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Key Points:
- Stream DOC dynamics are strongly linked to variations in the age of source waters
- Nonstationary flow-DOC relationships reflect changing hydrologic connectivity
- FDOM is a reliable proxy for long-term, high-resolution DOC time series

Supporting Information:
- Supporting Information S1

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Linking high-frequency DOC dynamics to the age of connected water sources

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Abstract We combined high-frequency dissolved organic matter fluorescence (FDOM) data with stable isotope observations to identify the sources and ages of runoff that cause temporal variability in dissolved organic carbon (DOC) within a peat-dominated Scottish catchment. FDOM was strongly correlated ($r^2 \sim 0.8$) with DOC, allowing inference of a 15 min time series. We captured 34 events over a range of hydrological conditions. Along with marked seasonality, different event responses were observed during summer depending on dry or wet antecedent conditions. The majority of events exhibited anticlockwise hysteresis as a result of the expansion of the riparian saturation zone, mobilizing previously unconnected DOC sources. Water ages from the main runoff sources were extracted from a tracer-aided hydrological model. Particularly useful were ages of overland flow, which were negatively correlated with DOC concentration. Overland flow age, which ranged between 0.2 and 360 days, reflected antecedent conditions, with younger water generally mobilizing the highest DOC concentrations in summer events. During small events with dry antecedent conditions, DOC response was proportionally higher due to the displacement and mixing of small volumes of previously unconnected highly concentrated riparian soil waters by new precipitation. During large events with wet antecedent conditions, the riparian saturation zone expands to organic layers on the hillslopes causing peaks in DOC. However, these peaks were limited by dilution and supply. This study highlights the utility of linking high-frequency DOC measurements with other tracers, allowing the effects of hydrologic connectivity and antecedent conditions on delivery of DOC to streams to be assessed.

1. Introduction

Dissolved organic carbon (DOC) is an important component of surface water quality in northern catchments, integrating hydrological, and biogeochemical processes that connect landscapes and riverscapes. In many northern temperate regions, DOC concentrations have been increasing over recent decades [*Dawson et al.*, 2009; *Monteith et al.*, 2007; *Worrall and Burt*, 2004]. Such increases have potentially significant impacts on the carbon budget [*Meybeck*, 1993; *Hope et al.*, 1997], ecosystem productivity [*Tank et al.*, 2010], and the cost of treating drinking water [*Ledesma et al.*, 2012]. Thus, it is essential to understand the interactive processes controlling the spatial and temporal variation of DOC in surface waters.

DOC is produced from the microbial degradation of soil carbon, which releases DOC into soil water [*Hope et al.*, 1994]. Subsequent transport of DOC occurs during hydrological events, when water flushes through soils, mobilizing DOC and transferring it to streams [*Boyer et al.*, 1996]. Numerous interactive processes influence the production and transport of DOC in the landscape, which result in temporal variability in DOC concentration in streams spanning subhourly to annual (i.e., seasonal) time scales [*Ågren et al.*, 2014; *Köhler et al.*, 2008; *Laudon et al.*, 2013]. The nature and connectivity of dominant flow paths within a catchment exert a strong influence on this temporal variability in stream water DOC, particularly the connectivity between organic-rich soils and stream channels [*Aitkenhead et al.*, 1999; *Casper et al.*, 2003; *Laudon et al.*, 2011; *Chaplot and Ribolzi*, 2014; *Dick et al.*, 2015; *Inamdar et al.*, 2011].

Until recently, DOC was typically sampled at weekly intervals or intensively sampled for occasional individual events [e.g., *Dawson et al.*, 2008]. However, at these sampling frequencies, it is difficult to capture the full temporal dynamics of DOC as flow paths, source areas, and factors affecting DOC production can be highly variable over short periods of time, as well as between seasons [*Pellerin et al.*, 2011; *Neal*, 2013]. Thus, our understanding of specific interactions and processes may be still overly simplistic. Fully capturing DOC temporal variations has recently become a possibility with the development of optical sensors that can infer subhourly DOC at time scales corresponding to hydrological and biogeochemical dynamics [*Kirchner et al*., 2004; *Fellman et al*., 2010; *Strohmeier et al*., 2013]. Probes that measure the fluorescent component of dissolved organic matter (FDOM) can provide a continuous in situ proxy of DOC in freshwaters [*Pellerin et al*., 2011; *Downing et al*., 2012; *Saraceno et al*., 2009; *Wilson et al*., 2013]. However, care is needed because fluorescence is affected by light attenuation and temperature. Therefore, calibration and correction of measured FDOM values derived from such probes is required to account for these effects [*Downing et al*., 2009].

Understanding changes in hydrological flow paths and associated water ages is fundamental to understanding the temporal dynamics of DOC [*Laudon et al*., 2011]. Natural tracers have been widely used to track flow paths and sources of water generating streamflow [*Wels et al*., 1991; *Buttle and Peters*, 1997; *Neal*, 1997; *McGlynn and McDonnell*, 2003; *Capell et al*., 2011]. Geochemical tracers are useful in distinguishing geographical sources of runoff, particularly the relative contribution of groundwater and soil water during storm events, which help explain temporal variations in DOC [*Laudon et al*., 2011; *Strohmeier et al*., 2013]. Similarly, isotopic tracers can be used to quantify the temporal dynamics of different sources and distinguish the role of water stored in the catchment prior to an event (pre-event water) compared with "new" water from the event itself (event water) [*Lischeid*, 2008; *Klaus and McDonnell*, 2013]. The relative contribution of preevent versus event water will likely affect the temporal variations in DOC concentration as DOC is mobilized from spatially dynamic sources. Recent advances in tracer-aided hydrological modeling now allow us to go beyond the traditional simplistic division of event and preevent water allowing the ages of water sources to be well constrained [e.g., *Birkel and Soulsby*, 2015; *Soulsby et al*., 2015]. Recent work has allowed such models to relate the age of streamflow to weathering-derived solutes [e.g., *Benettin et al*., 2015], but this link has not yet been established with DOC.

In this study, we use 13 months of high-frequency FDOM data from a peat-dominated headwater catchment in the Scottish Highlands. Importantly, we couple this with hydrochemical and stable isotope tracers to identify the dynamics of sources, flow paths, and ages of waters within the catchment that generate streamflow and cause temporal variation in DOC concentration. Previous work at this site includes modeling studies using weekly and daily DOC data [*Birkel et al*., 2014; *Dick et al*., 2015] and tracer studies to assess storage and runoff dynamics [*Tetzlaff et al*., 2014]. Studies have highlighted the importance of an extended, quasi-permanently saturated riparian zone as a key contributor of DOC and a mixing zone of source waters [*Tetzlaff et al*., 2014; *Lessels et al*., 2016]. Recent work from which this study has developed includes *Dick et al*. [2015], who used a coupled hydrological and DOC model to simulate daily DOC concentrations to determine the relative DOC fluxes from different landscape sources and relate this to temporal variability in hydrologic connectivity. In addition, *Soulsby et al*. [2015] integrated long-term daily isotope measurements in a runoff model to extract the ages of water fluxes from the main landscape units. The study presented here significantly extends this work by using 15 min DOC data and combining these with water flux ages from the main landscape units to relate, for the first time, the ages of source waters and flow paths to temporal dynamics in DOC concentrations. This study has two specific objectives:

1. To characterize high-frequency DOC concentration dynamics in stream water using real-time proxies derived from FDOM optical sensors, over a full seasonal cycle.
2. To use stable isotope tracers to derive source water ages, to determine how DOC concentration dynamics relate to temporal dynamics in water flux ages, flow paths, and connectivity within the catchment.

2. Study Site

The Bruntland Burn catchment (3.2 km^2) is situated in the Cairngorms National Park, NE Scotland and is a tributary of the larger Girnock experimental catchment [*Birkel et al*., 2011b]. Precipitation (P) is fairly evenly distributed throughout the year, with an annual mean of approximately 1000 mm (all mean values for period 1974–2014). Around 5% of annual precipitation falls as snow, though this can exceed 10% in colder years. Mean annual runoff is 700 mm and potential evapotranspiration 400 mm. Mean annual air temperatures are around 6°C, ranging from daily means of 1°C in winter to 12°C in summer.

