

A Hydropedological Approach to Describing Runoff Generation, Lateral Podzolization,
and Spatial and Temporal Patterns of DOC in a Headwater Catchment

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Abstract

The variations in discharge and water chemistry among and within headwater catchments are not well understood. Developing a better understanding of the processes that control these variations is crucial to determining how headwater catchments will respond to changes in climate and land use. This dissertation explores how hydrologic processes in headwater catchments may be better understood by utilizing a hydropedological framework, where similar soils are grouped together and considered to be representative of and developed by similar hydrologic and biogeochemical processes. In the first chapter, soil groups, called hydropedological units (HPUs) are found to be indicative of distinct water table regimes characterized by the interquartile range and median of shallow groundwater levels, the percent time water table exists in the soil, and the level of catchment storage at which groundwater responds. The second chapter explores the hydrological processes that may lead to the formation of HPUs in the catchment. By examining water table records and unsaturated water potential from tensiometers we found that lateral unsaturated flow regimes may be partially responsible for the patterns of lateral translocation observed in HPUs. Finally, the third chapter identifies two HPUs in the catchment as sources of streamwater dissolved organic carbon (DOC). While near-stream areas have typically been found to be DOC sources in headwater catchments, the HPUs identified as sources occur at high elevations in the catchment, near channel heads. Overall, these findings will be useful to better explain runoff generation, soil formation, and DOC export from headwater catchments. Headwater streams source water to larger bodies of water that are valuable natural resources. Therefore, explaining these processes is critical to predicting and responding to changes in climate and land use that may affect important water supplies.

To Frank McCulley.
Thanks for the spark.

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Attribution

Chapter 2

Chapter 1 is in revision at the journal Water Resources Research, it was originally submitted on 23 February 2014.

Kevin J. McGuire, Ph.D. (Virginia Tech, Forest Resources and Environmental Conservation and Virginia Water Resources Research Center) helped with the design of the sensor network, data analysis, and editing of the manuscript.

Scott W. Bailey, Ph.D. (United States Forest Service Northern Research Station) helped with the design and installation of the sensor network, data analysis, and editing of the manuscript.

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Introduction

Headwater streams make up over 50% of total stream length in the contiguous United States [Nadeau and Rains, 2007]. However, the processes controlling the generation of streamflow and water chemistry in headwater catchments are not well understood [Bishop *et al.*, 2008]. This lack of understanding of a large percentage of stream networks results in difficulties explaining trends and variability in catchment output, such as those observed in dissolved organic carbon (DOC) concentrations [Evans *et al.*, 2005; Roulet and Moore, 2006]. This, in turn, makes it challenging to make accurate predictions about the behavior of headwater catchments in a changing climate or with changes in land use. For these reasons, it is critical to continue building understanding of the controls on headwater catchment streamflow and water chemistry generation.

This dissertation explores the questions of how streamflow and stream chemistry are generated in watershed 3 (WS3) of the Hubbard Brook Experimental Forest (HBEF) in Woodstock, New Hampshire, USA. These questions were addressed by examining common hydrologic and biogeochemical characteristics of similar soils throughout the catchment, then examining how they may affect streamflow generation and water chemistry at the catchment outlet. This combination of hydrology and soil science, called hydrogeology [Lin *et al.*, 2006], offers a unique perspective on catchment patterns and processes, as utilizes the spatial variation in soils as a metric for describing catchment hydrological and biogeochemical processes. This dissertation is divided into 3 chapters exploring catchment processes using the concept of hydrogeology, as well as a literature review to provide context for the work within the fields of hydrology and soil science.

Chapter 1 identifies similarities in shallow groundwater responses among similar soils, called hydrogeological units (HPUs). Shallow groundwater responses were monitored using recording wells installed in the solum of HPUs throughout watershed 3. HPUs were found to have different water table regimes, as characterized by percent time water table was detected in the soil, the interquartile range and median of their water table response time series, and the level of overall catchment storage at which water table developed.

Following these findings, a view of the catchment as a spatial patchwork of areas with water table in the shallow soil emerges, where areas with water tables are sometimes isolated and sometimes connected, contributing flow to the stream network.

Chapter 2 examines saturated and unsaturated water flux in HPUs in WS3 in order to present hydrologic explanations of how the patterns of soil horizon thickness and presence/absence arise. Several HPUs showed evidence of lateral podzolization, where soil-forming processes occur downslope instead of vertically in a profile. It was hypothesized that this is the result, in part, of lateral unsaturated water flow downslope. In order to investigate this hypothesis, measurements of saturated and unsaturated hydraulic head were made using tensiometers and shallow groundwater wells in HPUs. Lateral unsaturated flow was detected in the HPUs showing evidence of lateral podzolization. These findings provide a mechanism by which elements may be moved and/or concentrated in the landscape. This helps explain some of the spatial patterns in stream water chemistry observed in WS3 [*Zimmer et al.*, 2013].

In chapter 3, the implications of some of the findings in chapter 1 and 2 are used to explain the variation in DOC concentrations in streamwater in WS3 observed in *Zimmer et al.* [2013]. Dissolved organic carbon (DOC) concentrations in soil water and groundwater in HPUs are compared to those in stream water samples throughout the stream network and fluorescent dissolved organic matter (FDOM) at the outlet of WS3. Soil water was sampled using suction lysimeters and groundwater using a network of shallow wells. FDOM was measured every 30 minutes at the outlet of WS3. Two HPUs, occurring near channel heads at high elevations in the catchment, were found to be sources of DOC for the stream network. Furthermore, near-stream soils, commonly considered to be DOC sources [*Boyer et al.*, 2000; *Laudon et al.*, 2011; *McGlynn and McDonnell*, 2003], were not found to contribute more DOC to the stream than other hillslope soils.

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Chapter 1: Literature review

1.0 Introduction

Deciphering how runoff is generated and spatial and temporal water chemistry varies in headwater streams is essential to understanding and protecting the water bodies that provide vital resources to people and ecosystems around the world. Currently, most environmental regulation aimed at protecting water quality is directed toward the much more visible, larger water bodies [Nadeau and Rains, 2007]. However, downstream water quality has been shown to be influenced by small but numerous and spatially dominant headwater catchments [Alexander et al., 2007; Freeman et al., 2007; Peterson et al., 2001]. In addition to water quality, the biodiversity and ecological health of fresh water systems are largely governed by processes occurring in headwater streams [Lowe and Likens, 2005; Meyer et al., 2007].

These important headwater systems are diverse and complex. Even within the same watershed, headwater catchments have variable geochemical output [McGuire et al., 2014; Wolock et al., 1997; Zimmer et al., 2013]. Catchment geochemical output not only varies spatially, but temporally over a range of flow conditions [Gomi et al., 2002]. Explanations of these variations range from differences in catchment size [Wolock et al., 1997] to differences in contributing area primarily driven by riparian characteristics [Dodds and Oakes, 2008; Sanford et al., 2007]. However, others have found that the processes driving runoff generation are more complex than can be captured by simple metrics of catchment characteristics [Sidle et al., 2000].

The lack of concise explanations for variability among catchments illustrates how little is known about the generation of stream chemistry and runoff in headwater catchments [Bishop et al., 2008]. Describing how these catchments function and developing descriptions of processes that are relevant across scales is an important step in understanding not only the variability in headwater catchment output but also variability at larger scales [McGuire et al., 2014; Tetzlaff et al., 2008]. This may be accomplished by focusing on first-order controls of runoff generation and stream water chemistry, such as

the connection and disconnection of different catchment reservoirs governed by threshold responses to precipitation [McDonnell, 2003]. To do this, dominant landscape units must be identified and monitored [McGlynn *et al.*, 2004]. By focusing on common patterns and processes of these landscape units at the hillslope scale, fundamental relationships may be identified, offering insight into processes that transcend spatial scales [Sivapalan, 2003; Uchida *et al.*, 2005]. However, controls on the landscape heterogeneity governing these patterns and processes are complex, therefore, expertise from multiple disciplines must be integrated in order to move toward a more complete understanding of headwater catchments [Troch *et al.*, 2009].

2.0 Catchment structure as a predictor of hydrologic/biogeochemical output

2.1 The variable source area concept

Since the early descriptions of runoff generation from Horton [1933], the likelihood of specific areas to contribute more or less runoff to a stream have been considered. Later, others would discuss explicitly the tendency of contributing areas to change throughout the duration of a storm, defining contributing areas as those where saturated overland flow occurs [Betson, 1964; Dunne and Black, 1970; Ragan, 1968]. Descriptions of the dominance of subsurface processes in generating streamflow [Harr, 1977; Hewlett, 1961; Hewlett and Nutter, 1970; Hursh, 1944; Hursh and Brater, 1941; Kirkby and Chorley, 1967; Sklash and Farvolden, 1979; Whipkey, 1965] further complicate the description of contributing area as it was recognized that infiltration [Horton, 1933; Ragan, 1968] or saturation [Dunne and Black, 1970] excess are not a requisite condition for stormflow generation.

The variable source area concept, presented in Hewlett and Hibbert [1967], offered a conceptual model of the processes producing streamflow via subsurface flow, and how contributing area changes throughout a precipitation event. They recognized that variations in flow pathways throughout the catchment are likely dependent on hillslope morphology and soil type [Hewlett and Hibbert, 1967; Hoover, 1943]. Indeed Sklash *et al.* [1986] showed variations in deuterium concentrations in a small catchment to further

confirm that water was traveling at different rates through hillslopes of varying morphology.

