, D., and Baker, A.: Functional properties of DOM in a stream draining blanket peat. Sci, Total Environ., 407, 566–573, 2008.

UKCIP: United Kingdom climate impacts projections. Department of Food, Environment and Rural Affairs, available at: http://ukcp09.defra.gov.uk/, last access: 2010.

Ussiri, D. A. N. and Johnson, C. E.: Sorption of organic carbon fractions by Spodosol mineral horizons, Soil Sci. Soc. Am. J., 68, 253–262, 2004.

Weishaar, J. L., Aiken, G. R., Depaz, E., Bergamaschi, B., Fram, M, and Fujii, R.: Evaluation of specific ultra-violet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37, 4702–4708, 2003.

Worrall, F., Burt, T. P., Jaeban, R. Y., Warburton, J., and Shedden, R.: Release of dissolved organic carbon from upland peat, Hydrol. Process., 16, 3487–3504, 2002.

Worrall, F., Harriman, R., Evans, C. D., Watts, C., Adamson, J., Neal, C., Tipping, E., Burt, T. P., Grieve, I., Montieth, D., Naden, P. S., Nisbet, T., Reynolds, B., and Stevens, P.: Trends in dissolved organic carbon in UK rivers and lakes, Biogeochemistry, 70, 369–402, 2004.

Worrall, F., Gibson, H. S., and Burt, T. P.: Production vs solubility in controlling runoff of DOC from peat soils – The use of event analysis, J. Hydrol., 358, 84–95, 2008.