Elevations range from 248 to 539 m a.s.l, with mean slopes of 13°. The catchment is predominantly granitic, bordered by schist and other metamorphic rocks. As a result of previous glaciation, the wide valley bottom is covered by glacial drift deposits up to 40 m deep. Overlying these deposits are soils that are predominantly organic rich, with three main hydropedological units spatially distributed throughout the catchment

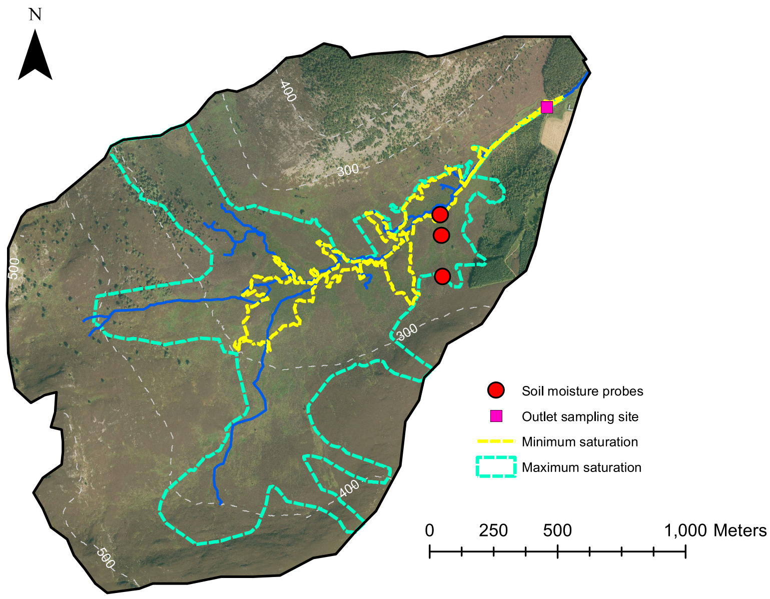

Figure 1. Bruntland Burn catchment showing topography, location of DOC sampling and FDOM sonde, location of soil moisture probes, and minimum and maximum extent of the quasi-permanently saturated riparian zone.

[*Tetzlaff et al.*, 2014]. Organic-rich soils dominate the catchment, with large areas of deep (up to 4 m deep) peats (Histosols) in valley bottoms and shallow (<0.5 m) peat on the lower hillslopes covering 22% of the catchment. The peat soils occupy riparian areas, receiving seepage from the upper hillslopes, and are highly water retentive. Therefore, they are quasi-permanently saturated, with a small dynamic storage range (~50 mm) and are highly responsive to precipitation events in terms of generating overland flow [*Soulsby et al.*, 2015]. Depending on antecedent conditions, the extent of the saturation area is highly variable and can range between 2 and 40% of the catchment (Figure 1). More freely draining podzols are found on the steeper hillslopes, covering around 55% of the catchment. They mostly drain vertically to sustain groundwater recharge, though lateral flow in the organic-rich upper horizons can be triggered during wet periods if the soils become saturated [*Geris et al.*, 2015]. Previous measurements of stream water DOC concentrations within the catchment show they range from ~2 to ~20 mg L^{-1}, broadly reflecting groundwater and organic soil water concentrations, respectively [*Dick et al.*, 2015; *Lessels et al.*, 2016]. The displacement of water from the peat-dominated riparian saturation area acts as the main source of streamflow resulting in "preevent" water typically accounting for >80% of flow [*Tetzlaff et al.*, 2014]. This water is DOC rich with concentrations varying between ~10 and ~60 mg L^{-1} [*Lessels et al.*, 2016]. Runoff coefficients are typically <10%, but these increase nonlinearly in wetter periods to >40% as the saturated zone in the valley bottom expands [*Tetzlaff et al.*, 2014]. Such expansion connects lateral flow in the upper horizons of the podzolic soils on the steeper hillslope to the channel network [*Tetzlaff et al.*, 2014].

The catchment land cover is dominated by heather (*Calluna vulgaris*) moorland on the steeper hillslopes and *Sphagnum* spp. and *Molinia caerulea* in riparian areas. It is uncultivated but extensively managed. Forest cover, mainly Scots Pine (*Pinus sylvestris*), is limited to small areas on steep slopes.

3. Data and Methods

Monitoring occurred between 22 July 2013 and 22 August 2014. Precipitation was measured every 15 min from a rain gauge ~1 km away from the catchment (operated by Marine Scotland) until 18 December 2013 before a new gauge was installed in the catchment itself (a period of cross comparison showed good agreement). Discharge was calculated at 15 min intervals from stage height measurements in a rated section at the catchment outlet using an Odyssey capacitance rod. Campbell time-domain reflectometry probes were used to measure volumetric soil moisture content (vsmc) at depths of 10, 30, and 50 cm within soil profiles along a hillslope transect (Figure 1).

In situ FDOM data were measured continuously and logged at 15 min time steps using an EXO2 multi sonde (Xylem Inc, NY, USA) situated at the catchment outlet (Figure 1). The sensor measures the fraction of DOC that absorbs light in the UV range of 365 nm (±5 nm) and emits at 480 nm (±40 nm). It was recalibrated every 3 months throughout deployment using quinine sulfate standards and expressed as quinine sulfate units (QSU), though drift was negligible. A wiper installed on the sensor reduced the risk of biofouling and the sensor was removed monthly for inspection. Additionally, the sonde measured water temperature (°C), specific electrical conductance (μS cm^{-1}), pH, and turbidity (Formazin Nephelometric Unit (FNU)). These were also calibrated on the same occasions as FDOM.

Discrete daily stream water samples were collected using an ISCO 3700 autosampler to determine DOC concentration. Samples were stored at 4°C and following filtration through 0.45 μm pore filters the samples were analyzed using a LABTOC Aqueous Carbon analyzer. This method is based on converting DOC to CO_2 using UV light before measuring the concentration using infrared gas analysis. The detection limit of DOC is 0.5 mg L^{-1}.

Daily precipitation and stream water samples were also collected for stable isotope analysis using ISCO 3700 autosamplers. These samples were preserved by paraffin to prevent evaporation losses and collected weekly before analysis in the laboratory using a Los Gatos DLT-100 laser isotope analyzer (precision of $\pm 0.4\permil$ for δ^2H; $\pm 0.1\permil$ for δ^{18}O). Due to the greater precision of deuterium, this was mainly used in our analysis, reported in δ notion according to the Vienna Standard Mean Ocean Water standards.

Data processing was carried out in the R programming language (R Core Team, 2014). First, the FDOM data were preprocessed using the robfilter package [*Fried et al*., 2012] to eliminate spurious data from instrument noise caused, for example, by leaves blocking the probe or removal of the sonde from the water for inspection. The FDOM data were then corrected for temperature, turbidity and inner filter effects using the method outlined by *Downing et al*. [2012]. Turbidity was low throughout the sampling period, with an average value of 0.28 FNU. There was only one larger peak in turbidity (136 FNU), which occurred midst the event with the largest instantaneous discharge (supporting information Figure S3). A linear regression model between sensor output and laboratory measured DOC was developed using 211 data points covering both base flow and high-flow conditions. A strong linear relationship was observed ($r^2 = 0.8$, $p < 0.0001$), which was used to predict DOC (supporting information Figures S1 and S2).

To be able to link the DOC dynamics to changes in water flow paths and water ages, we used the daily isotope time series in a separate modeling study [*Soulsby et al*., 2015] to estimate water ages of the main flow paths involved in runoff generation. The tracer-aided runoff model adopted was developed by *Birkel et al*. [2011a, 2011b, 2014] and *Birkel and Soulsby* [2015]. The model consisted of three conceptual stores representing the main landscape units: the hillslopes, the dynamically saturated riparian zone and groundwater. Key to the model is successfully capturing the nonlinear streamflow response by conceptualizing the hydrological connectivity of the catchment that links the three conceptual stores. By using isotopes to time-stamp and track the daily incoming precipitation and input and output fluxes through each of these stores, the age of the waters in the flux from the different landscape units could be estimated. This resulted in a predicted daily time series of the saturation overland flow age, hillslope water age and groundwater age. Within each of the stores complete mixing was assumed, but the stream water age is extracted by integrating the time-variant contribution of the differently aged water fluxes from the three stores, giving nonlinear mixing at the catchment scale. See *Soulsby et al*. [2015] for full details of how the flux ages used in this study were derived.