Determining what governs this variability is a persistent question in the field of hydrology. Authors have posited several controls governing the spatial and temporal distribution of contributing areas, including riparian morphology and hydrologic characteristics [Burt *et al.*, 2002; Buttle *et al.*, 2004; McGlynn *et al.*, 2004], hillslope topography [Anderson and Burt, 1978; Aryal *et al.*, 2002; Beven and Kirkby, 1979; Detty and McGuire, 2010b; Fujimoto *et al.*, 2008], and/or the subsurface topography of confining layers such as bedrock [Ali *et al.*, 2011; Freer *et al.*, 2002; Tromp-van Meerveld and McDonnell, 2006], dense glacial till [Hutchinson and Moore, 2000], or fragipans [Gburek *et al.*, 2006; McDaniel *et al.*, 2008]. Notwithstanding, the viability describing runoff generation through the lens of variable source areas has been called into question. For instance, McDonnell [2003] proposed a framework of networked threshold-governed reservoirs as a more effective way of describing runoff generation in catchments. This approach allows for more spatially variably contributing areas, rather than a saturated area extending up the hillslope from the stream.

2.2 Hillslope-riparian connectivity

One control on variable source area, and thus the chemical output and discharge of a catchment is the composition and morphology of the riparian zone. At the scale of small catchments, hillslopes and riparian areas have been described as dominant landscape units [Hooper, 1998; McGlynn *et al.*, 2004; Seibert and McDonnell, 2002]. The degree to which riparian zones connect with hillslopes has been identified as a control on catchment output [Buttle *et al.*, 2004; Cirimo and McDonnell, 1997; McGlynn *et al.*, 2004; Vidon and Hill, 2004]. This connectivity is controlled by the size and hydrologic characteristics of riparian areas [Burt *et al.*, 2002] and hillslope shape [Jencso *et al.*, 2009].

It is not only hillslope-riparian connectivity that governs streamflow generation but also the ability of riparian areas to buffer discharge from upland regions in the catchment.

Both the overall volume of riparian zones [McGlynn and McDonnell, 2003b] as well as the ratio of their size with that of hillslopes [McGlynn and Seibert, 2003] have been shown to control how they buffer discharge in small catchments.

Not only do riparian zones play a role in governing discharge, they also play a role in determining catchment chemical output. Hooper, et al. [1998] identified the importance of riparian zones to stream chemistry by finding a mixing model with hillslope end-members failed to describe the sources of stream water, due to the overarching effects of the riparian zone on the chemistry of runoff. Likewise, Burns et al. [2001] also concluded riparian areas were resetting hillslope water signatures, adding that this was likely the result of the magnitude of riparian storage related to that of the hillslope. Riparian zones and their changing connections with hillslopes have also been found to explain changing solute concentrations throughout events in a variety of systems [Burt, 2005; Inamdar and Mitchell, 2007; Katsuyama et al., 2009; Kendall et al., 1999; McGlynn and McDonnell, 2003a]. These effects are evident even beyond the headwater catchment scale, as Sanford [2007] proposed that the chemical variations seen in catchments over 10 km² can also be explained by variations in riparian size and buffering capacity.

While the riparian zone has been shown to exert control over catchment discharge and chemical output, the effects of upslope areas cannot be ignored. As illustrated above, riparian zone functioning is determined by morphology and hydrologic properties. However, the form and function of these zones has been shown to be partially controlled by upland characteristics [Ocampo et al., 2006; Vidon and Hill, 2004]. This suggests the characteristics of hillslopes in headwater catchments must be considered even when considering riparian zones as dominant catchment landforms.

2.3 Hillslope topography

Although the variable source area concept put forth by Hewlett and Hibbert [1967] identifies soil mantle thickness as a control on source area development, the effect of hillslope topography was not explicitly addressed. Later studies describing controls on

water table development identified hillslope concavity as a control on water table development, along with soil thickness and hydraulic properties [Beven, 1978; Dunne *et al.*, 1975; Freeze, 1972]. Anderson and Burt [1978] found water table development to be more prevalent in convergent slopes where event water was funneled into hillslope hollows, as opposed to divergent slopes where flow concentration did not occur.

In addition to hillslope concavity, the role of slope in water table development also became apparent. Dunne *et al.* [1975] observed that steeper hillslopes experienced less water table development than gentler slopes. Indeed in modeling variable source areas in catchments, TOPMODEL [Beven and Kirkby, 1979] predicts water table development using a topographic wetness index (TWI) calculated from local slope and area drained per unit contour length [Kirkby, 1975].

The inclusion of drainage area, or upslope accumulated area, to TWI to predict depth to water table in TOPMODEL [Beven and Kirkby, 1979] illustrates the importance of hillslope morphology, in predicting water tables. Several authors have identified digitally derived topographic attributes, e.g., the three-dimensional shape of a hillslope, as a driver of hydrological functioning, including water table development [Aryal *et al.*, 2002; Detty and McGuire, 2010b; Fujimoto *et al.*, 2008]. In fact, Jencso [2009] found a strong correlation between upslope accumulated area alone and hydrologic connection to the stream. As upslope accumulated area is an integrator of topographic characteristics [Jencso *et al.*, 2009], this reinforces previous findings identifying terrain attributes as a control on water table development and streamflow generation.

The predictive ability of terrain attributes and TWI with regard to water table occurrence is important not only in determining catchment or hillslope discharge, but also water chemistry. For instance, discrete saturated areas have been shown to be important to dissolved organic carbon (DOC) export during precipitation events in headwater catchments [Inamdar and Mitchell, 2006]. Predictors of water table development such as landform or TWI are therefore correlated with DOC [Creed and Beall, 2009; Hornberger *et al.*, 1994; Ogawa *et al.*, 2006]. Other chemical constituents in soil water throughflow

are also dependent on discrete saturated areas. TWI has been demonstrated to be a predictor of nitrate [Ogawa *et al.*, 2006; Welsch *et al.*, 2001] and dissolved organic nitrogen [Creed *et al.*, 2008; Ogawa *et al.*, 2006] in hillslope throughflow.

2.4 Impeding layer topography

Yet another important aspect controlling water table development and streamflow generation is the topography of subsurface impeding layers. In some catchments, surface topography alone is not an accurate predictor of water table development; instead the topography of the underlying bedrock [Ali *et al.*, 2011; Freer *et al.*, 2002; Tromp-van Meerveld and McDonnell, 2006], dense glacial till [Hutchinson and Moore, 2000] or fragipans [Gburek *et al.*, 2006; McDaniel *et al.*, 2008] dominates saturation patterns. As with the development of saturated areas, the same impeding layer control of soil moisture on hillslopes has also been observed [Chaplot and Walter, 2003; McNamara *et al.*, 2005].

Tromp-van Meerveld and McDonnell [2006] described the process governing this control over saturation as depressions in low permeability bedrock filling with water (reaching saturation) and then spilling, thereby generating downslope water flow. This process produces a threshold response to precipitation, as there is a requisite amount of precipitation that must be exceeded in order to produce runoff. Precipitation amounts below this will only partially fill storage reservoirs, generating no runoff. Depressions of many different magnitudes exist in these catchments, resulting in a spatial patchwork of areas with different thresholds of precipitation governing their response [Ali *et al.*, 2011; Lehmann *et al.*, 2007].

2.5 Hot spots and thresholds

As discussed previously, frequently saturated areas in catchments can have unique water chemistry, leading to stream chemistry that is dependent on the chemical output and structure contributing areas. Saturated areas in this context may be considered ‘hot spots’, as biogeochemical reactions create unique solute chemistry with the addition of a missing ingredient: water [McClain *et al.*, 2003]. Changes stream chemistry, not consistent with typical patterns, have been associated with different ‘hot spots’ in

catchments, such as elevated base cations from springs near streams at Hubbard Brook [Likens and Buso, 2006]. Additionally, hillslope saturation has been shown to play an important role in delivery of solutes to streams [Creed and Beall, 2009; Inamdar and Mitchell, 2006; van Verseveld *et al.*, 2009] and riparian zone characteristics [McGlynn and McDonnell, 2003a] and hydrologic connection with hillslopes [Pacific *et al.*, 2010] influence the timing and concentrations of solute export from catchments. This dependence of stream chemistry on zones of saturation or ‘hot spots’ in catchments illustrates the need to better understand not only the processes occurring in these zones, but also where and when these ‘hot spots’ occur spatially and temporally [Burt and Pinay, 2005; Uhlenbrook, 2006].

A potential tool in predicting the spatial and temporal dynamics of catchment hot spots is to group them in terms of response thresholds. Sidle [2000], among others [Detty and McGuire, 2010a; McDonnell, 2003; Spence, 2010; Tromp-van Meerveld and McDonnell, 2006], observed that runoff generation in small catchments occurs when a threshold of antecedent wetness and precipitation is exceeded. These threshold responses are observable at the catchment outlet, where discharge will only increase after a threshold amount of precipitation has been added to existing catchment storage [Detty and McGuire, 2010a]. Furthermore, McDonnell [2003] explained that threshold inputs are necessary to activate lateral throughflow, whether dependent on macropores or bedrock topography. Indeed threshold responses at the hillslope scale have been reported, whether dependent on bedrock topography [Ali *et al.*, 2011; Tromp-van Meerveld and McDonnell, 2006], the self organization of macropore flowpaths [Nieber and Sidle, 2010] or other factors such as soil depth [Buttle *et al.*, 2004]. It is the organization of these different threshold responses and the connection of flow pathways that produces stream runoff [Ali *et al.*, 2011; Sidle *et al.*, 2000; Spence, 2010].

A description of what thresholds for runoff production exist spatially in a catchment would therefore explain where and after how much precipitation ‘hot spots’ would activate. The biogeochemical functioning of soils in these ‘hot spots’ would then help predict the catchment chemical output resultant from a given amount of precipitation.

