AGU PUBLICATIONS

Water Resources Research

RESEARCH ARTICLE
10.1002/2015WR016927

Key Points:
- DOC is generated in shallow-to-bedrock soils
- Distal sources of DOC are detected at the catchment outlet
- Near-stream soils were not found to be DOC sources

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Citation:
Gannon, J. P., S. W. Bailey, K. J. McGuire, and J. B. Shanley (2015), Flushing of distal hillslopes as an alternative source of stream dissolved organic carbon in a headwater catchment, *Water Resour. Res.*, *51*, 8114–8128, doi:10.1002/2015WR016927.

Received 12 JAN 2015
Accepted 13 SEP 2015
Accepted article online 16 SEP 2015
Published online 12 OCT 2015

Flushing of distal hillslopes as an alternative source of stream dissolved organic carbon in a headwater catchment

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Abstract We investigated potential source areas of dissolved organic carbon (DOC) in headwater streams by examining DOC concentrations in lysimeter, shallow well, and stream water samples from a reference catchment at the Hubbard Brook Experimental Forest. These observations were then compared to high-frequency temporal variations in fluorescent dissolved organic matter (FDOM) at the catchment outlet and the predicted spatial extent of shallow groundwater in soils throughout the catchment. While near-stream soils are generally considered a DOC source in forested catchments, DOC concentrations in near-stream groundwater were low (mean = 2.4 mg/L, standard error = 0.6 mg/L), less than hillslope groundwater farther from the channel (mean = 5.7 mg/L, standard error = 0.4 mg/L). Furthermore, water tables in near-stream soils did not rise into the carbon-rich upper B or O horizons even during events. In contrast, soils below bedrock outcrops near channel heads where lateral soil formation processes dominate had much higher DOC concentrations. Soils immediately downslope of bedrock areas had thick eluvial horizons indicative of leaching of organic materials, Fe, and Al and had similarly high DOC concentrations in groundwater (mean = 14.5 mg/L, standard error = 0.8 mg/L). Flow from bedrock outcrops partially covered by organic soil horizons produced the highest groundwater DOC concentrations (mean = 20.0 mg/L, standard error = 4.6 mg/L) measured in the catchment. Correspondingly, stream water in channel heads sourced in part by shallow soils and bedrock outcrops had the highest stream DOC concentrations measured in the catchment. Variation in FDOM concentrations at the catchment outlet followed water table fluctuations in shallow to bedrock soils near channel heads. We show that shallow hillslope soils receiving runoff from organic matter-covered bedrock outcrops may be a major source of DOC in headwater catchments in forested mountainous regions where catchments have exposed or shallow bedrock near channel heads.

1. Introduction

One of the ways carbon moves through the landscape is as dissolved organic carbon (DOC) in soil water, groundwater, and stream water. In addition to its central role in carbon export from ecosystems, DOC in surface water is a key component of nutrient cycling [*Neff et al.*, 2003; *Brookshire et al.*, 2005] and facilitates the transport of metals [*Mierle and Ingram*, 1991; *Demers et al.*, 2010]. Understanding DOC pathways is important for describing carbon fluxes and export, as well as biogeochemical processes in catchments [*Pacific et al.*, 2010; *Laudon et al.*, 2011]. To facilitate this understanding, several authors have identified the importance of determining the spatial distribution of DOC sources to stream water in order to explain variations in DOC output from headwater catchments [*McGlynn and McDonnell*, 2003; *Raymond and Saiers*, 2010; *Ågren et al.*, 2014; *Peralta-Tapia et al.*, 2015].

The primary source of DOC in catchments without wetlands is generally described as stemming from near-stream areas [*Fiebig et al.*, 1990; *Bishop et al.*, 1994; *Sanderman et al.*, 2009; *Vidon et al.*, 2010; *Laudon et al.*, 2011; *Mei et al.*, 2012]. Using observations of water levels and soil water chemistry, several authors have suggested that saturation of near-stream zones by rising water tables mobilizes DOC from near-surface soil horizons high in organic carbon, thereby delivering water with elevated DOC concentrations to streams [*Easthouse et al.*, 1992; *Boyer et al.*, 1997; *Inamdar et al.*, 2004; *Winterdahl et al.*, 2011]. This process is consistent with the variable source area (VSA) concept of runoff generation [*Hewlett and Hibbert*, 1967], where stream contributing area extends from the near-stream area up the hillslope to varying degrees depending on the size of an event, antecedent conditions, soil properties, and topography [*Anderson and Burt*, 1978b; *Dunne*, 1983].

Because of the short flow path distances over which DOC is immobilized in mineral soil [*Guggenberger and Kaiser*, 2003; *Lajtha et al*., 2005; *Yano et al*., 2005], soils distant from the stream are not typically considered as dominant sources of DOC, particularly if flow is relegated to the soil matrix. However, several studies have shown that high DOC water from near-surface organic horizons can travel longer distances than typically described in mineral soil through preferential flow paths [*Kaiser and Guggenberger*, 2005; *Van Verseveld et al*., 2008; *Mei et al*., 2012; *Terajima and Moriizumi*, 2013]. Additionally, while typically not shown to be as prolific a DOC source as near-stream soils, hillslope soils may also be DOC sources in cases where flow paths from organic horizons on the hillslope provide opportunities for transport to the stream [*McGlynn and McDonnell*, 2003; *Terajima and Moriizumi*, 2013; *Ågren et al*., 2014].

Despite the contention that near-stream soils are DOC sources at many sites, several studies have suggested that these soils are not always DOC sources. A number of studies have identified stream reaches in which DOC concentrations decreased downstream [*Dawson et al*., 2001; *Laudon et al*., 2011; *Peralta-Tapia et al*., 2015]. This is not consistent with a uniform near-stream DOC source and instead suggests dilution by downstream sources and/or consumption from in-stream biogeochemical processing [*Kaplan et al*., 1980]. Additionally, *Grabs et al*. [2012] concluded that near-stream soils were not DOC sources upon observing that total organic carbon (TOC) in soil water did not increase on an event basis due to limited rise in near-stream groundwater levels. Finally, in work from the same catchment as this study, *Zimmer et al*. [2013] found that DOC concentrations in groundwater were not higher in near-stream soils than any other hillslope soils. In fact, the highest DOC concentrations observed in groundwater were from shallow soils near bedrock outcrops and upslope of channel heads [*Zimmer et al*., 2013].

In this study, we use a hydropedological framework to further describe and identify sources of stream water DOC in a headwater catchment. To highlight potential DOC source areas, we mapped the probable spatial extent of water table in soils throughout watershed 3 (WS3) at the Hubbard Brook Experimental Forest (HBEF) [*Gillin et al*., 2015] and compared it with DOC concentrations throughout the stream network. A shallow groundwater well and lysimeter network was then utilized to characterize DOC concentrations in soil and groundwater in different soils in the catchment. Finally, high temporal resolution in-stream fluorescent dissolved organic matter (FDOM) was used as a proxy for DOC [*Downing et al*., 2009; *Saraceno et al*., 2009; *Pellerin et al*., 2012] at the catchment outlet to compare the timing of fluctuations in DOC to water levels in shallow groundwater wells in different soils in the catchment. Through this combination of analyses at varying spatial and temporal scales, we addressed the following two research questions:

1. What source areas in the catchment drive spatial patterns of DOC concentrations observed in the WS3 stream network?
2. Can the spatial and temporal patterns in water table fluctuation in DOC source areas help explain temporal variations in stream water DOC concentrations at the catchment outlet?