4. Results

4.1. High-Frequency DOC Dynamics in Stream Water

Figure 2 shows the time series of precipitation, discharge, DOC and specific conductivity for the study period. The study began in summer 2013, which was the driest summer in 10 years. Following this, the winter period (December–February) was wet with total precipitation of 439 mm, 181% of the 1971–2000 winter average. The highest daily flows of 19 mm d^{-1} occurred on 29 January 2014 (Table 1). Conditions were drier than average in the following spring (March–May), prior to some larger rainfall events in June and another dry period in July. The highest instantaneous discharge of 0.24 mm 15 min^{-1} occurred in August 2014 in response to the highest single precipitation event, when 32.2 mm of rain fell in 1 day (Table 1). That month experienced precipitation 280% of the 1971–2000 August average.

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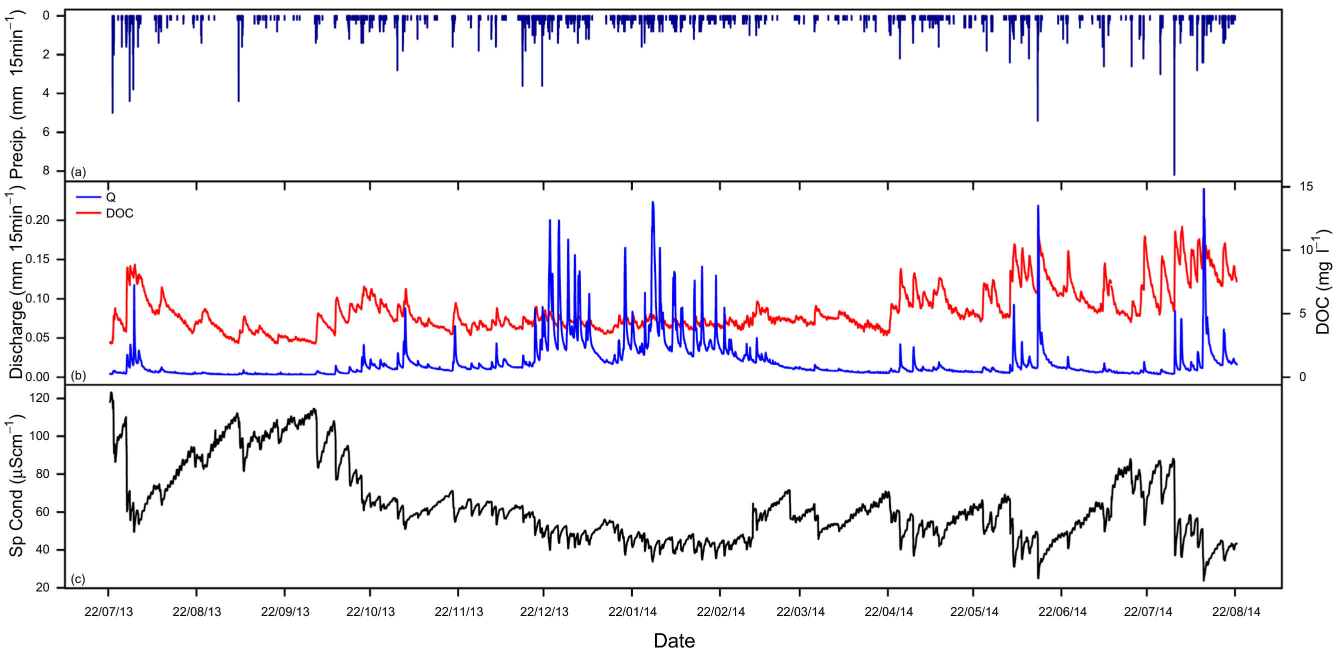

Figure 2. Time series of (a) precipitation, (b) discharge and predicted DOC derived from FDOM, (c) specific conductivity and pH. Equation used to predict DOC = 0.07 (FDOM) + 0.53.

Generally, increases in discharge resulted in increases in DOC concentrations inferred from the FDOM probe (Figure 2b). However, the relationship was nonlinear with the highest concentration of DOC not always corresponding to highest discharge in either summer or winter. As expected, lower DOC concentrations and less marked responses to events occurred during winter. The mean winter DOC concentration was 4.3 mg L^{-1}. During summer, concentrations were higher and had more marked responses to discharge. The minimum DOC concentration was 2.7 mg L^{-1} and occurred during low flow conditions in the exceptionally dry summer of 2013 (Table 1). The maximum DOC concentration (at 15 min) during the study period was

Table 1. Summary Statistics of Variables Measured in the Bruntland Burn for the Study Period 22 July 2013 to 22 August 2014

Data	Unit	Mean	Minimum	Maximum	Standard Deviation
Discharge (Q)	mm d^{-1}	1.97	0.318	19.20	2.54
	mm 15 min^{-1}	0.02	0.003	0.24	0.03
Precipitation	mm d^{-1}	2.97	0	32.20	5.07
	mm 15 min^{-1}	0.03	0	8.20	0.16
FDOM	QSU	63	28.52	192.29	22.70
Predicted DOC	mg L^{-1}	5.22	2.65	14.83	1.69
Measured DOC	mg L^{-1}	5	1.9	12.14	1.71
Turbidity	FNU	0.28	0	136.58	1.50
pH		6.8	5.67	7.68	0.34
Temperature	°C	8.65	0.52	21.90	4.61
Specific conductivity	μS cm^{-1}	63.11	23.77	123.20	19.26
Soil moisture	vsmc				
Peat		0.83	0.77	0.85	0.02
Peaty Gley					
10 cm		0.71	0.65	0.75	0.03
30 cm		0.39	0.32	0.40	0.02
50 cm		0.36	0.35	0.37	0.01
Podzol					
10 cm		0.32	0.23	0.44	0.04
30 cm		0.29	0.22	0.39	0.04
50 cm		0.28	0.21	0.35	0.04
Isotopes	(‰)				
Precipitation δ^2H		−55.51	−147.31	−12.34	26.06
Stream δ^2H		−56.7	−73.11	−49.52	3.88

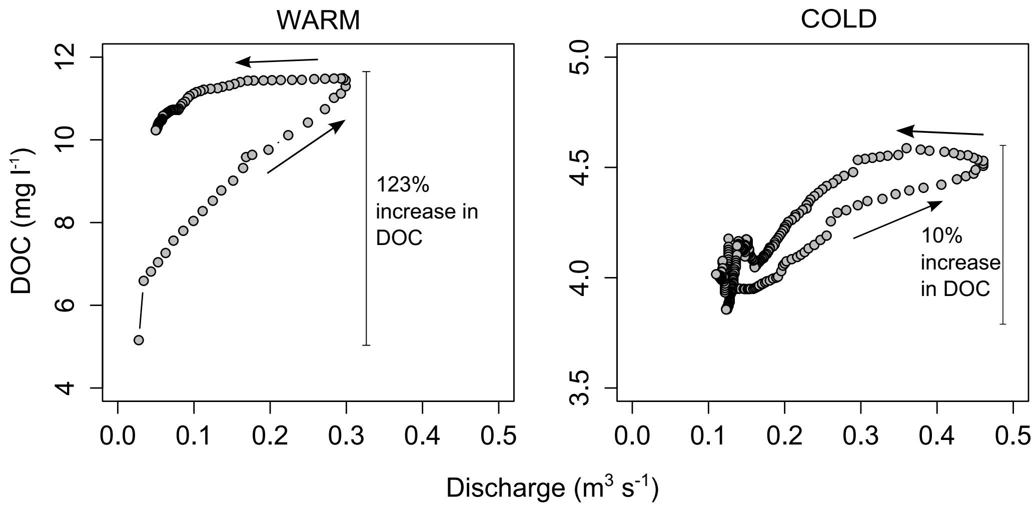

Figure 3. Discharge to DOC concentration plots showing anticlockwise hysteresis for: (a) an event, beginning 31 July 2014, with warm antecedent conditions (T_{14} = 15.6°C); (b) an event, beginning 19 February 2014, with cold antecedent conditions (T_{14} = 1.73°C).