Likewise the hydrological functioning of ‘activated’ zones, including whether or not they are contributing to runoff [Ambroise, 2004], would aid in predicting catchment discharge.

3.0 Soils predictors of catchment behavior

3.1 Topography as a predictor of soil attributes and morphology

Just as metrics describing the topography of a hillslope can be predictive of hydrologic behavior, they are also related to soil properties. For instance, simple topographic descriptors, such as slope, elevation, and TWI have been shown to be correlated with organic matter content in soil [Guo *et al.*, 2009] as well as various soil chemical properties [Gessler *et al.*, 1995; Moore *et al.*, 1993; Seibert *et al.*, 2007; Tsui *et al.*, 2004]. Additionally, soil morphological attributes may also be predicted by terrain [Gessler *et al.*, 1995; Moore *et al.*, 1993; Odeh *et al.*, 1994]. While many single topographic metrics may be predictive of specific soil attributes, a combination of many metrics is necessary for a more complete predictive model of spatial soil occurrence [Pennock *et al.*, 1987]. Indeed, Park and Burt [2002] found correlations between soil chemistry and several combined terrain attributes, suggesting a more descriptive metric of hillslope morphology was necessary to predict the occurrence of soil properties.

A useful metric describing hillslope topography may be landform. Pennock [1987] described how nine distinct landform types [Dalrymple, 1968] could be indicative of different soil morphologies. Similarly, Young and Hammer [2000] related several soil morphological features to specific landforms. As a computer model using digital elevation data can determine the locations of these landforms throughout a catchment, it is possible to predict the distribution of soils throughout a catchment [MacMillan *et al.*, 2000; Schmidt and Hewitt, 2004]. Although at a scale larger than would be necessary for a headwater catchment, the feasibility of this approach was demonstrated in Schmidt *et al.* [2005].

3.2 Hydrology as the driving factor in soil spatial distribution

As discussed in section 2.0, topographic attributes of a hillslope can be predictors of hydrologic behavior, just as they can be predictors of soil chemistry and morphology.

The dependence of hydrology and soil chemistry/morphology on topography is not a coincidence. Although *Jenny* [1941] did not explicitly identify hydrology as a control on soil development, it was included implicitly through the factors of climate and topography. More recent work, however, has specifically identified hydrology as a control on the development and distribution of soils in a watershed.

Hydrology has been identified as a control on soil composition and morphology [*Schaetzl and Anderson*, 2005], perhaps the primary control [*Daniels and Hammer*, 1992]. For instance, the amount of time a soil is saturated has been shown to control soil color [*Dunne et al.*, 1975; *Franzmeier et al.*, 1983; *Reuter and Bell*, 2003]. Additionally, *Moore et al.* [1993] related several soil characteristics to a topographic wetness index, additionally hypothesizing that subsurface flow paths are a control on soil spatial variability. As hypothesized by *Moore et al.* [1993], controls beyond saturation have also been identified. Several studies have identified lateral throughflow as a control on soil development, identifying patterns of Fe and Mn depletion and deposition indicative of translocation downslope, not only vertically in a profile [*Jankowski*, 2013; *McDaniel*, 1992; *Park and Burt*, 1999; 2002; *Sommer and Schlichting*, 1997; *Sommer et al.*, 2000]. Furthermore, these lateral flow processes have been linked to identifiable soil morphological characteristics, such as changes in horizon thickness due to horizontal translocation [*Bailey et al.*, 2014; *Jankowski*, 2013; *Sommer et al.*, 2000].

3.3 Soil characteristics as indicators of hydrologic regimes

As discussed above, soil morphology and chemical composition can be indicative of the hydrology that influenced their formation. Therefore, just as terrain can be used to predict soil characteristics, soil characteristics may also be used to predict hydrologic function. Indeed, *Park and Burt* [1999] suggested a detailed analysis of soil chemistry could predict hydrologic functioning. In a later study, *Park and van de Giesen* [2004] associated landforms with different soil development and thereby soil moisture regimes. By mapping landform occurrence they were able to identify areas of similar soil moisture regimes in a catchment. Pedotransfer functions, where soil characteristics indicative of hydrologic characteristics are indexed and used to predict hydrologic functioning, are

another example of a method for relating soil properties to hydrologic functioning [Pachepsky *et al.*, 2006].

4.0 Integration

As proposed by *Sivapalan* [2003] and *Uchida* [2005], an examination of common patterns and processes in headwater catchments has revealed relationships between soil properties, hydrologic function, and topographic position. Following the recent call for a more transdisciplinary approach to catchment hydrology [Troch *et al.*, 2009], these relationships integrate the fields of soil science and hydrology.

Because these relationships between soil, landform, and hydrology exist, it is hypothesized that a catchment may be divided into similarly functioning areas based on the predicted topographic location of soils [Lin *et al.*, 2006]. These similarly functioning areas may act as dominant landscape units, whose identification and description was called for by *McGlynn, et al.* [2004]. If the hydrologic responses of these areas are classified, and their response thresholds identified, they may be treated as the threshold governed storage areas described by *McDonnell* [2003]. Furthermore, during a precipitation event, above threshold areas may be treated as ‘hot spots’. If the chemical transformations taking place in these ‘hot spots’ can be described, they may be linked to the development of spatial and temporal patterns in stream chemistry. Likewise, knowledge of the hydrologic behavior of these areas may lead to a more thorough understanding of catchment discharge, potentially helping physically based models move toward getting the right answers for the right reasons [Kirchner, 2006]. Moving forward in this manner may therefore foster a better understanding of how our vital and relatively unknown headwaters function.

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Chapter 2: Organizing groundwater regimes and response thresholds by soils: a framework for understanding runoff generation in a headwater catchment.

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Abstract

A network of shallow groundwater wells in a headwater catchment at the Hubbard Brook Experimental Forest in New Hampshire was used to investigate the hydrologic behavior of five distinct soil morphological units. The soil morphological units were hypothesized to be indicative of distinct water table regimes. Water table fluctuations in the wells were characterized by their median and interquartile range of depth; proportion of time water table was present in the solum, and storage-discharge behavior of subsurface flow.

Statistically significant differences in median, interquartile range, and presence of water table were detected among soil units. Threshold responses were identified in storage-discharge relationships of subsurface flow, with thresholds varying among soil units. These results suggest that soil horizonation is indicative of distinct groundwater flow regimes. The spatial distribution of water table across the catchment showed variably connected/disconnected active areas of runoff generation in the solum. The spatial distribution of water table and therefore areas contributing to stormflow is complex and changes depending on catchment storage.

1.0 Introduction

The spatial distribution of soil moisture and depth to water table throughout a catchment are critical components in any attempt to understand streamflow generation [Freeze, 1972; Sidle *et al.*, 2000; Western *et al.*, 1999]. Water table fluctuations are often studied in order to describe runoff generation processes [Bachmair and Weiler, 2012; Sklash and Farvolden, 1979; Tromp-van Meerveld and McDonnell, 2006]. An improved understanding of where and when water tables develop in a headwater catchment would therefore be a valuable tool to help understand runoff generation and transport at the catchment scale.

Authors have posited several controls governing the spatial and temporal distribution of water tables, including riparian morphology and soil hydrologic characteristics [Burt *et al.*, 2002; Buttle *et al.*, 2004; McGlynn *et al.*, 2004], hillslope topography [Anderson and Burt, 1978; Beven and Kirkby, 1979; Detty and McGuire, 2010a; Dhakal and Sullivan, 2014; Penna *et al.*, 2014], and/or the subsurface topography of confining layers such as bedrock [Ali *et al.*, 2011; Freer *et al.*, 2002; Tromp-van Meerveld and McDonnell, 2006], dense glacial till [Hutchinson and Moore, 2000; Rodhe and Seibert, 2011], fragipans [Gburek *et al.*, 2006; McDaniel *et al.*, 2008], or other layers of contrasting conductivities [Rulon *et al.*, 1985]. Mapping the extent of these features may assist in the prediction of potential saturation regions in the subsurface given an amount of antecedent moisture and precipitation. However, bedrock, till, or fragipan hydrogeologic characteristics and topographies are not easily mapped or predicted, making understanding their importance to spatial runoff generation processes challenging.

Even when predictions of saturated regions in a catchment are possible, they indicate little about runoff generation [Bracken and Croke, 2007]. As described in Ambroise [2004], a distinction must be drawn between active and contributing areas. An active area may be any saturated area in the catchment. Contributing areas imply hydrologic connection to the stream with sufficiently high hydraulic conductivity to produce runoff at the catchment outlet at the timescale of storm events. Hydrologic connectivity and flux are higher in saturated or near-saturated soil than in soil with lower water content.

Therefore, while any saturated area may be considered an active area in terms of subsurface flow, if it is not connected hydraulically to the stream at the event timescale, it is not considered a contributing area. Threshold responses (defined as the absence of a response in the dependent variable until a threshold value of the independent variable is exceeded [Zehe and Sivapalan, 2009]) of water table rise in soil profiles to precipitation and antecedent wetness describe the function of distinct hydrologic regimes, such as whether or not areas are likely to be active and/or contributing areas under certain conditions. Threshold responses in catchment discharge have been identified in a variety of landscapes and are a promising tool for deciphering catchment hydrological processes [e.g., Detty and McGuire, 2010b; Penna *et al.*, 2011; Penna *et al.*, 2014]. Additionally, threshold subsurface flow responses have also been identified [Ali *et al.*, 2013]. When compared spatially throughout a catchment, threshold water table responses may offer insight into how water tables develop and contribute to streamflow. This may offer insights into how shallow water tables throughout a catchment relate to discharge and spatial and temporal variations in streamwater chemistry.