2. Site Description

This study was carried out at the Hubbard Brook Experimental Forest (HBEF) near North Woodstock, NH in the White Mountain National Forest. We focused on watershed 3 (WS3) (Figure 1), the 42 ha hydrologic reference watershed for paired watershed studies [*Hornbeck et al*., 1970; *Likens et al*., 1970; *Hornbeck*, 1973] and not experimentally manipulated. HBEF has a humid continental climate, with average temperatures of -9°C in January and 18°C in July [*Bailey et al*., 2003]. It receives 1400 mm of precipitation a year, of which a quarter to a third falls as snow.

The bedrock in WS3 is Silurian sillimanite-grade pelitic schist and calc-silicate granulite of the Rangeley formation. The soil parent materials are basal till and water-reworked glacial drift of varying thickness, texture, and hydraulic conductivity deposited during the late Wisconsinan glacial period [*Bailey et al*., 2014]. The average slope in WS3 is 28%, with a dominantly southern aspect, and elevation ranging from 527 to 732 m. The catchment is covered by mature forest composed of American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*), with balsam fir (*Abies balsamea*), red spruce (*Picea rubens*), and white birch (*Betula papyrifera var. cordifolia*) dominating areas with shallow soils [*Likens*, 2013].

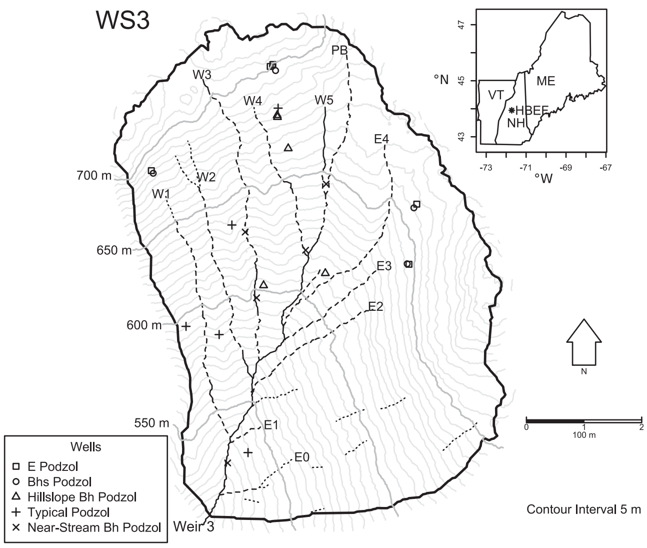

Figure 1. Map of watershed 3. The inset map indicates the location of HBEF in northern New England. Perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. Shallow groundwater wells are indicated by symbols designating the soil morphological unit (HPU) where the well is installed. Tributaries to the main stem in watershed 3 (Paradise Brook, PB) are labeled at their channel heads (E0-4 and W1-5).

Soils in WS3 have been broadly characterized as well-drained Spodosols (known as podzols outside of US soil taxonomy) [*Likens*, 2013]. Podzolization, the defining soil forming process in Spodosols, involves leaching of organic materials, Fe, and Al from surficial horizons (eluviation) and subsequent deposition (illuviation) of organometallic coatings (spodic materials) in subsurface horizons. Generally, podzolization is thought to occur at the point or pedon scale. However, *Bailey et al.* [2014] found distinct variations in horizonation supporting a functional classification of soil units with a broader range of drainage classes and evidence of podzolization occurring at pedon to hillslope scales. Soil units, defined as hydropedological units (HPUs) [*Gannon et al.*, 2014], describe distinct soil morphological groups with utility for describing spatial patterns in hydrological and biogeochemical processes. HPUs were found to be indicative of distinct spatial variations of carbon accumulation [*Bailey et al.*, 2014] and shallow groundwater regimes [*Gannon et al.*, 2014] in the solum. The solum is defined as the portion of the soil profile from the surface to the base of the B horizon. It is the approximate rooting zone and with respect to the geologic parent material it is a zone with greater alteration due to mineral weathering, development of soil structure, and lower bulk density. Finally, the solum is the zone of carbon accumulation in soil, with carbon concentrations that generally decrease with depth. Accumulation of carbon pools varies depending on the type, thickness, and bulk density of O, A, and B horizons.

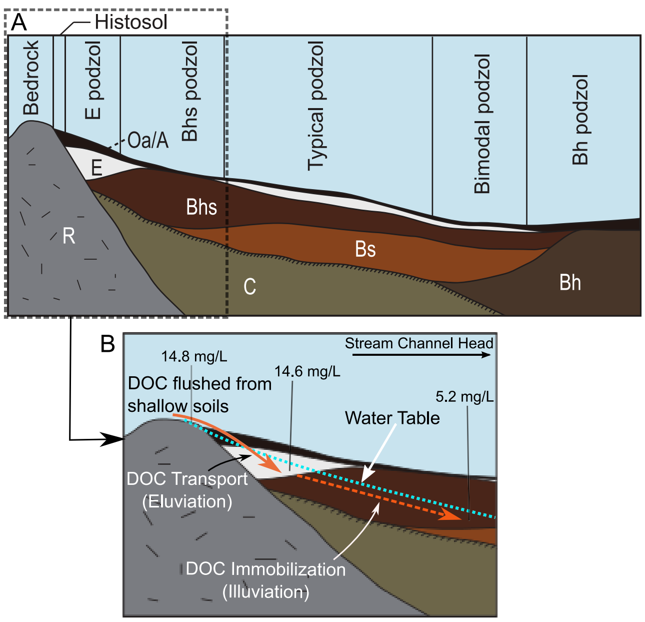

Figure 2. HPU conceptual model for WS3 (A) and conceptual model of DOC delivery to transient shallow groundwater in E and Bhs podzols (B) (modified from *Bailey et al.* [2014]). Water flows over the impervious bedrock surface through the forest floor, obtaining high DOC. This bedrock runoff then flows directly into the shallow soils downslope. Concentrations noted left to right in Figure 2b are median DOC from bedrock runoff (n = 4), E podzol groundwater (n = 45), and Bhs podzol groundwater (n = 66).

According to the above functional classification, five HPUs, all podzol variants, were described in WS3 (Figure 2). Three of the HPUs, E, Bhs, and Bh podzols, were named for the dominant mineral horizon where one horizon comprised the majority of each profile. The horizonation in typical podzols best meets the central concept of a Spodosol, with a thin and discontinuous E horizon overlying a sequence of moderately expressed Bhs and Bs horizons. Bimodal podzols are characterized by a typical podzol profile with an additional Bh horizon at the base of the solum. E and Bhs podzols are found on portions of the watershed divide where bedrock is covered by a thin layer of organic material or exposed as outcrops. E podzols form a complex, where interspersed lichen and moss-covered bedrock outcrops and pockets of organic soils overlay shallow bedrock. Bhs podzols are just downslope of the E podzol complex, where glacial parent materials are transitioning to deeper deposits. Typical and Bh podzols are in deeper glacial drift, with typical podzols common on backslopes and Bh podzols on benches and adjacent streams. Bimodal podzols were generally found in a narrow transition zone between typical and Bh podzols, of limited spatial extent in the catchment [*Gillin et al*., 2015], and were therefore excluded from this analysis.