14.8 mg L^{-1} corresponding to the highest flow intensity measured on 11 August 2014 (Table 1). The highest *daily* mean DOC concentration was 11.2 mg L^{-1} on 3 August 2014.

Throughout the study period, we captured 34 events, allowing the DOC responses occurring during events to be investigated in detail. Figure 3 shows the hysteresis plots of two events which are typical of fairly consistent responses during summer and winter events. One during July 2014, when the average temperature 14 days preceding the event (T_{14}) was 15.6°C. The other after much colder preceding conditions during February 2014, when T_{14} was 1.7°C. During the "warm" event, DOC concentration increased from 5.2 mg L^{-1} at low discharge (0.03 m^3 s^{-1}) to a maximum of 11.5 mg L^{-1} as discharge peaked at 0.3 m^3 s^{-1}; an overall DOC increase of 123%. During the "cold" event in February, DOC concentration increased from 4.2 mg L^{-1} at flows of 0.13 m^3 s^{-1} to a maximum of 4.6 mg L^{-1} as discharge peaked at 0.46 m^3 s^{-1}; an overall DOC increase of 10%.

We also explored the nonlinearities in the flow-concentration relationships during the summer months (June–August). Figure 4 focuses on summer events and shows the percentage increase in discharge from the beginning to the peak of an event versus the corresponding percentage increase in DOC concentration. The events were classified into two categories: those with wet and with dry antecedent conditions (13 and 5 events, respectively). Events were classed as dry or wet when precipitation total 14 days preceding (P_{14}) was less or greater than 35 mm, respectively. During wet antecedent conditions the percentage increase in DOC ranged from 9 to 73%. During dry antecedent conditions ranges were higher (58–129%) even though discharge increases were smaller. The gradient of the relationship between DOC and discharge was steeper for dry antecedent conditions as even minor increases in discharge resulted in large increases in DOC. There was no relationship between T_{14} and the percentage increase in DOC between these summer events. Figure 5a illustrates a rewetting period during the 10 year return period drought at the end of July 2013. The DOC increase was caused by a small peak at the beginning of the event preceding the large discharge peak. Daily measurements (Figure 5b) would not have detected this DOC increase during small peaks.

The overwhelming majority of events analyzed (32 out of 34) exhibited an anticlockwise hysteresis. Lag times between the peaks in discharge and in DOC varied between 15 min and 12 h. The average lag time was 5 h. The two clockwise hysteresis loops, when DOC peaked prior to discharge, occurred in intense summer precipitation events after wet antecedent conditions. The lag time for these events was short, only 30 min. There was no relationship observed between antecedent conditions (P_{14} and T_{14}) and lag time.

4.2. Temporal Dynamics in Water Sources, Flow Paths, and Ages

To understand how soil moisture dynamics drive changes in flow paths and hydrological connectivity generating streamflow, time series of volumetric soil moisture content (vsmc) of the soils in the three main

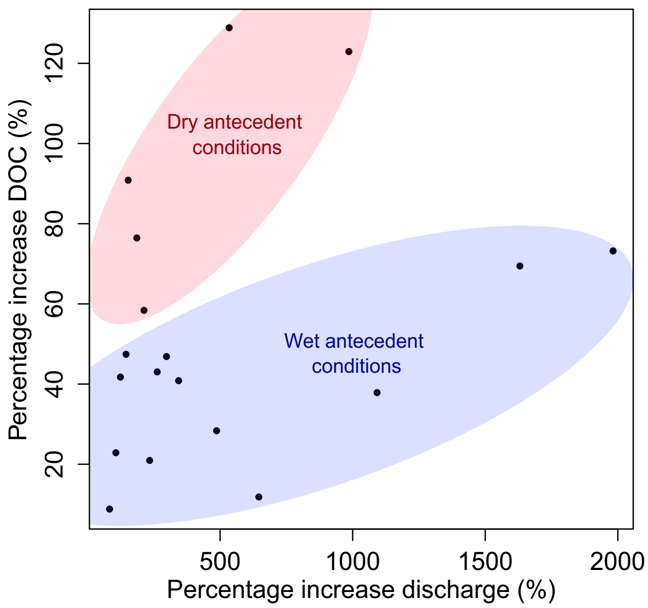

Figure 4. Percentage increase in discharge versus the percentage increase in DOC for 18 summer events.

landscape units are shown in Figure 6. The peat soils in the valley bottom showed little variability in soil moisture and remained at or close to saturation (∼83% vsmc) throughout the year (Figure 6a). Constant seepage from upslope areas and incident precipitation resulted in a dominance of saturation overland flow which can be readily observed in the field and is evident from groundwater levels in observation well networks [see *Blumstock et al.*, 2016]. The peaty gleys on the lower slopes (Figure 6b) were similarly wet, remaining close to saturation (around 70%) in the organic upper horizon throughout the sampling period. The deeper minerogenic horizons had a lower vsmc of around 38%, but also showed little variability. The podzols on the steeper hillslopes showed a much more dynamic response throughout the profile with clear wetting and drying at all depths (Figure 6c) which also corresponds to increased water table levels [*Blumstock et al.*, 2016]. Maximum vsmc was 44% in the organic-rich surface horizon during larger events and minimum was 23% during dry periods in summer 2013 and spring 2014. Near-continuous vsmc of around 40% occurred during the winter wet period in December 2013 to January 2014.

Specific conductivity declined when discharge increased (Figure 2). This gives an index of the total solute concentration in stream waters and the inverse relationship with discharge generally reflects the dilution of groundwater. Dry periods were dominated by high conductivities (maximum was 123 μS cm^{-1}), whilst wet periods and events caused low specific conductivities (Table 1). The lowest measurement of 23 μS cm^{-1} occurred during the largest daily rainfall event in August 2014 (Table 1). Simple hydrograph separation using specific conductivity showed that the relative groundwater (GW) contribution was dominant during the dry period in summer 2013 (supporting information Figure S4). During this period, the lowest DOC concentrations were recorded (Figure 2b). As the winter wet period progressed, GW contributions steadily decreased to around 20% on average. The lowest relative GW contribution (highest soil water contribution)

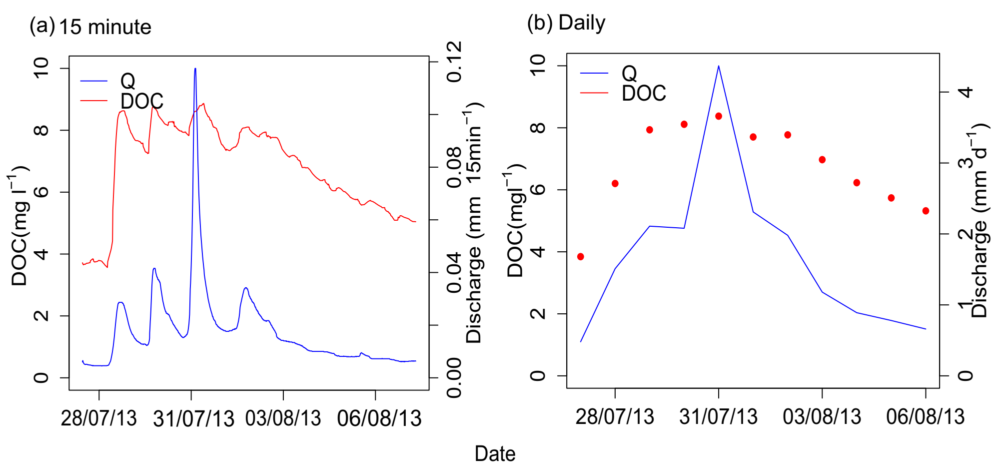

Figure 5. Time series of DOC and discharge for (a) 15 min data and (b) daily data, during an event following a 10 year return period drought at the end of July 2013.