Spatial and temporal variations in the streamwater chemistry of headwater catchments have been observed at a variety of scales [Likens and Buso, 2006; Zimmer *et al.*, 2013]. Contrasting longitudinal patterns in streamwater chemistry have been observed within branches of the same stream even in small headwater catchments [Asano *et al.*, 2009; Palmer *et al.*, 2005; Zimmer *et al.*, 2013]. In scenarios where bedrock, soil parent material, and vegetation are similar across the stream network, other factors must be the cause of such variation. One such potential cause of these observed variations is differing spatial distributions of water tables in subcatchments that suggest distinct active flowpaths unequally distributed throughout the catchment [O'Loughlin, 1981]. Saturated areas are thought to be hot spots for biogeochemical activity [McClain *et al.*, 2003], regardless of their connection to the stream. Distinct chemical signatures developed in these areas due to variations in redox conditions or water contact time with subsurface materials, may therefore be relevant to streamwater chemistry at an event timescale and/or beyond [Zimmer *et al.*, 2013]. Thus identifying response thresholds, characteristic water table behavior, and the spatial distribution of contributing and non-contributing

areas is vital to understanding streamflow generation and regulation of solute composition in headwater catchments.

Several studies have identified hydrological controls on soil development [Bailey *et al.*, 2014; Park and Burt, 2002; Zaslavsky and Rogowski, 1969], expanding the classic soil formation factors of Jenny [1941], which only indirectly identifies hydrologic influences by way of climate and topography. For instance, intermittently saturated soils have been shown to contain redoximorphic features and elevated carbon accumulation [He *et al.*, 2003; Moore *et al.*, 1993; Rabenhorst and Parikh, 2000]. Likewise, several studies have identified lateral throughflow as a control on soil development, detecting patterns of Fe and Mn depletion and deposition indicative of translocation downslope, not only vertically in a soil profile [McDaniel, 1992; Park and Burt, 2002; Sommer *et al.*, 2000].

In this study we utilized five soil morphological units that have been recognized in watershed 3 (WS3) at the Hubbard Brook Experimental Forest (HBEF), USA [Bailey *et al.*, 2014; Zimmer *et al.*, 2013]. Soils were grouped based on the characteristics of the solum. The solum is the soil to the base of the B horizon. Compared to the C horizon it is relatively weathered, with greater development of soil structure (i.e., particle aggregation), a lower bulk density, and varying carbon accumulation depending on thickness and type of B horizons. Additionally, it is approximately equivalent to the rooting zone. In contrast, the underlying C horizon is less affected by soil forming processes, reflecting geologic properties of relatively unaltered parent material. Varying depths and thicknesses of diagnostic soil horizons in the solum, hypothesized to be the result of differences in hydrologic flowpaths, have been identified at HBEF and shown to occur along topographic sequences. Using a well network to monitor groundwater responses in the solum, we compared the water table dynamics and estimated subsurface flow rates under different storage regimes across soil units. The primary questions addressed in this study are: 1. Can soil units defined by morphological differences be used to indicate specific solum groundwater dynamics and/or the spatial distribution of solum groundwater in a headwater catchment? 2. Can insights from examining solum groundwater regimes in different soils provide information about runoff generation and

contributing/recharge areas in a catchment?

2.0 Site Description

This study was carried out at the Hubbard Brook Experimental Forest, in watershed 3, the hydrologic reference watershed for a series of paired watershed experiments [Hornbeck, 1973; 1975; Hornbeck *et al.*, 1970; Likens *et al.*, 1970] (Figure 1). Hubbard Brook is located near North Woodstock, NH, USA in the White Mountain National Forest. The climate is humid continental, with average January and July temperatures of -9°C and 18°C, respectively. Precipitation is evenly distributed throughout the year with about a quarter to a third of the 1400 mm annual precipitation occurring as snow [Bailey *et al.*, 2003].

Watershed 3 is 42 ha, south facing, steep (average slope of 28%), and ranges in elevation from 527 to 732 m [Likens, 2013]. The catchment is forested with mature, northern hardwood species, American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*). On shallow to bedrock areas balsam fir (*Abies balsamea*), red spruce (*Picea rubens*) and white birch (*Betula papyrifera var. cordifolia*) dominate [Likens, 2013].

Watershed 3 is underlain by sillimanite-grade pelitic schist and calc-silicate granulite of the Silurian Rangeley Formation. The soil parent materials are ablation and basal tills of varying thickness, texture, and hydraulic conductivity deposited during the late Wisconsinan glacial period [Bailey *et al.*, 2014]. The major soil type is a podzol with a sandy loam texture, which has been characterized as a well-drained Haplorthod with 0.5 m average solum thickness [Likens, 2013]. However, distinct variations of soil horizonation and a broader range of drainage classes have been identified in WS3, and are hypothesized to be the result of variations in soil forming processes driven by groundwater regime. These variations have been grouped into soil morphological units [Bailey *et al.*, 2014] named according to their dominant pedogenic horizon. For example, the solum of an E podzol is dominated by an E horizon, a leached layer that is highly weathered and has a low carbon content. Bhs and Bh podzols are similarly dominated by

Bhs and Bh horizons, respectively, with higher carbon content. The exceptions are the typical podzol, which has horizonation more typical of the classic concept of a Spodosol, with moderate expression of both E and B horizons, and the bimodal podzol, which is characterized by an anomalous Bh horizon at the base of the solum in an otherwise typical podzol. A conceptual model of these soil units along an idealized hillslope is shown in Figure 2. E, Bhs, and Bh podzols were hypothesized by *Bailey et al.* [2014] to be indicative of the lateral translocation of spodic materials downslope (lateral podzolization), a process similar to that identified by *Sommer et al.* [2000]. Upon initial analysis of existing wells in Bh podzols from *Detty and McGuire* [2010a] and *Bailey et al.* [2014], differences were identified in water table fluctuations leading to the separation of Bh podzols into near-stream Bh podzols and hillslope Bh podzols. Bimodal podzols were not included in this analysis as they are considered to be a transitional soil unit between typical podzols and Bh podzols, occupying a small percentage of the catchment compared to other units.

3.0 Methods

3.1 Well network

This study is based on data from a shallow groundwater well network spatially distributed throughout WS3 (Figure 1). The network of 25 wells was designed to monitor water table dynamics across different soil units throughout the catchment and is a composite of wells established by previous studies and wells installed specifically for this analysis. Seven wells installed by *Detty and McGuire* [2010a; b] had soil morphology characterized in adjacent soil pits by *Bailey et al.* [2014]. An additional seven wells with detailed soil characterization were installed by *Bailey et al.* [2014] in order to have three wells in each soil unit identified in WS3. In this study, 11 more wells were installed and soils were characterized, in order to bring the total number of wells in each soil unit to five, including five wells each in Bh podzols found in near-stream areas as well as other settings more distant from streams. Wells from previous studies have associated multi-year datasets that were used to test the representativeness of the time period of this study (August 2011 – August 2012).

At each well, a small soil pit was hand excavated to ~10 cm into the C horizon (40 to 100 cm; 65 cm average) and pedogenic horizons were described. Each soil profile was assigned to one of the categories based on horizon presence and thickness. Wells were constructed of standard dimension ratio (SDR) 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. Wells were either installed with a 10 cm hand auger immediately upslope of the characterization pit or in the backfilled pit. The auger was used to bore 10 cm into the C horizon so that the base of the well screen was inserted into the C horizon. Wells were installed on top of bedrock in the cases where a C horizon was not present. Local washed sand was used to backfill 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. Each well was equipped 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) recorded at 10 minute intervals. Data was available for the 25 wells used in this study for the period of August 2011 – August 2012; however, several wells had records extending to August 2007. To be sure this data period was not anomalous, and therefore suitable to use to characterize water table regimes in soil units, we compared the water table data from year to year where possible. Because of the large number of water table measurements per year ($n > 50,000$), examining statistical tests for differences in the distributions of water table measurements will always detect differences even when the distributions are very similar [*Gardner and Altman*, 1986]. Therefore, similar to the analyses used in this study, the median and interquartile range (IQR) were used to examine the water table records for multiple years. The median and IQR were within 1.5 cm of previous years in all 7 of the wells with up to 3 years of water table data. This suggests the period of data used in this analysis was not anomalous.

Topographic metrics for each well were derived from a low-pass filtered, 5-meter resolution, LiDAR derived digital elevation model (DEM). This DEM was determined by *Gillin* [2013] to produce topographic metrics most similar to field measured values. Upslope accumulated area (UAA) was calculated using a multiple flow direction

algorithm defined in *Seibert and McGlynn* [2007]. The maximum slope algorithm [*Travis et al.*, 1975] was used to calculate slope. Distance from stream was calculated as the Euclidean distance to the nearest intermittent or perennial stream channel on a stream network mapped from observations of streamflow and evidence of fluvial channel development (Figure 1).

3.2 Water table dynamics

In an effort to quantify differences observed in the water table dynamics of wells in different soil units, three metrics describing water table fluctuation in the solum were examined: median water level, interquartile range of water level, and percent time water table existed above the C horizon.

The distribution of water level measurements was defined as all data where water level was recorded to be anywhere within the solum. While permanent water tables undoubtedly existed at depth within the C horizon, *Detty and McGuire* [2010a] found that the upper C horizon saturated quickly following events and saturated hydraulic conductivities above the subsoil were higher. This led to the conclusion that water tables in the solum may develop on top of the C horizon [*Detty and McGuire*, 2010a]. We acknowledge that solum water tables likely rise up from the C horizon in some settings and develop on top of the C horizon in others, however, because this study focused on solum water table dynamics, water tables above the C horizon were considered regardless of their origin. Therefore, percent time of water table existence was defined as the number of measurements where the record was above the subsoil (i.e., above the top of the C horizon) divided by the total number of measurements in the record times one hundred. For calculation of the interquartile range and median of each water table record, water table measurements were normalized to range from 0 (ground surface) to 100 (base of solum), in order to more uniformly compare all well records. Records of water level below the C horizon were categorized as non-detects, therefore a median groundwater level was more appropriate than a mean. Differences between metrics among soil units were tested for statistical significance using the Kruskal-Wallis analysis of variance and Tukey's honestly significant difference test at a significance level of 0.05.