Previous work describing runoff generation in WS3 suggests water is transported to the stream via preferential flow in the top 10–30 cm of the solum in addition to matrix flow from contributing areas [*Stresky*, 1991; *Detty and McGuire*, 2010a]. *Detty and McGuire* [2010a] explained an observed threshold streamflow response as a combination of preferential flow in shallow horizons and matrix flow as contributing areas expanded rapidly up hillslopes. Additionally, *Gannon et al*. [2014] found that a spatial patchwork of HPUs with water table in the solum connected to the stream to generate stormflow above thresholds in antecedent soil moisture plus precipitation.

3. Methods

3.1. Well Records and Samples

Water table data for this study are from a spatially distributed shallow groundwater well network throughout WS3 (Figure 1). The well network was designed to monitor water table dynamics across five different HPUs throughout the catchment (Figure 1), and was established by three different studies. *Detty and McGuire* [2010a, 2010b] installed 28 wells, 7 of which were used for this study. These well locations had soil morphology characterized in adjacent soil pits by *Bailey et al*. [2014]. Seven additional wells paired with detailed soil characterizations were installed by *Bailey et al*. [2014] in order to bring the number of wells in each HPU to three. Finally, 11 wells were added and soils characterized by *Gannon et al*. [2014], to bring the total number of wells to 26 and the number in each HPU to a minimum of 5 (Figure 1).

Wells were installed either with a 10 cm hand auger or in a small backfilled soil pit and were constructed of SDR (standard dimension ratio) 21 PVC pipe with a 3.76 cm inner diameter and a 31 cm screen length consisting of 0.025 cm width lateral slots with 0.32 cm spacing between slots. An auger was used to set the base of the well screen 10 cm into the C horizon, below the solum. In cases where a C horizon was not present, wells were installed on top of bedrock. The volume immediately surrounding the well screen in each hole was filled with local washed sand to a depth just above the screened interval, and then native soil was backfilled and carefully compacted above the screened interval to the soil surface. Water level was logged at each well with a 1.5 m Odyssey Water Level Logger that used capacitance measured along a Teflon coated wire suspended in the well to determine water level (Dataflow Systems Pty Ltd). Data were recorded at 10 min intervals.

Water table was measured as height of the groundwater within the solum relative to the top of the C horizon, or bedrock if the C horizon was absent. Semipermanent to permanent saturation likely exists deeper in the C horizon in WS3, but for the purpose of examining hydrologic regimes related to DOC sources this deeper zone was not considered.

Prenart soil suction lysimeters, wells, and bedrock runoff collectors were also sampled to measure DOC concentrations. Lysimeters were installed by boring a hole from the surface to the desired depth and then pushing the lysimeter to the end of the bored hole. Lysimeters were installed at two to three sites for each HPU adjacent to the characterized soil pit. Lysimeters were installed near the top of the B horizon and at 30–40 cm depth in Bhs (three sites, five lysimeters total) and hillslope Bh podzols (three sites, eight lysimeters total) and near the top and bottom of the B horizon in typical podzols (three sites, four lysimeters total). Due to the thin solum of E podzols only one lysimeter was installed in the middle of the E horizon, which was the dominant horizon for this HPU (two sites, two lysimeters total). To sample the lysimeters, 50 kPa of suction was placed on a sample bottle attached to the lysimeter. The bottle was allowed to collect water for 24 or 12 h if predicted nighttime temperatures would freeze the collected water. Samples were collected at the end of this period. Samples from multiple lysimeters in the same soil profile were kept separate. Wells were also sampled for DOC concentrations. Wells were purged to remove at least one borehole volume of water and then sampled using a peristaltic pump. Included in this analysis are 45 samples from five wells in E podzols, 66 samples from six wells in Bhs podzols, 17 samples from three wells in typical podzols, 77

Table 1. Sampling Periods Referred to in This Study[a]

Sampling Period				
Start	End	Sampling Description	Daily Discharge (mm/d)	% Exceedance (2000–2014)
9 Jul 2009		Synoptic stream water	4.5	14.5
1 Apr 2010		Synoptic stream water	6.7	9.1
18 Jun 2010		Synoptic stream water	0.7	64.5
6 Aug 2010		Synoptic stream water	0.3	79.9
21 Aug 2010		Synoptic stream water	0.1	91.1
1 Oct 2010		Synoptic stream water	77.0	0.0
25 Mar 2010	13 Feb 2013	Wells: 34 days	N/A	N/A
2 Oct 2011		Outlet FDOM	22.1	1.2
7 May 2012		Outlet FDOM	27.4	0.8
11 Mar 2013	11 Apr 2013	Wells, lysimeters: 6 days	4.9 (mean)	13.2
25 Jun 2013	28 Jun 2013	Wells, lysimeters: 3 days	3.3 (mean)	20.2
2 Jul 2013		Bedrock	31.9	0.6
3 Jul 2013		Bedrock	10.2	5.5
7 Oct 2014		Bedrock	2.4	28.8
8 Oct 2014		Bedrock	5.0	13.0

[a]For 1 day sampling efforts, only a start date is given, and for longer periods both a start and end dates are given. For multiday sampling periods, daily discharge is either given as a mean daily discharge for the entire period or listed as not applicable (N/A). Daily discharge and % exceedance were calculated using daily discharge data from the catchment outlet from 2000 to 2014. Data from samples on 9 Jul 2009, 1 Apr 2010, 18 Jun 2010, 6 Aug 2010, 21 Aug 2010, and 1 Oct 2010 were previously published in *Zimmer et al.* [2013].

samples from six wells in hillslope Bh podzols, and 11 samples from three wells in near-stream Bh podzols. Finally, small (~4 cm) funnels were installed in constrictions on the surface of a bedrock exposure to collect runoff at three sites. Polyester wool was packed into the base of the funnel to prevent particulate matter from entering the sample. Timing and flow conditions for these samples are detailed in Table 1.

Groundwater and soil solution samples were not filtered prior to analysis as DOC measured in filtered and unfiltered samples at Hubbard Brook have been shown not to differ [*Buso et al*., 2000]. Analysis of the samples for DOC concentrations was carried out at the Forestry Sciences Laboratory in Durham, NH, USA with a Shimadzu TOC-5000A. Samples were refrigerated after collection and analyzed within 2–3 weeks. The detection limit was 0.1 mg/L and precision on triplicate samples was less than 10%. Lysimeter and well samples were taken on 6 days during snowmelt, from 11 March 2013 to 11 April 2013, and on 3 days spanning a summer storm, from 25 June 2013 to 28 June 2013. Additional groundwater samples used in this analysis were taken on 34 dates from 25 March 2010 to 13 February 2013. Not all wells and lysimeters were sampled on each date, as some did not yield sufficient sample volume. Bedrock runoff was sampled on 2 July 2013, 3 July 2013, 7 October 2014, and 8 October 2014. Sample periods are summarized in Table 1.