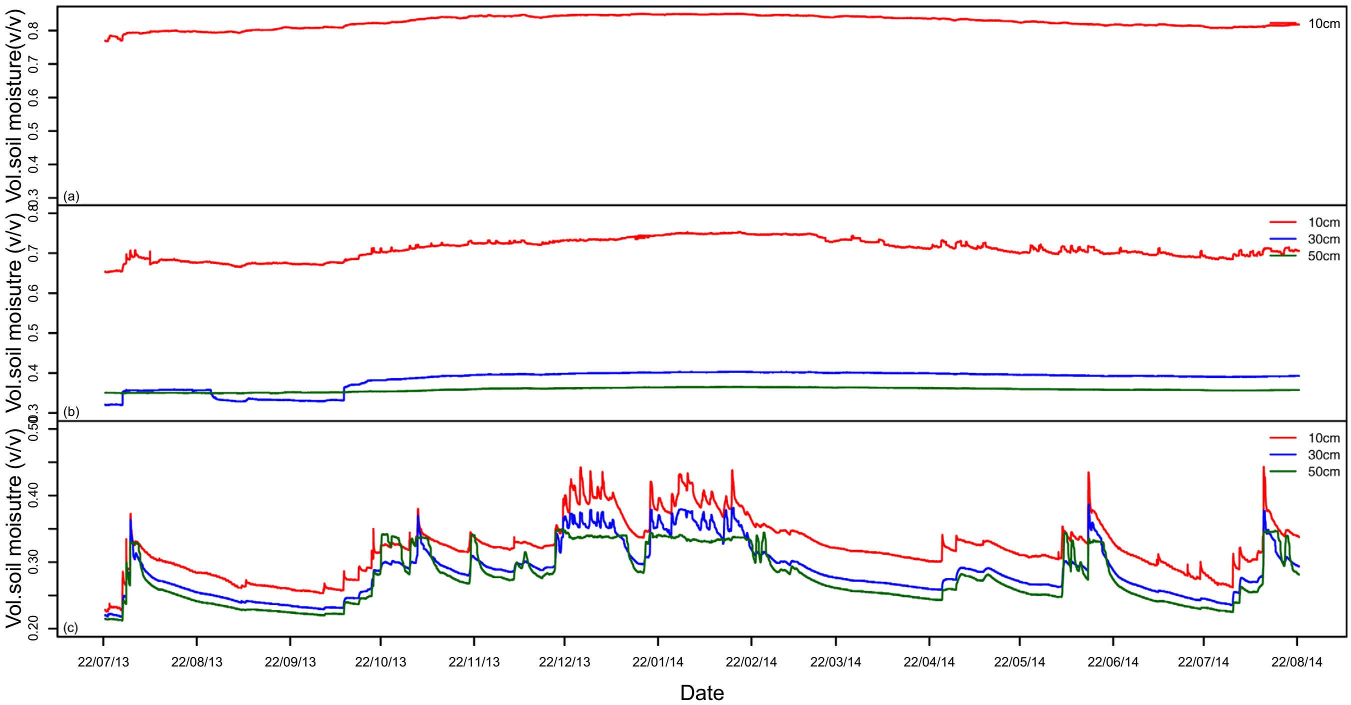

Figure 6. Time series of soil moisture (vsmc) in (a) a valley bottom riparian peat soil, (b) a peaty gley soil on the lower hillslopes, and (c) a podzol on the upper hillslopes.

occurred during the largest instantaneous discharge in August 2014. This corresponded to the maximum predicted DOC concentration on a 15 min frequency (Figure 2b).

Stable isotopes δ^2H were used to gain further insight into the temporal dynamics of different water sources and to allow the daily water ages in their fluxes to be tracked. Figure 7a illustrates the high variability and seasonality in δ^2H signatures in precipitation (mean = −55.5‰, range = 135‰), with enriched values in summer and depleted values in winter. This variability was damped in stream water signatures (mean = −56.7‰, range = 23.6‰) although a similar seasonality was observed (Figure 7b). Persistently high winter precipitation resulted in more depleted δ^2H signatures in stream water. A more direct linkage between precipitation input and stream water response was apparent during the event at the end of summer 2014. Results from the simple, isotope-based, two-component hydrograph separation model (supporting information Figure S5), suggested that, most of the time, stream water was dominated by preevent water and event water contributed less than 10%. Only on four occasions did event water exceed 50%; these generally occurred during wet winter periods when soils were most saturated; connectivity between hillslopes and the stream was highest and overland flow and shallow subsurface runoff generation processes were dominating. The maximum event water contribution was 71% and occurred during an event in the winter wet period (31 January 2014). However, high event water contributions also occurred during smaller events when Q_{14} was low after the dry period in the summer of 2013 and during small discharge events in July 2014.

Over the study period, the median age of stream water derived from coupled flow-tracer modeling by *Soulsby et al*. [2015] was 2.5 years (±1.5 SD). This represents the integration of nonstationary water ages in fluxes from different landscape units; i.e., overland flow from quasi-permanently saturated areas, near-surface flow from hillslopes, and deeper groundwater discharge (Figure 7c). Youngest stream water occurred during events dominated by recent overland flow (~2.5 months old), which occurred during the largest daily discharge event during the winter wet period (31 January 2014). This event also had the highest antecedent flows (Q_{14}) and soils were closest to saturation throughout the catchment (Figure 6). These findings are consistent with the results of the isotope hydrograph separation with a high new water contribution. During this winter wet period, the hill slopes with relatively young water (mean age ~ 1 week) became connected to the riparian zone, and overland flow (OF) age was on average 10 days old (Figure 7d).