3.3 Groundwater flux

Groundwater flow was estimated at each well in order to make comparisons among the responses of different soil units. We calculated total catchment storage from 20 Feb 2011 to 30 June 2012 and evaluated well response for different levels of storage.

The hydrologic lumped, conceptual rainfall runoff model HBV light [Seibert and Vis, 2012; Steele-Dunne et al., 2008; Uhlenbrook et al., 1999], a version of HBV [Bergström, 1995; Lindström et al., 2005], was adapted to MATLAB and used to calculate storage in the catchment and snow melt input. Storage was represented for this analysis by the combination of the soil and groundwater storages from HBV. This combined storage value was intended to represent variation in the overall storage or wetness state of the catchment through time. This model was chosen because it has been shown to perform well in snow-dominated catchments [Bergström, 1995; Seibert, 1997] as well as other catchments around the world [Lidén and Harlin, 2000; Steele-Dunne et al., 2008] and represents catchment storage (as presented in Detty and McGuire [2010b]) well. HBV was calibrated for WS3 by selecting the optimal parameter set from a 100,000 iteration Monte Carlo simulation using streamflow and snow water equivalent in a multi-objective calibration using the Nash-Sutcliffe Efficiency (NSE) [Nash and Sutcliffe, 1970] and relative volume error following Lindström [1997] and the NSE of snow water equivalent. The same parameters were varied as in Seibert et al. [2000] with the exception of MAXBAS, which is a channel routing parameter that is unnecessary due to the small size of WS3. The multi-objective calibration efficiency for the optimum parameter set was 0.79. The storage dynamics from the model were considered to be representative of actual catchment storage based on a linear relationship between storage calculated from a representative soil moisture transect in Detty and McGuire [2010b]. The calculated storage from Detty and McGuire [2010b] was used to corroborate the model, and was not used for calibration. Observed and modeled storage metrics, were highly correlated ($r = 0.95$). While magnitudes differed in the two calculated metrics, the strong linear relationship indicated the storage dynamics were captured by the model.

Following the procedure outlined in *Detty and McGuire* [2010b] for examining threshold changes in catchment discharge, the modeled storage was then added to the daily input, whether it was measured precipitation or model calculated snowmelt input. The resulting dataset represented the ‘effective storage’ in the catchment: catchment storage from HBV plus precipitation and snowmelt inputs on a daily time step.

Subsurface flow within the solum was then calculated for the water level record of every well using Darcy assumptions. The hydraulic gradient at each well was assumed to be parallel to the local, DEM derived ground surface slope at the well location (i.e., the kinematic approximation), and transmissivity was calculated based on the hydraulic conductivity - depth relationship for WS3 presented in *Detty and McGuire* [2010a]. Subsurface flow (q_{ssf}) above the C horizon (L^2/T) was calculated as:

$$q_{ssf} = T(z) \tan b$$

where z is the water table height (L) above the subsoil, b is the local slope, and T is transmissivity (L^2/T), calculated as:

$$T(z_i) = \int_{z_i}^z \frac{K_o}{f} \{ \exp(-fz_i) - \exp(-fZ) \}$$

where K_o is hydraulic conductivity (L/T) at the ground surface, z_i is the initial (highest in the profile) depth to water table, and Z is the depth to C horizon, and $f(L^{-1})$ is the slope of the line fit to the log transformed hydraulic conductivity-depth relationship [*Detty and McGuire*, 2010b].

Subsurface flow (q_{ssf}) for each well was then examined across all levels of catchment storage. This was done by binning modeled effective storage into 10 mm bins and calculating the mean subsurface flow response for each bin at each well. The result was an estimate of Darcian flow for each effective storage bin, allowing an examination of subsurface flow as a function of the effective catchment storage.

For each bin of effective storage for each well, a Wilcoxon rank sum test was performed to identify bins in which mean discharge was significantly different from zero (significance level of 0.05). The subsurface flow activation threshold for each soil unit was identified as the mean storage level for all wells in the group at which the subsurface flow significantly deviated from zero.

4.0 Results

4.1 Water table dynamics

Water table records from wells in different soil units showed distinct patterns of water table fluctuation (Figure 3). The consistency of these differences among wells in the same soil units over the study period is illustrated further in Figure 4. These two figures exemplify the characteristic differences in water table dynamics among soil units.

Transient water table incursions into the solum were very infrequent in typical podzols (Figure 3). Also, water tables seldom rose above the bottom 30% of the soil profile in typical podzols (Figure 4). E and Bhs podzols were shown to have more frequent water table presence (Figure 3) which was also higher into the soil profile (Figure 4). Hillslope and near-stream Bh podzols had higher water tables for longer periods of time (Figure 4). Hillslope Bh podzols, however, had only seasonally persistent water table while near-stream Bh podzols had perennial water table (Figures 3 and 4). Furthermore, hillslope Bh podzols had higher magnitude fluctuations in water level, whereas near-stream Bh podzols had relatively smaller magnitude fluctuations (Figures 3 and 4).

When the distributions of percent profile saturation above the subsoil in each soil unit were compared, statistically significant differences were observed (Figure 5). The presence or absence of water table in wells yielded statistically significant differences among soil units (Figure 5a). Wells in soil units hypothesized to receive groundwater flow from upslope (E, Bhs, hillslope Bh, near-stream Bh) had a significantly higher percentage of their record where water table was observed above the subsoil. Water tables were present in these wells ranging from about 25-100% of the time. Wells in the vertically developed typical podzols detected water table far less frequently, with water table present about 0-10% of the time, with the exception of one well, which had water

table just under 40% of the time, but only for a small portion of the solum thickness (Fig. 4).

The difference in water table fluctuations of the two subsets of Bh podzols can be observed in Figure 3, showing a representative time series of water level data for each soil unit, and Figure 4, showing cumulative density functions of the water table data for each well in each soil unit. Hillslope Bh podzols had persistent water tables only in the non-growing season and had higher magnitude water table fluctuations than near-stream Bh podzols (Figure 3). The lower slope center portion of the ECDF (Empirical Cumulative Density Function) for near-stream podzols in Figure 4 also shows that water tables were more persistent and fluctuated less. Differences between near-stream and hillslope Bh podzols were also related to the topographic position of the well (Figure 6): Hillslope Bh podzol wells had consistently higher interquartile range of water table recordings, occurred at distances >10 m from streams, and had upslope accumulated areas (UAA) <150 m².

Wells in soil units with horizonation hypothesized to be indicative of lateral podzolization processes (E, Bhs, and hillslope Bh podzols), had consistently higher water level than typical podzols. Interquartile ranges of these groups, however, did not differ from one another, with the exception of near-stream Bh podzols, which were smaller, indicating less variable water table fluctuations.

Median normalized water level likewise showed differences in well responses (Figure 5c). Hillslope and near-stream Bh podzols were not different from one another as both exhibit persistent saturation for part of the year. E, Bhs, and typical podzols, despite having different dynamics, shown by the percent time and interquartile range metrics, had similar median water levels relative to their respective soil profile depths as their water tables did not persist beyond event responses (Figure 3).

4.2 Storage – Groundwater flux relationships

Distinct response thresholds to catchment effective storage, defined in section 3.3, were observed for estimated groundwater flow in the solum for each of the soil units (Figure 7). With increasing storage in the catchment, water table in wells showed no measurable response until a storage threshold was exceeded. This storage threshold differed among wells included in this study. When wells were grouped by soil unit, however, response thresholds were similar, with differences observed between units. While the podzols hypothesized to be dominated by lateral flow on the hillslope had similar thresholds (E, Bhs, and hillslope Bh), typical podzols and near-stream Bh podzols had very different responses.

Saturated flow in the solum of typical podzols, where vertical soil development through unsaturated percolation was hypothesized to dominate, showed a very high threshold, requiring over ~90 mm of effective storage before a response was observed. For two wells, the responses to precipitation in the solum were too brief and infrequent to elicit any statistically significant response using this analysis. Therefore, the effective storage needed to elicit a detectable response in these two wells is over 140 mm (Figure 7). Furthermore, when typical podzols had measurable discharge, it was of a magnitude not exceeding $0.1 \text{ cm}^2/\text{min}$.

In wells where lateral processes are hypothesized and water table was more frequent, thresholds were substantially lower and discharge much higher. In E and Bhs podzols, the response threshold was in the 70-80 mm storage bin, while in hillslope Bh podzols it was in the 50-60 mm bin (Figure 7). During the growing season, Figure 3 shows E and Bhs podzols responding when Bh podzols did not. Later in the same time series, when vegetation was dormant, hillslope Bh podzols responded with greater magnitude to smaller events, leading to the lower threshold observed for hillslope Bh podzols (Figure 7). Discharge for these podzols was also higher, nearing $0.4 \text{ cm}^2/\text{min}$ for E, Bhs, and hillslope Bh podzols.

Near-stream Bh podzols were observed to have persistent discharge that increased steadily with increased storage, therefore no threshold response was observed.

Furthermore, these near-stream soils showed low discharge, whose maximum was about $0.1 \text{ cm}^2/\text{min}$. Differences in response thresholds were not only seen between soil units, but also along transects of wells in a topographic sequence (Figures 8, 9).