3.2. Spatial Extent of Water Table Rise Into the Solum

In order to examine the potential contributing area to streamflow, the probable extent of water table in the solum in the catchment was mapped for two dates where water chemistry was available every 50 m along the active stream network as reported in *Zimmer et al.* [2013]. As a representative higher flow condition, 9 July 2009 was chosen; daily average streamflow on that date had a 14.5% exceedance probability calculated using discharge measurements from 2000 to 2014. A low flow date was also examined, on 6 August 2010 when daily average streamflow had a 79.9% exceedance probability [*Zimmer et al*., 2013]. The spatial extent of each HPU was derived from the model in *Gillin et al.* [2015], which predicted (with 80% accuracy) the HPU distribution based on a terrain analysis using a 5 m digital elevation model. HPUs were mapped for each cell in a 5 m grid of WS3 by selecting the HPU with a probability of 0.5 or higher according to the soil predictive model. This approach left 5% of cells in the catchment uncategorized. Water table was then mapped in HPUs throughout the catchment based on an analysis from *Gannon et al.* [2014] where it was shown that water table occurred at different threshold values of combined catchment storage and precipitation in different HPUs. The modeled area of each HPU was therefore shown on the map as having a water table if modeled catchment storage from *Gannon et al.* [2014] plus measured rainfall on the sampling date exceeded the threshold needed to bring the water table up into the solum. This technique is similar to one used with the same data set in *Gillin et al.* [2015], where water table dynamics were predicted over the entire catchment and compared with water level data from wells.

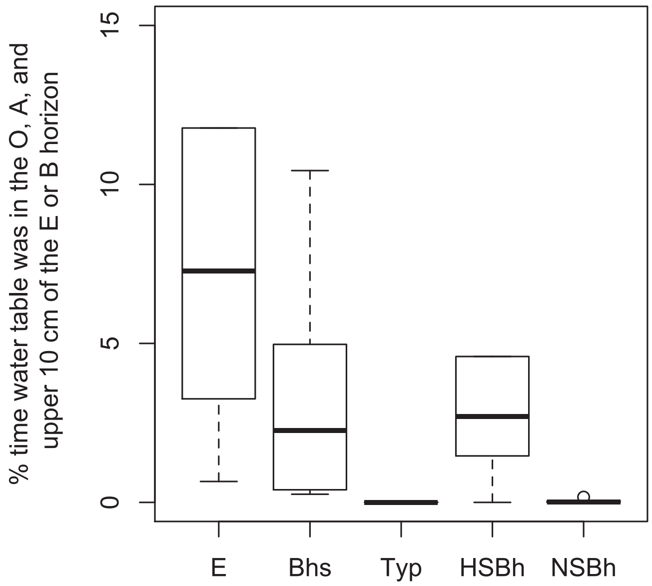

Figure 3. Percent time in 2 years that wells in each HPU recorded water table in the O, A, and upper 10 cm of the E or B horizon (n = 5 per group). HPUs shown are E podzols (E), Bhs podzols (Bhs), typical podzols (Typ), hillslope Bh podzols (HSBh), and near-stream Bh podzols (NSBh). The middle line in each box corresponds to the median of the data, the hinges are the boundaries of the interquartile range (IQR), the whiskers are the first and third quantile ±1.5 times the IQR, and points are outliers beyond the range of the whiskers. One outlier was excluded from the E podzol group (44%) and the hillslope Bh podzol group (74%) in order to shorten the *y* axis.

3.3. FDOM

A flow-through FDOM fluorometer (WETLabs, Philomath, OR) was installed in WS3 just upstream of the V notch weir. The fluorometer measured the concentration of fluorescent, humic-like DOM using a single excitation/emission pair (370/460 nm; with 10 and 120 nm full width, respectively, at half maximum excitation/emission band-pass filters). FDOM is a strong proxy for DOC [*Pellerin et al*., 2012]. Every 30 min a sample was pumped through the fluorometer. After a 2 min sample flush and warm up period, repeated FDOM measurements were made for 30 s at 1 Hz and logged with a Campbell Scientific CR1000 data logger (Campbell Scientific, Logan, UT). The last 20 measurements of each measurement burst were used to calculate median, mean, and standard deviation. The blank corrected output sample voltage was then multiplied by an instrument-specific conversion factor supplied by the manufacturer to convert to ppb quinine sulfate equivalents (QSE, fluorescence of 1 ppb quinine sulfate dehydrate in 0.1 N H_2SO_4). The sensor had a confirmed linear response ($r^2 > 0.99$) up to 167 ppb QSE. FDOM values were corrected for temperature [*Downing et al*., 2012]. Turbidity was not measured during the study, but during 2013–2014 turbidity never exceeded 16 NTU (J. Potter, University of New Hampshire, unpublished data, 2015), despite six storms with greater peak flows than the two storms presented here; turbidity interference is negligible at these levels [*Saraceno et al*., 2009].

4. Results

4.1. Water Table Fluctuations and Subsurface DOC Concentrations

The percentage of time water table occurred in the upper part of the soil profile was examined by comparing the percent time water table was in the O horizon, A horizon (if present), and top 10 cm of the solum below the O and/or A horizon (Figure 3). Figure 3 shows that wells in E, Bhs, and hillslope Bh podzols recorded saturation in the upper portions of the soil profile where percent soil organic matter is generally higher. Wells in near-stream Bh podzols and typical podzols did not exhibit saturation in upper portions of the soil profile.

Groundwater in E and Bhs podzols had the highest concentrations of DOC, with a mean of 14.6 mg/L in E podzols and 5.2 mg/L in Bhs podzols (Figure 4a). Groundwater DOC concentrations in near-stream soils were no higher than hillslope Bh podzols or typical podzols. Median DOC concentration in groundwater in typical, hillslope Bh, and near-stream Bh podzols were all less than 1.5 mg/L (Figure 4a).

In typical podzols, water sampled from suction lysimeters had higher DOC concentrations than that in the groundwater according to a Wilcoxon rank sum test (p-value < 0.05, Figure 4a). However, in E and Bhs podzols, the pattern was opposite; groundwater in these soils had higher DOC than water sampled from suction lysimeters according to a Wilcoxon rank sum test (p-value < 0.05, Figure 4a).

4.2. Spatial Patterns in Stream Water DOC Concentrations

The potential area contributing to streamflow was examined by producing maps of the probable extent of water table within the solum in the catchment for high and low flow: 9 July 2009 and 6 August 2010,