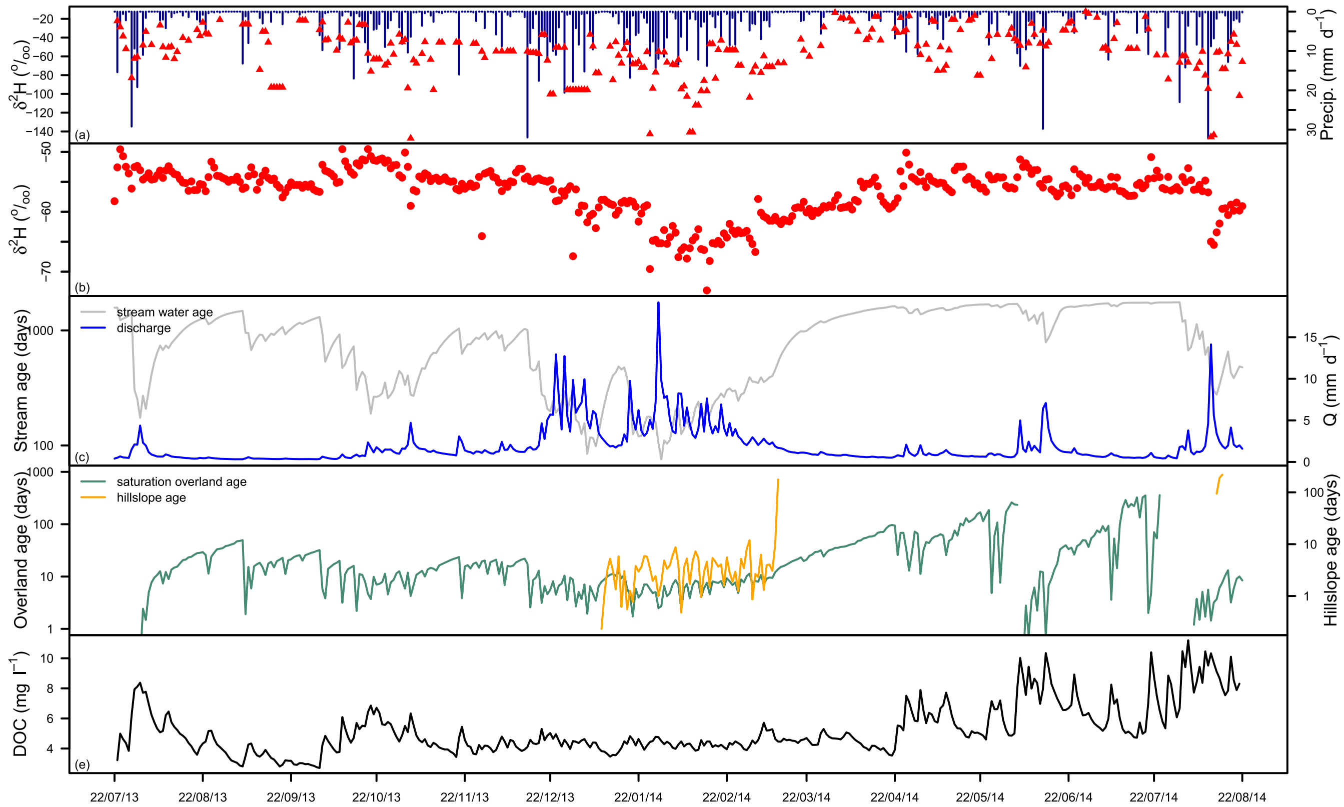

Figure 7. Daily time series of: (a) precipitation (blue bars) and δ^2H signatures of precipitation (red triangles), (b) δ^2H of stream water, (c) median water flux age of stream water against discharge, (d) median water age of fluxes from the hillslope and the saturation area, and (e) daily DOC.

According to the modeling results, the only other time the hillslopes were connected during the study period was for 3 days during the largest rainfall event from 12 to 14 August 2014. This is broadly consistent with the soil moisture data for the podzols shown in Figure 6.

Outside the winter wet period, the youngest stream waters ($\sim$6 months old) occurred during the July 2013 event. This event had the lowest antecedent Q_{14}. Results from the hydrograph separation implied that, prior to the event, groundwater was almost the entire source of water to the stream (95%). This contribution decreased to 30% at peak discharge. Overland flow during this event was very young ($<$1 day old). Due to the dryness of the catchment during this period, the steeper hillslopes remained disconnected and there were no hillslope fluxes, so flows were generated from the riparian area which had more limited water stored to mix with incoming precipitation. This was similar to dry periods in summer 2014 (end of June and beginning of July). The model predicted that overland flow ceased during this period. However, this was likely an artefact of the model's limitations as even during the driest periods a few wet zones usually still remain. The oldest stream water ages ($\sim$4 years) occurred between events, during dry periods, when GW was the dominant contribution to the stream.

Daily ages of overland flow and stream water were negatively correlated with daily DOC concentrations (Table 2). Daily DOC concentrations were derived from the continuous time series to be consistent with daily water age estimates. During events when stream water was characterized by a predominance of younger water sources, higher DOC concentrations were found. These relationships were nonstationary and in 6 out of the 13 months studied, overland flow and stream water age were more significantly correlated with DOC than discharge. Correlations between DOC concentrations and overland flow age were significant ($p < 0.01$) in all months apart from March 2014. In March, the catchment was still drying up after the winter wet period, resulting in a gradual decrease in discharge and gradual increase in stream water and overland flow age. Temperatures were still low and DOC production was limited by temperature. The strongest correlation between DOC and overland flow age occurred in August 2013 ($r^2 = 0.8$, $p < 0.0001$). When multiple linear regressions (MLR) were explored between daily DOC and discharge, as well as overland flow age, the

Table 2. Summary of Monthly r^2 and p Value of DOC, Discharge (Q), Overland Flow (OF) Age, and Stream Water (SW) Age Relationships

Month	DOC Versus Q r^2	DOC Versus OF Age r^2	DOC Versus SW Age r^2	DOC Versus Q + OF Age r^2	DOC Versus Q + SW Age r^2
Aug 2013	0.77***	0.8***	0.85***	0.91***	0.90***
Sep 2013	0.68***	0.36**	0.49***	0.69***	0.75***
Oct 2013	0.58***	0.71***	0.83***	0.81***	0.85***
Nov 2013	0.73***	0.67***	0.58***	0.91***	0.88***
Dec 2013	0.28*	0.45***	0.36**	0.49***	0.38*
Jan 2014	0.5***	0.59***	0.24*	0.68***	0.53***
Feb 2014	0.4**	0.37**	0.05	0.53***	0.40*
Mar 2014	0.07	0.02	0.01	0.11	0.22*
Apr 2014	0.69***	0.37**	0.05	0.73***	0.70***
May 2014	0.7***	0.55***	0.38**	0.80***	0.71***
Jun 2014	0.49***	0.39**	0.46***	0.60***	0.59***
Jul 2014	0.18*	0.38**	0.03	0.51**	0.19
Aug 2014	0.2*	0.44*	0	0.61*	0.28

*Significant at $p < 0.05$, **significant at $p < 0.001$, and ***significant at $p < 0.0001$.

relationships were improved. Excluding March, the relationship between DOC and discharge, as well as overland flow age, had an average coefficient r^2 of 0.65 and p value < 0.01. The correlations between DOC and stream water age also produced significant results but not as strong and consistent across months as overland flow age. Again, when combined with discharge in MLR the relationships were improved. In all cases, there was no relationship in March mainly due to the lack of substantial flow increases.

5. Discussion

5.1. Temporal Dynamics in DOC Concentration

The high-resolution FDOM data allowed us to investigate the temporal variability in DOC with an unprecedented level of detail over a 13 month period. As shown in many other studies, on a seasonal scale, the DOC concentrations and responses to discharge were lower in winter and early spring, and higher in summer and autumn [*Dawson et al*., 2008; *Raymond and Saiers*, 2010*; Strohmeier et al*., 2013; *Birkel et al*., 2014; *Jones et al*., 2014] as a result of DOC production and mobilization from soil organic matter being temperature dependent [*Birkel et al*., 2014; *Dick et al*., 2015]. However, the transport of DOC to the stream was often restricted during the summer due to limited hydrological connectivity, particularly in the exceptionally dry summer of 2013 when the lowest stream concentrations of DOC were observed. Groundwater levels across the catchment at this time showed that the catchment hillslopes and much of the surface riparian zone were disconnected from the stream network *[Blumstock et al*., 2016]. Thus, deeper sources of groundwater low in DOC ($\sim$2 mg L^{-1}) dominate runoff.

The FDOM probe provided a unique opportunity to observe and compare high-resolution DOC dynamics and responses to discharge on an event scale throughout the whole study period. The steepness of the hysteresis loops varied due to the temperature influence on DOC production, with warmer temperatures allowing more DOC to be readily available for mobilization [*Raymond and Saiers*, 2010; *Pellerin et al*., 2011; *Strohmeier et al*., 2013]. Aside from temperature controlled seasonal responses, there were also distinctly different responses depending on wet or dry antecedent conditions resulting in nonlinearity between DOC and discharge during summer events alone. Antecedent wetness conditions have been identified as a control over DOC response during events in previous studies [*Raymond and Saiers*, 2010; *Oswald and Branfireun*, 2014], and results here suggested they are highly important in explaining DOC concentration dynamics within the Bruntland Burn.