Two common sequences of soil units along transects were examined to serve as examples of the ways thresholds vary along hillslopes in the catchment. In the sequence from E – Bhs – typical podzol, thresholds were lowest in the highest elevation wells, the E and Bhs podzols (Figure 2, Figure 8). Moving closer to the stream, thresholds increased: E and Bhs podzols had lower thresholds whereas thresholds in typical podzols were higher (Figures 7, 10b, 8). Conversely, in another common sequence of soil units, typical – hillslope Bh, thresholds changed in the opposite direction (Figure 8). Typical podzols further from the stream had the highest response thresholds, whereas hillslope Bh podzols further downslope required a much lower requisite storage to elicit a response (Figure 8, 10B). The same pattern is observed in the transition between typical podzols and near-stream Bh podzols (Figure 9).

While response thresholds generally increased with smaller UAA and greater distance from the stream, the relationship was not consistent (Figure 10). For instance E, Bhs, typical, and hillslope Bh podzols all had overlapping ranges of UAA and distance from the stream; only near-stream Bh podzols separated entirely, with lower response thresholds, lower distance to the stream, and higher UAA (Figure 10a, b). While typical podzols only occurred on greater slope gradients and Bh podzols on lesser slope gradients, E and Bhs podzols occurred over almost the entirety of the range observed for wells used in this study (Figure 10c). Finally, the differences between hillslope and near-stream Bh podzols were highlighted when topographic metrics were examined with thresholds. Near-stream Bh podzols not only had the lowest detectable threshold but also the highest upslope accumulated area (Figure 10a) and were the closest to the stream (Figure 10b). Their topographic similarities were in slope, where they occupied the same range (Figure 10c).

5.0 Discussion

5.1 Soil horizonation as an indicator of complex water table dynamics

Distinct water table regimes, described by the median and interquartile range of water levels and percent time water table exists in the solum, were observed in each soil unit (Table 1). Variations in soil morphology, including the presence of redoximorphic features [He *et al.*, 2003; Rabenhorst and Parikh, 2000]. and horizonation [Bailey *et al.*, 2014] have been shown to be indicative of saturation dynamics. Moore *et al.* [1993] identified relationships between soil properties and topography, hypothesized to be the result of different flowpaths and He *et al.* [2003] and Rabenhorst and Parikh [2000] identified differences based on time of saturation. However, in this study soil units were defined by characteristic horizonation throughout the entire profile, rather than discrete features or horizons within the solum [Bailey *et al.*, 2014]. Furthermore, the differences observed in water table regimes across soil units in WS3 were compared to water table dynamics having to do with the fluctuation, flow magnitude, and duration of flow occurring in a soil unit. This suggests soil units observed in WS3 can be used to understand solum flow dynamics and water table regimes in a catchment.

E and Bhs podzols have shallow profile depths and a large proportion of shallow or exposed bedrock in contributing areas (Figure 2). E podzols were characterized by a soil profile dominated by a thick E horizon and occur in complexes with bare bedrock outcrops and organic horizons directly on bedrock. Bhs podzols were likewise characterized by a thick Bhs horizon, and occurred immediately downslope of E podzols. This sequence of podzols therefore appears to have formed as a result of frequent periods of downslope saturated water flux, driven by vertical flow constriction due to shallow bedrock, creating the eluviated E podzols upslope of the depositional Bhs podzols [Bailey *et al.*, 2014; Sommer *et al.*, 2000]. The result is two pedons in a sequence on a hillslope that show downslope soil forming properties generally seen vertically within a single pedon [Sommer *et al.*, 2000]. This is supported by the frequent incursion of water table into the solum, high interquartile ranges of water levels, and low median water level (Figure 5). Additionally, the threshold storage required to elicit a response in these soil units was lower than typical podzols (Figure 7).

Typical podzols were characterized by a thin E horizon over moderately thick spodic horizons, indicating vertical leaching and immobilization of spodic (Bhs and Bs) materials downward through the soil profile [Lundström *et al.*, 2000; Sauer *et al.*, 2007]. The existence of this horizonation in typical podzols would require a relatively inactive water table regime consisting primarily of unsaturated vertical fluxes, with only brief periods of water table incursion into the solum during extreme events. Indeed, our analysis showed these podzols were saturated very infrequently, with low interquartile ranges of water table measurements, never more than about 1/3 of the profile saturated (Figure 4), and a median water table that was without exception equal to the depth of the top of the parent material C horizon (Figure 5). Activation thresholds for these wells were likewise the highest of all soil units, with the lowest magnitude discharge (Figure 7). These conditions could result from a combination of small contributing area, C horizon topography steep enough to permit drainage, and/or a more permeable C horizon, any of which could create the drainage conditions necessary for limited water table incursion into the solum of typical podzols. Bailey *et al.* [2014] showed that typical podzols are the most commonly encountered soils in the catchment. Furthermore, Gillin [2013] suggested that the typical podzol was the dominant soil unit in the catchment at approximately 50% of the area, which suggests that no more than 50% of the catchment is active within the solum in all but the most extreme precipitation events.

Two soil units that were typically found lower on hillslopes and with higher upslope accumulated areas were also found to be indicative of frequent incursions of groundwater into the solum: hillslope and near-stream Bh podzols. Both podzols were characterized based on a profile dominated by a thick Bh horizon, hypothesized to be formed by frequent saturation leading to lateral transport of spodic materials [Bailey *et al.*, 2014]. This saturation was likely a result of flowpath convergence and/or from water rise originating in the deeper C horizon. Both podzols had the highest median water levels and were the most frequently saturated (Figure 5). The difference in hydrologic response between these soil units was likely related to a combination of topographic variables. Near-stream Bh podzols were closer to streams and had higher upslope accumulated areas (Figures 5,8). They also exhibited lower interquartile ranges of water level,

presumably because of higher conductivity soil in the near-stream zone that likely resulted from glacial lag deposits and alluvial material [Detty and McGuire, 2010b]. The higher conductivity in near-stream areas provides a transmissivity feedback [Bishop et al., 2004], limiting water table rise in relation to overall flux magnitude [Detty and McGuire, 2010b]. This transmissivity feedback is also responsible for the low magnitude discharge observed in near-stream Bh podzols in Figure 7.

Several authors have proposed that topography is not a suitable predictor of water table behavior along a hillslope [Devito et al., 2005; Haught and van Meerveld, 2011; Penna et al., 2014; Tromp-van Meerveld and McDonnell, 2006; Western et al., 1999]. Soil thickness [Buttle et al., 2004], bedrock topography [Freer et al., 2002; Tromp-van Meerveld and McDonnell, 2006], and confining layer topography [Hutchinson and Moore, 2000] are all identified as controls on water table dynamics potentially more important than surface topography. Furthermore, the need for characteristics that are capable of acting as surrogates for the integration of these controls has been acknowledged [Graham et al., 2010; Zehe et al., 2005]. We found no one surface topographic metric was able to consistently predict soil units (Figure 10). Water table regimes at well sites in WS3 are controlled by surface and C horizon topography, hydraulic properties, bedrock topography, portion of upslope area that is bedrock outcrop, and surface slope. Yet soil horizonation is a robust predictor of water table dynamics. We therefore propose that soil units in WS3 act as a suitable characteristic describing the many controls on water table fluctuations, integrating their myriad hydrologic effects.

5.2 Soil units as hydrogeological units

Bailey et al. [2014] identified the soil units in WS3 because they observed variations in soil horizon thickness and presence/absence beyond the ranges of recognized soil series in the region. These variations occurred at a fine spatial scale and were therefore not included in medium intensity soil surveys where they would have been excluded by minimum map unit/polygon area requirements. However, Bailey et al. [2014] found differences in carbon pools in soil units as well as evidence for varying hydrologic regimes, hypothesizing that these soil units are indicative of distinct hydrologic and

biogeochemical conditions. Our analysis has shown that these soil units are indicative of distinct water table regimes and threshold water table responses to catchment storage consistent with the conditions hypothesized to create individual soil units (Table 1). The soil units are therefore indicative not only of variations in soil horizonation, but the coupling of biogeochemical processes and hydrologic regimes. Our work suggests there are feedbacks between water table regime and soil formation, the understanding of which may lead to new insights into critical zone processes concerning the structure and function of ecosystems [Chorover *et al.*, 2011]. The term “hydropedological unit” has been used to describe similar feedbacks elsewhere [Tetzlaff *et al.*, 2014], but has not been previously defined. Following our investigation, we propose defining the term “hydropedological unit” as a grouping of variations in soil morphology that directly relate influence of water table regime, flowpaths, and saturation to soil development.

A hydropedological unit is therefore a functional grouping of soils by hydrologic behavior and indicating potential implications for biogeochemical processing, runoff production, and the structuring of natural communities. This system of grouping soils may be most useful in catchment or other studies where local differences in water movement outweigh the role of varying vegetation or other soil forming factors on local gradients in soil morphology and chemistry. In contrast, the theory of Jenny [1941] only implicitly considers the role of water as a soil forming factor within the context of climate, which explains patterns of soil distribution at much broader scales than considered here, and even less explicitly in the role of parent material, relief, time and organisms in their influence on water movement.

5.3 Implications for runoff generation

The highest threshold responses observed in this study were in mid-slope positions, while the lowest occurred near the top and bottom of hillslopes. Typical podzols, which had the highest response thresholds, dominated the catchment, accounting for an estimated 50% of the catchment area [Gillin, 2013] and primarily occurred along mid-slope positions. While E and Bhs podzols almost always occurred together on the landscape, they were also almost always separated from hillslope Bh podzols by typical podzols (Figure 2).