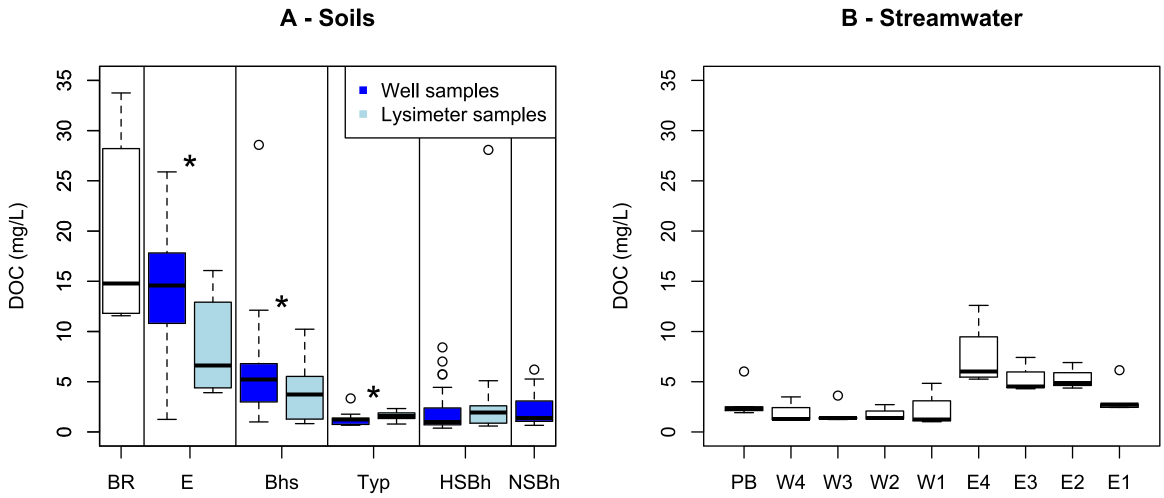

Figure 4. Concentration of DOC (mg/L) in bedrock runoff (BR) and groundwater, and lysimeter samples in (a) the five HPUs and at (b) the outlets of WS3 (Paradise Brook, PB) and eight tributaries in WS3. Figure 4a shows groundwater and lysimeter water for each HPU except near-stream Bh podzols (NSBh), as no lysimeter samples were available. For bedrock runoff (BR), n = 5. For E podzols (E), n = 45 for groundwater and 12 for lysimeter samples. For Bhs podzols (Bhs), n = 66 for groundwater and 28 for lysimeter. For typical podzols (Typ), n = 17 for groundwater and 16 for soil water. For hillslope Bh podzols (HSBh), n = 77 for groundwater and 31 for lysimeter samples. Finally, for near-stream Bh podzols, n = 11 for groundwater. A star shown between two grouped soil water and groundwater boxplots indicates a significant difference according to a Wilcoxon rank sum test, p-value < 0.05. Figure 4b shows DOC in stream water for all sample dates in *Zimmer et al*. [2013] at the outlet of WS3 (Paradise Brook, PB), four tributaries on the western side of the catchment (W1, W2, W3, and W4) and four tributaries on the eastern side of the catchment (E1, E2, E3, and E4). The middle line in each box corresponds to the median of the data, the hinges are the boundaries of the inter-quartile range (IQR), the whiskers are the first and third quantile $\pm$1.5 times the IQR, and points are outliers beyond the range of the whiskers.

respectively. On 9 July, the date with higher flow, the storage plus precipitation level according to modeled storage from *Gannon et al*. [2014] was 85 mm. Therefore E, Bhs, hillslope Bh, and near-stream Bh podzols would be expected to have saturation above the B/C horizon interface (Figure 5). The mean response threshold for typical podzols was more than 85 mm [*Gannon et al*. 2014] and therefore they were not mapped as having water table in the solum. On 6 August 2010, near base flow conditions, the storage plus precipitation level was 55 mm [*Gannon et al*., 2014], meaning only Bh podzols would be expected to have saturation above the B/C horizon interface. Therefore, only Bh podzols were mapped for this date in Figure 5.

Stream samples with the highest DOC concentrations on 9 July 2009 from *Zimmer et al*. [2013] were generally at channel heads (Figure 5). Furthermore, in stream reaches with a high percentage of bedrock-controlled E and Bhs podzols in their channel heads, DOC concentrations decreased downstream as the source area made up of near-stream Bh and hillslope Bh podzols increased (Figure 5). Finally, water tables in the solum were observed near channel heads in E and Bhs podzols (Figure 5). While only a portion of this area likely contributed directly to stormflow (e.g., due to water travel time in these soils), there were several sampling sites in the stream network where most of the soils in the contributing area were E and Bhs podzols (Figure 5).

On 6 August 2010, during lower flow conditions and with water table only in Bh podzols, stream DOC concentrations were consistently low (<4.5 mg/L) throughout the wetted portion of the stream network. The only exceptions were the two sampling points high on a western tributary (W3) with primarily bedrock contributing area. These two points had the highest stream water DOC concentrations (>5.5 mg/L) in the catchment on this date.

Stream water DOC concentrations at the outlets of western tributaries W1, W2, W3, and W4 and eastern tributaries E1, E2, E3, and E4, and the main stem (Paradise Brook, PB) from all six sampling dates in *Zimmer et al*. [2013] are shown in Figure 4b. Stream water samples were collected from July 2009 to October 2010 while lysimeter and groundwater samples were collected from March 2010 to July 2013. Both data sets sampled dates that cover a broad range of flow conditions (Table 1). However, because the two data sets were not acquired simultaneously, below we compare the distributions of groups of samples rather than making site or date-specific comparisons. Paradise Brook had slightly higher median DOC (2.3 mg/L) than lysimeter (LW) and groundwater (GW) samples in near-stream Bh (GW = 1.4 mg/L), hillslope Bh (GW = 1.0 mg/L, LW = 2.0 mg/L), and typical podzols (GW = 1.2 mg/L, LW = 1.6 mg/L). Similarly, the western tributary outlets had low median DOC concentrations (W1 = 1.3 mg/L, W2 = 1.4 mg/L, W3 = 1.4 mg/L, and

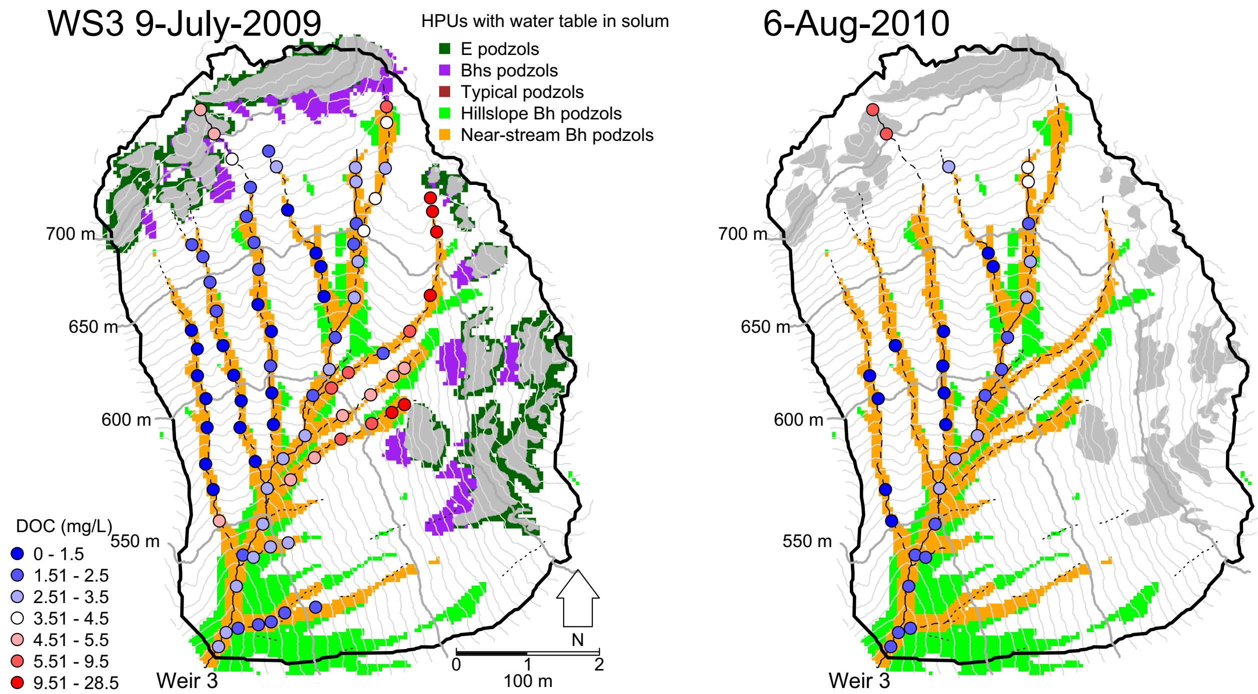

Figure 5. Map of HPUs with water table in their solum on 9 July 2009 and 6 August 2010 according to the modeled storage value and threshold of water table response from *Gannon et al*. [2014] and predicted HPU locations from *Gillin et al*. [2015]. Spatial stream water DOC concentrations (mg/L) on the same two dates are shown as colored circles, samples were collected every 50 m when water was present in the channel [*Zimmer et al*., 2013]. Grey areas on the maps denote areas with exposed or organic matter-covered bedrock as mapped by *Gillin et al*. [2015]. Perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. The contour interval is 5 m.