Previous research has found both clockwise hysteresis [*Hornberger et al*., 1994; *McGlynn and McDonnell*, 2003; *Hood et al*., 2006; *Raymond and Saiers*, 2010; *Jeong et al*., 2012] and anticlockwise hysteresis [*Inamdar et al*., 2004; *Rusjan et al*., 2008; *Saraceno et al*., 2009; *Pellerin et al*., 2011; *Strohmeier et al*., 2013; *Laudon et al*., 2011]. Clockwise hysteresis, with higher DOC on the rising limb, has been attributed to the initial flushing of DOC from organic-rich soils in riparian zones before decreasing as the event continues and deeper mineral soil waters from the hillslopes enter the streams with lower DOC [*McGlynn and McDonnell*, 2003; *Hood et al*., 2006]. A second possible cause for clockwise hysteresis is the temporary depletion of DOC supply [*Hornberger et al*., 1994; *Raymond and Saiers*, 2010]. This was likely the case for the two events which had clockwise hysteresis as they followed previous events with large flushes of DOC. Overall, we found mostly anticlockwise hysteresis relationships across events, with peak DOC concentration on the hydrograph's falling limb. *Dick et al.* [2015] identified the importance of saturated peats in the riparian zone in the Bruntland Burn, delivering around 84% of DOC to the stream. The delayed contributions of DOC were most likely a result of the extending riparian saturation zone, which increases in area during wet periods, increasing hydrological connectivity and allowing the transport from otherwise disconnected sources that are rich in DOC [*Inamdar et al.*, 2004; *Pellerin et al.*, 2011]. As *Inamdar et al.* [2004] explained, the lag between the peak discharge and peak DOC is associated with the mobilization and movement of DOC from the saturated areas to the catchment outlet. *Mei et al.* [2014] explored factors controlling lag times suggesting event duration and hydraulic properties of riparian soils as primary controls. Further analysis is required to determine what caused the lag times within the Bruntland Burn ranging between 15 min to 12 h. Preliminary analysis suggests antecedent conditions (T_{14} and P_{14}) do not control this lagged response. Event characteristics (e.g., the magnitude, intensity, and duration of precipitation events) are likely to exert an important influence on lag times.

The high-frequency data allowed us to explore event dynamics in detail, capturing 34 event peaks with 15 min precision and covering a range of events in terms of discharge, season and antecedent conditions. However, data from FDOM probes require careful preprocessing [*Pellerin et al.*, 2011; *Saraceno et al.*, 2009; *Downing et al.*, 2012]. The correction for interferences is necessary due to the potential effects of temperature, light attenuation, and turbidity on FDOM [*Downing et al.*, 2012; *Wilson et al.*, 2013; *Saraceno et al.*, 2009]. Furthermore, routine DOC samples must continue to be collected and analyzed over the study period, so that an understanding of the relationship between DOC and FDOM can be established [*Wilson et al.*, 2013; *Pellerin et al.*, 2011]. In this study, the strong relationship between routine DOC samples and corrected FDOM ($r^2 = 0.8$) confirmed the use of FDOM as a consistent proxy of DOC.

5.2. Influence of Temporal Dynamics in Water Sources, Flow Paths, and Water Flux Ages on DOC Concentration

The use of geochemical and isotopic tracers provided crucial additional insights into the hydrological controls of DOC transport to the catchment outlet. As demonstrated in previous studies, storm events correspond with the highest DOC concentrations. During events, the relative importance of groundwater contributions decreases as near-surface flow pathways with higher DOC concentrations dominate [*Strohmeier et al.*, 2013; *Birkel et al.*, 2014; *Tiwari et al.*, 2014]. During low flows groundwater contributions which are low in DOC are dominant. This is why the lowest DOC concentrations occurred in the dry summer of 2013 when near-surface sources of streamflow had dried up [*Birkel et al.*, 2014; *Tiwari et al.*, 2014; *Blumstock et al.*, 2015]. However, during the wet winter, when the relative contribution of groundwater steadily decreased, DOC concentrations remained low. It is evident that during the winter periods there is an overriding influence of temperature that is causing seasonality in DOC production [*Dawson et al.*, 2011; *Raymond and Saiers*, 2010].

The isotopic damping in stream waters, and the generally low event water contributions, imply the main source of stream water, and DOC, is from the mixing and displacement of soil waters in the riparian zone caused by incident precipitation [*Tetzlaff et al.*, 2014; *Laudon et al.*, 2004; *McGlynn and McDonnell*, 2003]. The riparian soils are at, or close to, saturation all year round, hence, this extended area provides a large store of water available for mixing [*Tetzlaff et al.*, 2014; *Birkel and Soulsby*, 2015]. *Tetzlaff et al.* [2014] described the riparian zone as an "isostat" mixing waters of different ages, and setting the isotopic signature of the stream under most conditions. During events, as the riparian saturation zone expands through incident precipitation and increased connectivity with upslope sources, newer water mixes with and displaces the old water in the riparian zone. This results in stream water being dominated by DOC-rich preevent water. During the wettest periods, the saturation zone may cover up to 40% of the catchment area [*Tetzlaff et al.*, 2014]. Other studies have recognized the importance of the riparian zone in both the generation of runoff [*McGlynn and McDonnell*, 2003; *Birkel et al.*, 2011a; *Jencso et al.*, 2010] and as the main source of DOC [*Fiebig et al.*, 1990; *Bishop et al.*, 1994; *Ågren et al.*, 2014; *Dick et al.*, 2015; *Ledesma et al.*, 2015; *Strohmeier et al.*, 2013; *Pacific et al.*, 2010].

By using the daily isotopes in a tracer-aided runoff model from a previous study we extracted estimates of the ages of the main fluxes from the dominant landscape units, gaining insights into hydrological connectivity, mixing processes and storage dynamics [*Soulsby et al.*, 2015]. We advanced on this previous study by

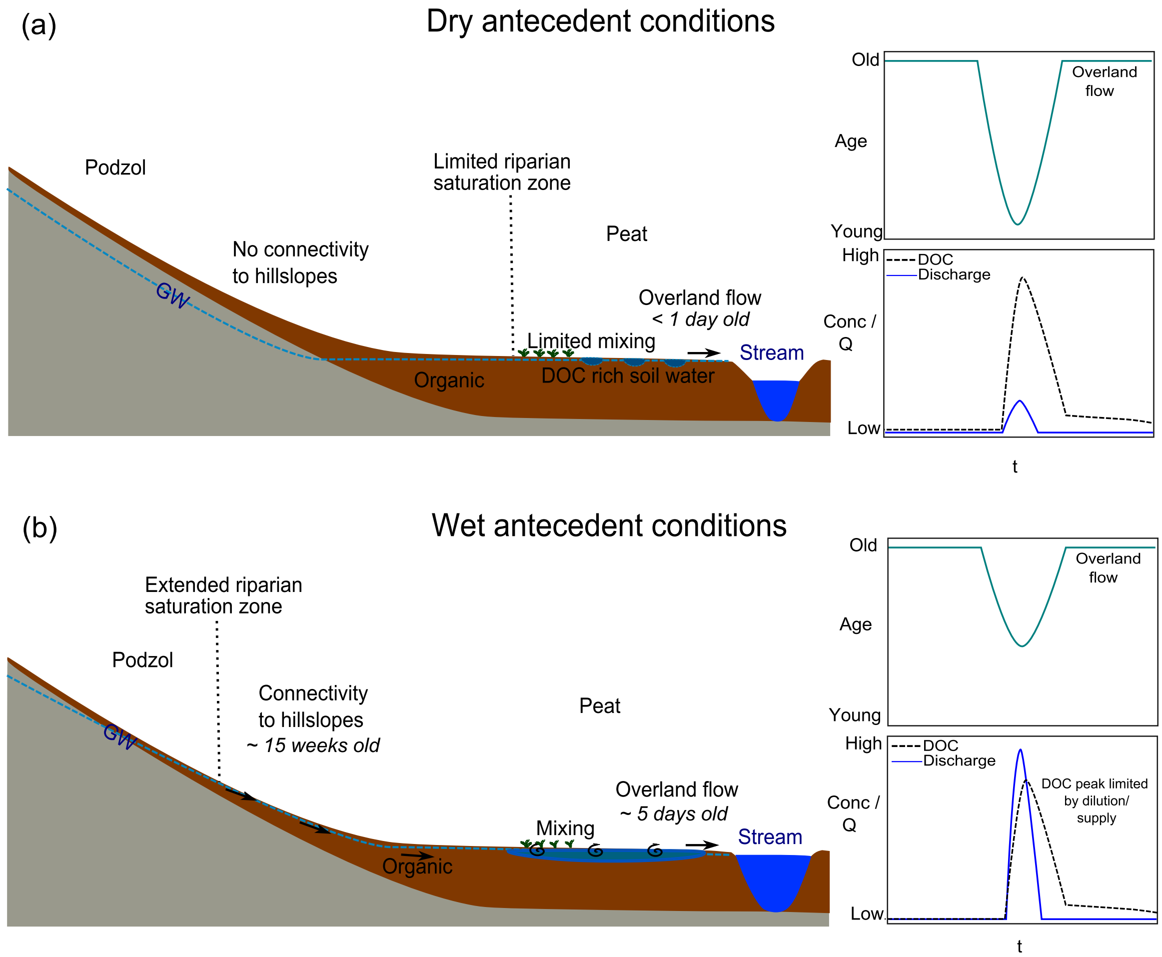

Figure 8. Conceptual diagram illustrating the role of antecedent conditions, during summer events, on hydrological mechanisms influencing DOC flushing.