Hillslope and near-stream Bh podzols were likewise sometimes separated from each other by typical podzols. This paints a picture of stormflow generation via a spatial patchwork of water table occurrence within the solum, and therefore lateral subsurface flow in the solum of the catchment, rather than an uninterrupted saturated area extending up from streams. A system such as this highlights the importance of the active vs. contributing areas of *Ambroise* [2004]. For example, water tables occurred in E and Bhs podzols far from the stream at frequently exceeded thresholds of catchment storage necessary for water table occurrence. Furthermore, there are large areas of the catchment separating E and Bhs podzols from the stream that only had water tables in the solum during extreme events (typical podzols). While portions of E and Bhs podzol areas may connect with intermittent or ephemeral channels, in many cases water tables occur upslope and infiltrate to deeper storage before the areas of saturation reach a stream channel. When water from these soils does enter stream channels it often flows into portions of the stream network where the stream is surrounded by typical podzols, likely indicating the stream is losing water to surrounding soils. During larger events, when thresholds are exceeded in typical podzols, E and Bhs podzols are more likely to connect to the stream (Figure 1). Therefore, if water tables connected to the stream channel generate stormflow, there are active areas in the catchment that are not contributing areas unless a high threshold of catchment storage is exceeded. However, water in these areas is moving further downward into the C horizon.

Water in the C horizon may take one of several paths to the stream network. While generally lower conductivity [*Detty and McGuire, 2010b*], the C horizon in WS3 has been shown to be heterogeneous, with lenses of higher conductivity material [*Bailey et al., 2014*]. Furthermore, preliminary ground penetrating radar results have shown the C horizon to be 0-9 m thick. Therefore, most water entering the C horizon will take a slower flowpath to the stream, recharging the larger C horizon groundwater reservoir. However, as high conductivity areas of till are present throughout the catchment, there also exists the possibility of groundwater following such a pathway to the stream. Some water moving from water tables in E and Bhs podzols into the C horizon may contribute flow to streams in this way.

Other authors have discussed discontinuous active areas on hillslopes [McNamara *et al.*, 2005; Spence, 2010; Stieglitz *et al.*, 2003]. Furthermore, as distance from the stream increases, some authors have found a decreased correlation of groundwater levels with streamflow [Haught and van Meerveld, 2011; Penna *et al.*, 2014; Seibert *et al.*, 2003]. The spatial patchwork of solum water table occurrence in WS3 is consistent with the behavior presented in these other studies. However, we have identified an integrative characteristic (i.e., hydrogeological unit) that is consistently indicative of water table behavior. Looking at the catchment through this lens provides a framework for mapping continuous/discontinuous water table occurrence in the solum of the catchment through time. As mentioned above, the role of discontinuous water tables in generating streamflow is currently unknown, as is their potential influence on stream chemistry. However, the insights offered in this study may provide an approach to more closely investigate the effects of patchy regions of subsurface saturation located throughout a catchment.

In addition to being a useful tool for examining the role of discontinuous solum water tables, our findings may be useful for examining the evolution of contributing area throughout events. Our observations are consistent with others suggesting distinct hydrologic regimes in near-stream areas [Cirimo and McDonnell, 1997; McGlynn and Seibert, 2003; Ocampo *et al.*, 2006]. We detected persistent water tables in near-stream Bh podzols with lower magnitude water fluctuations, presumably the result of higher saturated hydraulic conductivity in the near-stream zone [Detty and McGuire, 2010b]. Upslope of these soils were almost always typical podzols, which our threshold analysis has shown to have very infrequent water table incursion into the solum. Therefore, the observation of persistent water tables in the near-stream zone and typical podzols immediately upslope is consistent with the majority of event water being mobilized from the near-stream zone [McGlynn and McDonnell, 2003]. A direct connection between hillslope groundwater and the stream likely only occurs during large events, where water tables develop in the lower portion of typical podzol profiles. The discontinuities evident

from our analysis suggest most hillslope water takes longer, deeper flow paths to the stream, likely through the glacial parent material of the C-horizon.

6.0 Conclusions

We have shown that variations in soil horizonation across the landscape in WS3 at the Hubbard Brook Experimental Forest were indicative of specific water table regimes. Descriptors of water table regime that can be determined by examining soil horizonation include percent time a water table exists, median water level, interquartile range of water level fluctuations, and the threshold storage at which a water table will develop in the solum. The water table regimes associated with soil units across the landscape were consistent with the hypothesized flow regimes necessary to create the observed soil horizonation. As a result, we introduced the term hydrogeological unit to describe variations in soil horizon presence/absence and thickness that correspond to the hydrologic behavior of a soil.

We used a technique where catchment storage levels were compared to water table occurrence in the solum to determine storage thresholds for the generation of subsurface flow above the parent material. This method revealed isolated areas where water table occurred at lower storage thresholds than areas closer to the stream with larger contributing areas, painting a picture of a spatially disconnected patchwork of water table occurrence in the solum of the catchment. Response thresholds were related to soil horizonation: an integrator of several surface and subsurface properties including topography, rather than distance from the stream or contributing area.

Soil horizonation is therefore a useful tool for examining water table dynamics throughout a catchment. Upon characterizing the flow regimes associated with different soil morphologies in a catchment, different soil groups (hydrogeological units) may be used as an indicator to predict regions of the catchment where water tables are likely to develop. Additionally, we have shown these hydrogeological units to be indicative of distinct and consistent water table regimes. This framework, where distinct soil units indicative of hydrologic regimes and biogeochemical processes are identified, may be a

useful tool for examining runoff generation processes and patterns in surface water chemistry in headwater catchments.

Figures and Tables:

Table 1. Qualitative descriptions of the water table regimes for each soil unit (HPU) based on the findings of this study.

Soil Unit (HPU)	Water table regime summary
E Podzol	<i>frequent, near instantaneous response to precipitation and short recession period, nearly entire solum experiences saturation</i>
Bhs Podzol	<i>frequent, near instantaneous response to precipitation with a longer recession period than E podzols, nearly entire solum experiences saturation</i>
Typical Podzol	<i>brief, infrequent water tables near the base of the solum, only at high catchment storage</i>
Hillslope Bh Podzol	<i>seasonally persistent, lower magnitude event responses than E and Bhs podzols, nearly entire solum experiences saturation</i>
Near-stream Bh Podzol	<i>perennially persistent, lower magnitude event responses than hillslope Bh podzol, rarely if ever experience full solum saturation</i>

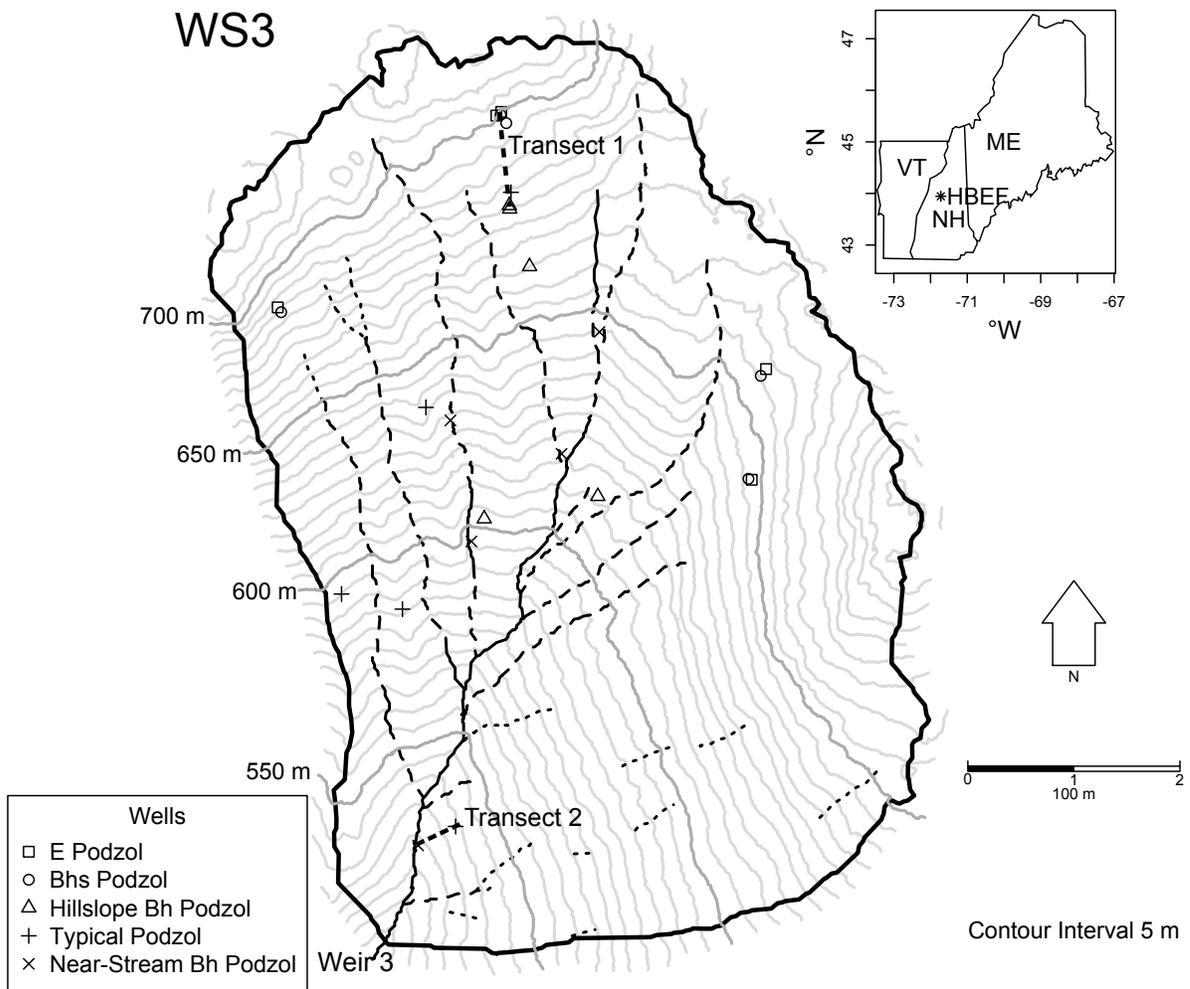


Figure 1. Map of WS 3. Perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. Shallow groundwater wells are indicated by symbols on the map. Soil morphological units are indicated by different shaped symbols. Transect 1 (Figure 8) and transect 2 (Figure 9) are shown by bold, dashed lines. The inset map indicates the location of HBEF in northern New England.