W4 = 1.3 mg/L) compared to groundwater and lysimeter water in near-stream Bh, hillslope Bh, and typical podzols. The eastern tributary outlets, however, had median stream water DOC concentrations (E1 = 2.7 mg/L, E2 = 4.9 mg/L, E3 = 4.5 mg/L, E4 = 6 mg/L) consistently higher than hillslope Bh, near-stream Bh, and typical podzols. Only E (GW = 14.6 mg/L, LW = 6.6 mg/L) and Bhs podzols (GW = 5.2 mg/L, LW = 3.7 mg/L) had higher median DOC concentrations than the outlets of the eastern tributaries.

Surface water sampled by bedrock runoff collectors had a median DOC concentration of 14.8 mg/L. DOC concentrations in bedrock runoff were therefore higher than the mean DOC concentration at the outlet of all tributaries and the mean of all subsurface water other than groundwater in E podzols.

4.3. Temporal Patterns in DOC Concentrations at the Catchment Outlet

The timing of the FDOM response at the outlet of WS3 was compared to water table fluctuations in the solum among HPUs to examine how outlet FDOM varied with potential source areas (Figure 6). Water levels were plotted against FDOM fluctuations for the same storm, noting the C horizon depth and soil surface in order to show the degree of saturation in different HPUs as well as how close water levels were to the surface (Figure 6).

Water levels in all wells that responded to the events on 2 October 2011 and 7 May 2012 (Figure 6) peaked before FDOM at the outlet. The primary observable contrast in the water level response of HPUs in relation to outlet FDOM was on the recession limb of the FDOM and water table responses. Water levels in E and Bhs podzols continued receding throughout the FDOM recession during both events, illustrated by their vertically elongated hysteresis loops (Figure 6). Additionally, in most cases E and Bhs podzols also had water levels closer to organic-rich surface horizons than the other HPUs. Water levels in hillslope Bh podzols receded with FDOM during the October storm (Figure 6a) but during the May storm water tables stayed high throughout the FDOM recession (Figure 6b). Very little water level fluctuation was observed in near-stream Bh podzols during either event, resulting in generally flat relationships between FDOM and water table levels (Figure 6). The minimal response of near-stream Bh podzols was especially evident during the May event. FDOM at the outlet had a defined peak while water levels in near-stream Bh podzols increased no more than 10 cm and in one case had no increase (Figure 6b). Therefore, wells in the HPUs with the

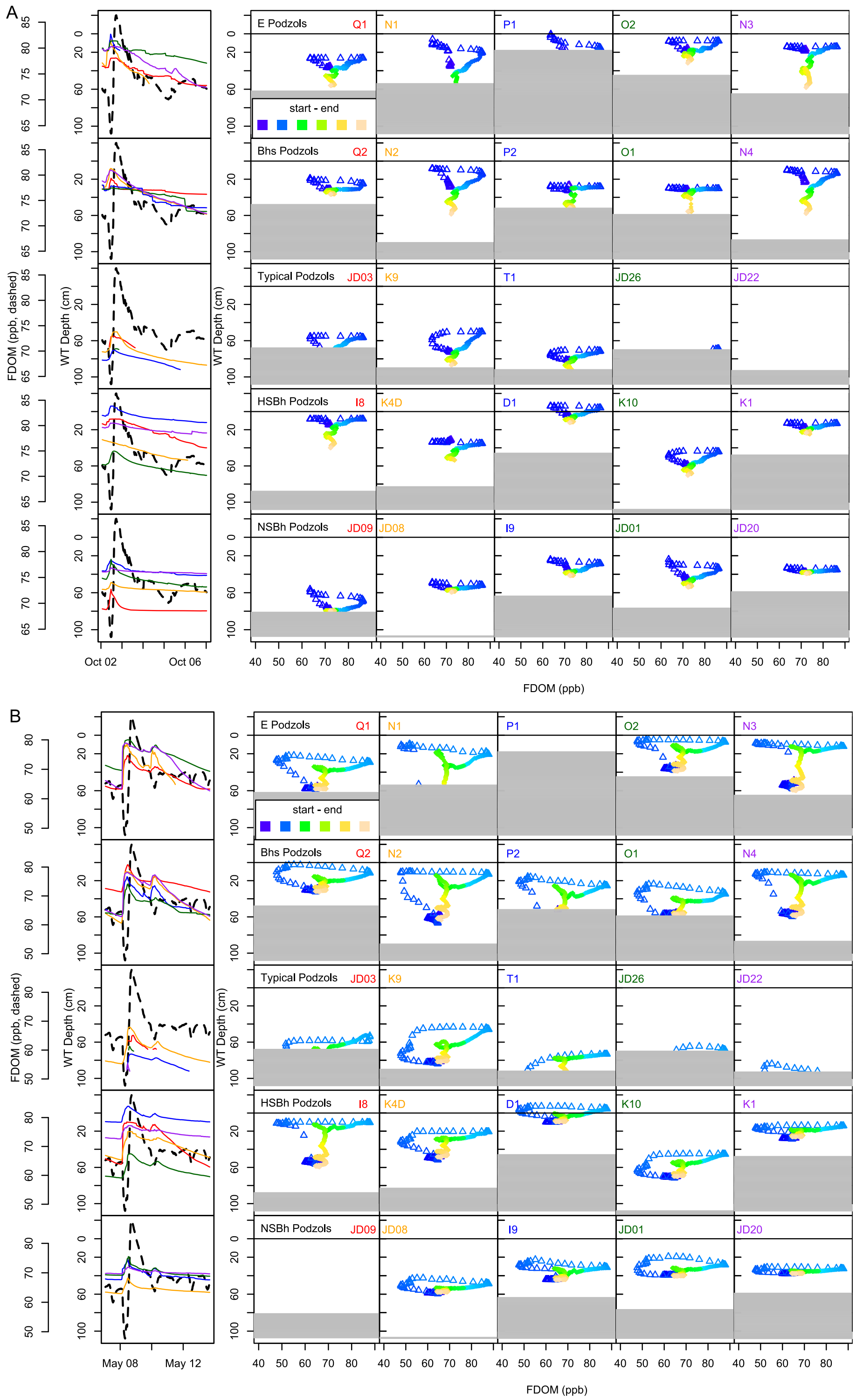

Figure 6. FDOM at the catchment outlet and water table at five example wells in each HPU. Figure 6a is an event occurring on 2 October 2011 and Figure 6b is from 7 May 2012. In the plots on the left, FDOM is indicated by a dashed line and water table levels are indicated by colored solid lines. The color of each well record on the left corresponds to the well name of the same color in the plots on the right. Plots on the right are water table (*y* axis) plotted against catchment outlet FDOM (*x* axis), the color of the plots goes from blue at start to beige at the end of the event. Points on the rising limb of the FDOM time series are shown as upward facing, open triangles and points on the falling limb are shown as smaller, filled diamonds. The filled grey area at the bottom of the plots on the right denotes the C horizon at each well. A horizontal line at the ground surface (0 depth) is shown for each plot on the right.

highest DOC concentrations in groundwater, E and Bhs podzols, had water level responses that most closely tracked FDOM fluctuations at the outlet.