linking the hydrological interpretations from the model to the mechanisms responsible for transporting DOC. The model captures the water flux dynamics fairly well, however, limitations were identified and there is some uncertainty in estimating the flux ages precisely [*Soulsby et al.*, 2015]. Nevertheless, the relative ages of water fluxes from different landscape units have less uncertainty and remain a useful basis for understanding processes governing DOC mobilization. Hydrochemical data collected from the catchment indicate that the majority of DOC is coming from surface flow pathways hence the saturation overland flow age was a particularly useful predictor. The high-frequency DOC data identified the influence antecedent conditions have on the DOC response during events. Overland flow age is influenced by and integrates antecedent conditions. Hence, it has a stronger relationship with DOC than discharge during months with more extreme conditions. For the first time, we used this approach of extracting overland flow age to explain the mechanistic processes responsible for causing the response in DOC and delivery to the stream to be dependent on antecedent conditions. We conceptualized the identified linkages between sources, flow paths, connectivity, consequent water flux ages and DOC concentrations in Figure 8. During small events after dry periods (Figure 8a), high stream DOC concentrations occurred caused by very small discharge increases (for example, July 2014). This resulted in nonlinearity between DOC and discharge. During such events, although only minor increases in discharge occurred, the overland flow age is very young (<1 day old). Dry antecedent conditions result in a reduction in stored water in the riparian zone, compared to wetter periods. Therefore, limited mixing occurs with older waters causing overland flow age to decrease. Overland flow age had a stronger relationship with DOC than discharge during these dry periods (13 August and 14 July). This is in agreement with studies by *James and Roulet* [2009] and *Brown et al.* [1999], who found higher new event water contributions during dry periods. Yet this contradicts findings by *Shanley* *et al*. [2002] who suggested dry antecedent conditions result in increased infiltration causing a greater displacement of old water to the stream. However, *Shanley et al*. [2002] also identified spatial variability in this relationship due to infiltration being dependent on soil transmissivity and surface saturation. Considering the Bruntland Burn is predominantly peat in the riparian zone and close to saturation throughout the year, infiltration is limited in these main areas of carbon storage even during dry antecedent conditions.

These small discharge events during dry periods are enough to displace a minimal amount of highly concentrated DOC-rich soil waters from areas that were previously transport limited (Figure 8a). The small increase in discharge at the beginning of the event caused the large increase in DOC due to the flushing of a modest volume of concentrated soil DOC (Figure 5). Following this, the increased discharge did not increase DOC further as it was limited by DOC supply, resulting in the nonlinearity between DOC and discharge. This is consistent with *Raymond and Saiers* [2010] and *Oswald and Branfireun* [2014] where events that occurred after drier conditions resulted in higher DOC concentrations due to the generation of DOC in soils ready for mobilization. During dry periods, the breakdown of carbon in the soils continues, adding to the carbon available to be flushed out during the next event [*Worrall et al*., 2002; *Inamdar et al*., 2011].

After wet antecedent conditions the riparian saturation zone expands upslope, connecting to the upper organic horizons of the podzols, providing an additional source of DOC (Figure 8b). Upslope expansion of saturation is evident from the peaks in the podzol soil moisture data (and groundwater well data shows the rise of the water table into the soil profile), especially during the winter period and large August event in summer 2014 (Figure 6). This connection to the organic horizons of the podzols likely also contributes to the flush of DOC during wet periods in the summer. The event in August 2014 corresponded to the maximum DOC concentration recorded at a 15 min frequency, indicating the importance of this hydrological connectivity. *Dick et al*. [2015] used modeling to infer that the connectivity to the upper hillslopes contributes around 16% of the total DOC load to the stream, via the riparian area. During wetter periods, overland flow age did not decrease as much compared to dry periods. Wetter antecedent conditions allow mixing with greater volumes of stored waters in the riparian zone and the hillslope contributions enhance the displacement of preevent waters [*James and Roulet*, 2009] (Figure 8b). This is consistent with a study by *Casper et al*. [2003] that found wetter antecedent conditions resulted in a decrease in event water contributions due to more mixing with preevent soil waters.

The DOC peaks during summer events occurring in wet antecedent conditions were limited. There was a lower gradient between the percentage increase in discharge versus percentage increase in DOC compared to dry antecedent conditions (Figure 4). One hypothesis for this limitation is a dilution effect [*Pacific et al*., 2010; *Oswald and Branfireun*, 2014; *Buffam et al*., 2007]. During large rainfall events, the expansion of the saturation area into the hillslopes results in soil moisture peaks in the hillslopes and the flush of DOC from the organic-rich layers in the podzols. However, the saturation in upper organic-rich layers does not last long and as runoff begins to decrease, the flow paths deepen to the minerogenic layers, which are poor in organic material. This water mixes in the riparian zone causing a dilution in DOC. A second hypothesis is a supply limitation. During large events, DOC becomes limited due to exhaustion of DOC in soil water and therefore, the event progressively becomes diluted in DOC [*Jones et al*., 2014; *Worrall et al*., 2002; *Buffam et al*., 2007]. Overland flow age provided a better predictor of DOC than discharge during wet periods (December 2013, January 2014, and August 2014) as it takes account of the antecedent conditions which influence DOC transport to the stream.

6. Conclusions and Wider Implications

We examined the link between DOC dynamics and tracers in a peat-dominated catchment in the Scottish Highlands with the overall goal of identifying the causes of temporal variation in DOC concentration. In addition to the influences of temperature and discharge on temporal dynamics in DOC, our study highlighted the specific importance of antecedent conditions, flow paths, connectivity and the ages of water sources.

High-frequency measurements allowed us to explore DOC dynamics in detail, capturing 34 event peaks which covered a range of seasons and antecedent conditions. Using FDOM as a proxy for DOC revealed:

1. Marked seasonality, with highest DOC concentrations (~15 mg L^{-1}) in summer events and lower concentrations (~4 mg L^{-1}) in winter.
2. Nonlinearities in the flow-concentration relationships in summer events as a result of different event responses depending on dry or wet antecedent conditions.
3. Almost all events displayed anticlockwise hysteresis relationships; consistent with the expansion of the riparian saturation area, increasing hydrological connectivity across peat soils and mobilizing DOC.
4. Wide range in lag time (15 min to 12 h) between discharge and DOC peak, likely to be linked to event characteristics.

Using stable isotope tracers in a tracer-aided model to determine the ages of water fluxes from different landscape units and to directly link this to DOC dynamics has helped to better understand the landscape controls on this important carbon pathway. In particular, overland flow age was a good predictor for DOC transport because it reflects antecedent conditions. During small events with dry antecedent conditions, DOC response was proportionally higher caused by the displacement of a small volume of previously unconnected, highly concentrated soil waters. During large events with wet antecedent conditions, the large volume of water causes the expansion of the riparian saturation zone to organic layers on hillslopes resulting in peaks in DOC. However, DOC peaks in such events are limited due to either dilution effects or supply limitation.

The value of in situ FDOM sensors was highlighted in providing insights into the processes responsible for DOC transport on a subevent event scale. Future work should focus on obtaining higher-frequency tracer data and using this data in integrated ways to answer specific questions about flow pathways and mechanisms of DOC transport.

Wider implications from this study include the importance of the riparian area in regulating the quality and age of waters, hence the need to encompass these sensitive areas in land management strategies. Furthermore, the influence of antecedent conditions on temporal DOC dynamics has been highlighted, which will likely become more significant in the future with changes in precipitation and temperature resulting in more extreme conditions. Hence, gaining further understanding of DOC dynamics will improve our ability to evaluate the effects of climate change on this integral component of water quality.

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