A short-lived decrease in FDOM occurred during the initial hydrograph rise in both the October and May storms (Figure 6). This decrease occurred simultaneously with initial water table increases in the wells and is therefore likely indicative of a first flush of dilute stream channel storage.

5. Discussion

5.1. DOC Sources

Stream water DOC concentrations in several reaches in WS3 decreased down the stream network toward the outlet (Figure 5) [*Zimmer et al*., 2013]. Similar patterns have been observed in the larger Hubbard Brook valley [*Likens and Buso*, 2006; *McGuire et al*., 2014] and in other stream network studies [*Kaplan et al*., 1980; *Dawson et al*., 2001; *Laudon et al*., 2011]. There are two possible explanations for the decrease in DOC concentrations downstream: (1) dilution from a lower concentration source; or (2) in-stream DOC removal [*Demers et al*., 2010]. While rapid in-stream DOC removal has been shown to occur at Hubbard Brook [*McDowell*, 1985; *Demers et al*., 2010] and other sites [e.g., *Kaplan et al*., 1980], removal rates are typically determined during low flow conditions. DOC removal rates are likely less of a factor during higher flow conditions when residence times are shorter and landscape factors more strongly influence DOC patterns [*Tiwari et al*., 2014; *Creed et al*., 2015]. Therefore, as suggested by the low DOC concentrations we observed in near-stream Bh podzols (Figure 4), the decreasing DOC we observed downstream during events is more likely due to dilution from contributions of lower concentration source areas rather than in-stream removal.

Further evidence that near-stream soils were not major DOC sources was found when comparing water table fluctuations and DOC concentrations in stream and groundwater. Water tables were not observed in the O horizon or shallow B horizon in near-stream Bh podzols (Figure 3). This is consistent with findings from *Gannon et al*. [2014] and *Detty and McGuire* [2010b], who both found that near-stream soils showed limited event-scale water table rise. *Detty and McGuire* [2010b] attributed this to the higher hydraulic conductivities of glacial deposits and alluvial material in near-stream areas. Furthermore, DOC concentrations in the groundwater of near-stream soils in WS3 were similar or lower than those of hillslope soils (Figure 4a). Finally, DOC concentrations at several tributary outlets in the catchment were higher than those of groundwater in near-stream soils (Figure 4b). A DOC concentration that is higher in stream water than in near-stream soils implies other catchment DOC sources besides near-stream soils.

In contrast to the low DOC concentrations in groundwater found in near-stream soils, upland E and Bhs podzols had the highest DOC concentrations in groundwater recorded in this study (Figure 4). E and Bhs podzols had the thickest O horizons of any of the HPUs [*Bailey et al*., 2014] (Table 2), with water table frequently rising into the upper part of the solum, and high water throughput due to upslope areas of shallow bedrock and outcrops [*Gannon et al*., 2014]. The probable extent of saturation of near-surface soils predicted in the catchment suggests there were transient water tables near the channel heads of WS3 that connected E and Bhs podzols with the stream network during the high flow synoptic sampling (Figure 5; 9 July 2009). These channel head areas, with the highest percentage of E/Bhs podzol contributing area, also had the highest stream water DOC concentrations [*Zimmer et al*., 2013] (Figure 5). Additionally, DOC concentrations at the outlets of eastern tributaries, which had more E and Bhs podzol area in their channel heads, were also higher than at the outlets of the western tributaries, which had lesser influence of E and Bhs podzol areas. FDOM fluctuations at the catchment outlet were lagged compared to water table fluctuations in E and Bhs podzols, but otherwise showed similar temporal patterns (Figure 6), further indicating they were likely a DOC source. This was especially the case on the recession limb, where FDOM concentrations decreased during the same general period the E and Bhs water tables subsided. Therefore, similar to the evidence presented in *Peralta-Tapia et al*. [2015] in support of shallow flow

Table 2. Representative Total Solum Thickness, O Horizon Thickness, and Total Profile C Content for HPUs in WS3[a]

HPU	Total Solum Thickness (cm)	O Horizon Thickness (cm)	Total Profile C (kg/m^2)
E	61	20.8	20.9
Bhs	88	8.5	27.8
Typical	76	6.3	18.6
NSBh and HSBh	72	3.9	21.0

[a]Modified from *Bailey et al*. [2014].

path contributions, the proximity of E and Bhs podzols to the dynamically expanding and contracting stream network in WS3 [*Zimmer et al*., 2013] suggests DOC was delivered to streamflow from shallow soil horizons in upslope shallow bedrock areas.

Soils in the upper portion of the catchment near the bedrock-controlled ridges appear to be the primary source of DOC to channel heads in WS3. E and Bhs podzols predominate this area and were shown to have the highest groundwater concentrations of DOC. However, the high DOC concentrations in groundwater in these soils may not be completely explained by groundwater rising into shallow soil horizons as noted in other studies [*Boyer et al*., 1996; *Hinton et al*., 1998; *Seibert et al*., 2009] and as suggested above. The conceptual model [*Bailey et al*., 2014] proposed for this catchment describes lateral podzolization, delineating zones of eluviation and illuviation along hillslope catenas downslope from shallow-to-bedrock areas [*Bourgault et al*., 2015; *Gillin et al*., 2015] (Figure 2). In these areas, the podzolization process occurs in a downslope direction at the hillslope scale rather than vertically at a point scale [*Sommer et al*., 2000]. Therefore, the shallow to bedrock areas upslope of E podzols act as though they were an O horizon in a vertically developed profile. DOC concentrations in water from O horizons are typically high [*Cronan and Aiken*, 1985; *McDowell and Likens*, 1988]. Indeed, water in O horizons at Hubbard Brook has also been shown to have much higher DOC than in B horizons in studies using suction lysimeters [*McDowell and Wood*, 1984; *McDowell and Likens*, 1988, this study, Figure 4a] and zero-tension lysimeters [*Dittman et al*., 2007]. Likewise, water sampled from bedrock outcrops in this study had high DOC (Figure 4). As indicated by the higher DOC concentrations in groundwater compared to shallower lysimeter samples in E podzols (Figure 4a), water from shallow-to-bedrock areas moves to these soils immediately downslope. E podzols, like E horizons, are eluviation environments where mineral soil horizons lack organometallic complexes and have high DOC throughput in soil water and groundwater (Figure 2). Downslope from E podzols, Bhs podzols form accumulation environments where DOC concentrations in groundwater begin to decrease as organic carbon is immobilized as spodic materials (Figure 2).

While *D'Amore et al*. [2015] identified similar shallow to bedrock areas with high DOC, they noted that it was unlikely these areas would connect to streams. We posit two possible ways that high DOC water from these areas can arrive at the stream. First, in areas dominated by eluvial processes (E podzols), DOC concentrations in groundwater are similar to runoff collected from organic material-covered bedrock (Figure 3). Therefore, in cases where the stream network is directly below eluvial areas, matrix flow may carry high DOC water to the stream. Second, due to the shallow soils and bedrock outcrops in the E/Bhs podzol region, water storage is limited and water flux downslope is high. This causes water tables in these soils to respond quickly to events and rise high into the soil profile (Figure 3), where macropore pipe volume is highest at Hubbard Brook [*Stresky*, 1991]. While most DOC is removed from water over short distances in mineral soil, preferential flow has been shown to transport high DOC water further than matrix flow [*Kaiser and Guggenberger*, 2005; *Van Verseveld et al*., 2008; *Terajima and Moriizumi*, 2013]. Furthermore, preferential flow has previously been identified as a major component of stormflow generation in WS3 [*Detty and McGuire*, 2010a]. Therefore, similar to the processes described in *Jardine et al*. [1990], we propose that preferential flow pathways may also provide the short travel time necessary to deliver DOC to the stream network before it is adsorbed by mineral soil horizons.

Several studies have investigated the interplay among riparian, hillslope, and wetland landscape units in controlling DOC concentrations in stream water [*McGlynn and McDonnell*, 2003; *Andrews et al*., 2011; *Dick et al*., 2014]. The applicability of our findings is that in mountainous catchments, where bedrock ridges and shallow to bedrock areas are common, such bedrock-controlled portions of the landscape may be important to incorporate into existing DOC source conceptualizations. While higher concentration DOC sources such as high riparian water tables or wetlands may mask bedrock-area contributions in some catchments, the identification of this DOC source offers an additional tool for explaining the spatial extent of DOC source areas and fluctuations of DOC at the catchment outlet.

5.2. Implications for Carbon Sequestration and Mobility

While near-stream soils did not contribute high concentrations of DOC to the stream network in WS3, *Bailey et al*. [2014] found larger carbon pools in Bh podzols compared to typical podzols in WS3. Moreover, Bh podzols had the highest proportion of their carbon in the deeper B horizons rather than the near-surface O and A horizons. Hence, there were likely two reasons these soils were not DOC sources. First, in contrast to other studies [*Boyer et al*., 2000; *McGlynn and McDonnell*, 2003], they did not experience high water tables which intersect more soluble carbon in their O and A horizons. Second, despite the large pools of carbon in the lower Bh horizons, the carbon form is likely more stable. *Bourgault et al*. [2015] found that soil carbon in these Bh podzols was mostly incorporated with colloidal amorphous organometallic complexes, which tend to be more stable forms of soil carbon. The B horizons in Bh podzols were also seasonally if not perennially saturated. These observations suggest that although there is high water flux through near-stream soils, the carbon was simply not as mobile.

Changes in groundwater fluctuations or frequency of saturation in these near-stream Bh podzols could have implications for carbon storage and release. The amount of precipitation in the northeastern United States has been increasing and is predicted to continue to increase with changing climate [*Hayhoe et al*., 2007; *Campbell et al*., 2011]. These increases in precipitation, as well as a shift in seasonality to more winter rainstorms [*Hayhoe et al*., 2007], may lead to more variations in water table conditions, which could mobilize carbon stored higher in the soil profile or change redox regimes or microbial activity in a way that could destabilize carbon storage at depth.

Based on the findings from *Gannon et al*. [2014], changes in catchment moisture that exceed storage thresholds may increase the frequency of water table rise into the solum, which has been linked to variations in soil development through carbon eluviation and illuviation over short distances [*Bourgault et al*., 2015; *Gillin et al*., 2015]. *Nauman et al*. [2015] and *Barrett and Schaetzl* [1998] have shown that depodzolization, including large losses of accumulated subsoil carbon, may occur at time scales of decades due to changes in vegetation and accompanying changes in soil pH and moisture. Thus, it is possible that trends in hydrologic conditions could lead to temporal trends in DOC export from catchments with hydrologically controlled podzolization processes.

5.3. Implications for Flow Paths and Runoff Processes

The identification of upslope portions of the channel head region of the catchment (i.e., outcrops, organic soils, and E and Bhs podzols) as a source of stream water DOC also implies they are important to streamflow generation. If contributing areas are considered to include some portion of the spatial extent of saturated shallow soils in the catchment, water table mapped in Figure 5 indicates that E and Bhs podzols likely contribute to streamflow when the catchment is wet and the intermittent portions of the stream network are active. Furthermore, the water table in near-stream areas extends minimally up side-slopes (Figure 5) as near-stream areas are very efficient at transmitting hillslope water to the stream due to their higher hydraulic conductivities deeper in the soil profile [*Detty and McGuire*, 2010b]. This suggests an elaboration of the conceptual model of streamflow generation from the classic idea of a variable source area [*Hewlett and Hibbert*, 1967]. While water tables expand and contract in the near-stream zone to varying degrees depending on topography [*Anderson and Burt*, 1978a], their rise and outward extent is largely limited by high hydraulic conductivity. In contrast, water tables that occur in shallow soils near channel heads account for a majority of the contributing area expansion in this catchment. To the extent that these areas contribute to streamflow during events, their high DOC concentration means that they contribute disproportionately as an important DOC source to stream water.

6. Conclusions

In this study, we found that the process generally attributed to mobilizing DOC to streamflow in headwater catchments, i.e., near-stream water tables intersecting shallow, high DOC soil horizons, was not a major driver at Hubbard Brook WS3. We present a new conceptual model where DOC is delivered to the stream primarily in channel head areas where bedrock outcrops covered by a layer of organic material were sources of DOC to groundwater in the soils downslope. DOC concentrations in near-stream groundwater were similar to or lower than hillslope groundwater and water tables were not observed in the upper horizons of near-stream soils. Rather, soils in channel head areas with primarily bedrock-controlled contributing areas had the highest DOC concentrations in soil water and groundwater. Water tables rose into these soils during events, indicating they likely contribute water to channel heads, where the highest DOC in stream water was observed. Furthermore, water table fluctuations in these soils matched the timing of fluorescent dissolved organic matter (FDOM) concentration fluctuations observed at the outlet of WS3 better than any soil type in the catchment. Finally, our predictions of probable water table extent by way of mapping water table in soils in the catchment suggested that the variable source area in WS3 consists of a limited expansion of water table from the near-stream zone with much more active expansion zones in channel head areas. This channel head variable source area represents a DOC source area distal from the stream network.

Acknowledgments
The data used in this study will be available for download at www.hubbardbrook.org. This study was supported by the National Science Foundation under grants EAR 1014507, DBI/EAR 0754678, and LTER DEB 1114804 and the Northeastern States Research Cooperative. We thank Joel Detty and Margaret Zimmer for installation of many of the wells used in this analysis, Patricia Brousseau and Rebecca Bourgault for soil pit characterizations, and Margaret Burns for field work assistance. Furthermore, we would like to thank Hjalmer Laudon and Jonathan Malzone who provided early reviews of the manuscript and improved it significantly. Hubbard Brook Experimental Forest is operated and maintained by the U.S. Forest Service, Northern Research Station, Newtown Square, PA. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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