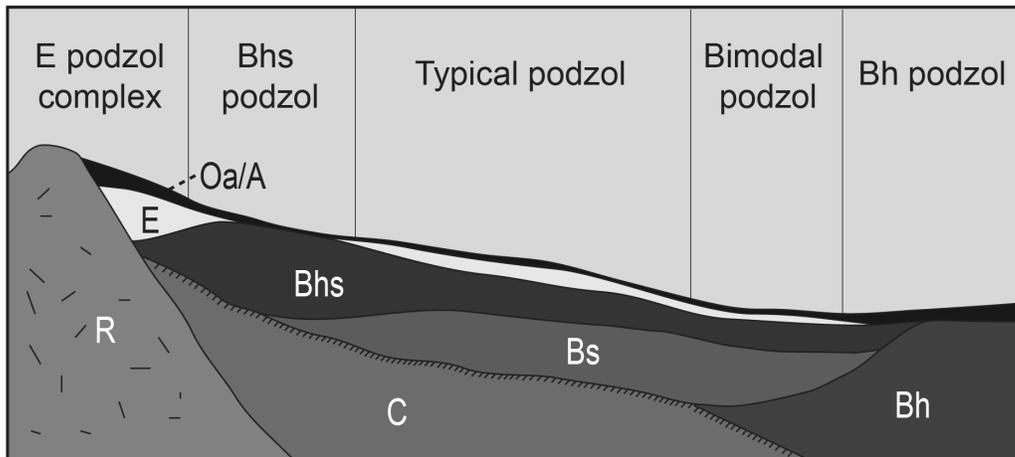


Figure 2. Schematic conceptual diagram showing soil horizonation along a typical soil unit sequence [Bailey *et al.*, 2014]. Mean depth to C horizon is 70 cm. Vertical scale is exaggerated. E, Bhs, Bh podzols, and the Bh horizon of Bimodal podzols were hypothesized to be indicative of frequent lateral flux in the solum. Typical podzols and the portion of bimodal podzols above the Bh horizon were hypothesized to be indicative of primarily vertical flux.

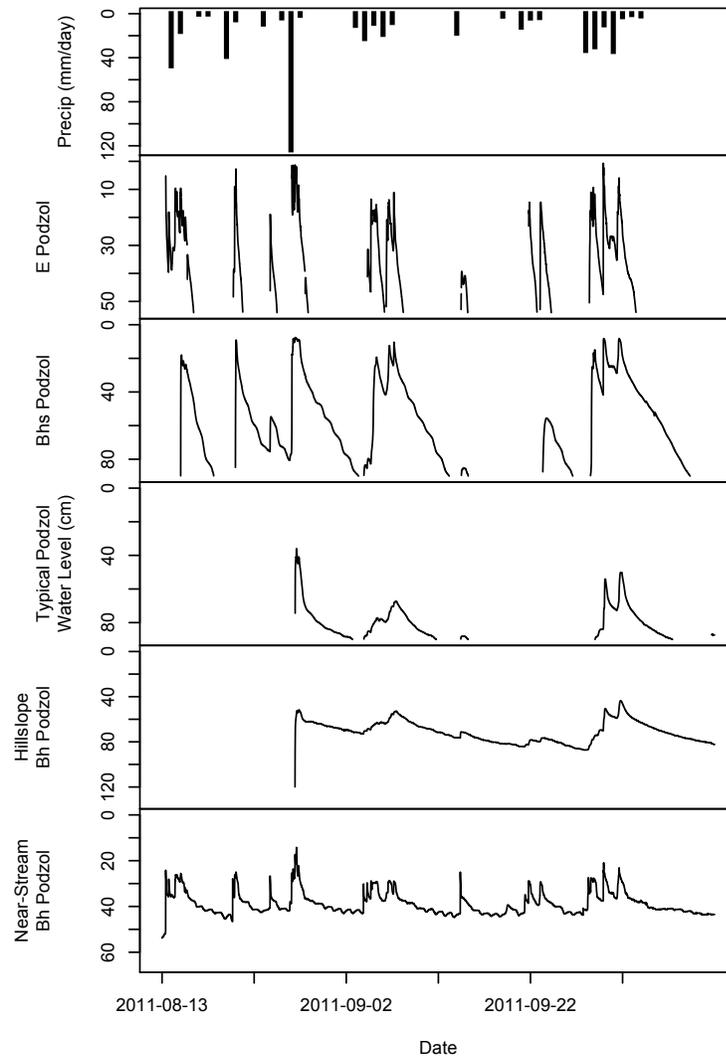


Figure 3. Example time series of precipitation and water table recordings within the solum for one characteristic well in each soil unit. The y-axis of each plot extends from the C horizon to the ground surface. Periods without data indicate a lack of water table in the solum at the site. Modified from *Bailey et al.* [2014].

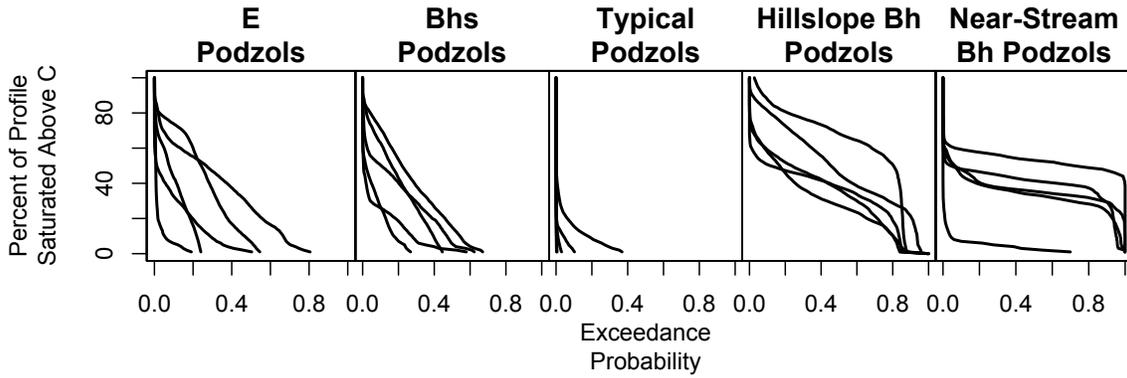


Figure 4. Empirical cumulative density functions (ECDFs) show the probability a water table exists at a given percentage of the total depth of a soil profile. Soil profiles in this figure are considered to begin at the C horizon and extend to the surface. ECDFs were constructed from 1 year of 10-minute water level data from all wells in each of the soil units used in this analysis. Each line in each plot represents the water level time series from a well in that soil unit. (n = 5 wells per soil unit)

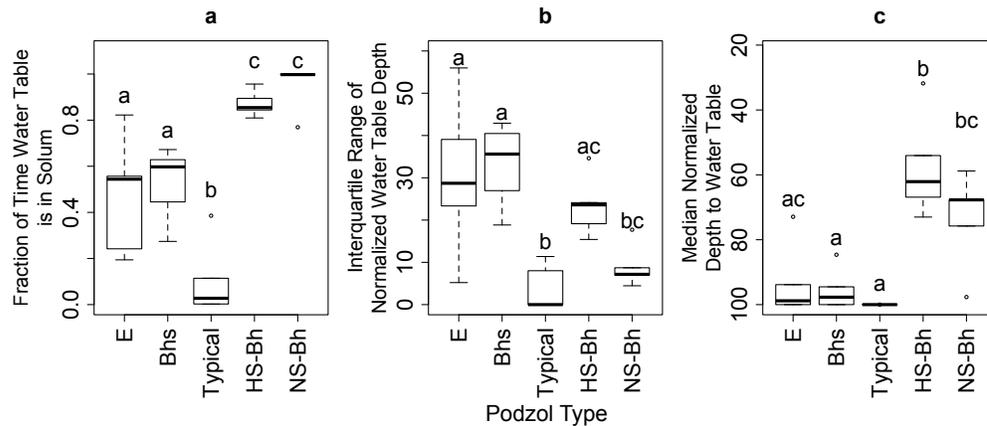


Figure 5. Box plots showing the separation of soil unit water table regimes for different dataset measures. Letters above groups indicate statistically significant differences according to a Wilcoxon rank sum test (significance level 0.10). The fraction of total time a water table was detected in the solum is presented in panel a. Water table records were normalized from 0 (ground surface) to 100 (relatively unaltered parent material (top of C

Horizon)) for comparison of interquartile range (b) and median depth to water table (c). The middle line in each box corresponds to the median of the data, the upper and lower bounds of the boxes are of the interquartile range (IQR), the whiskers are the first and third quartile plus or minus 1.5 times the IQR, and points are outliers beyond the range of the whiskers. The soil types shown are E podzols (E), Bhs podzols (Bhs), typical podzols (Typical), hillslope Bh podzols (HS-Bh), and near-stream Bh podzols (NS-Bh).

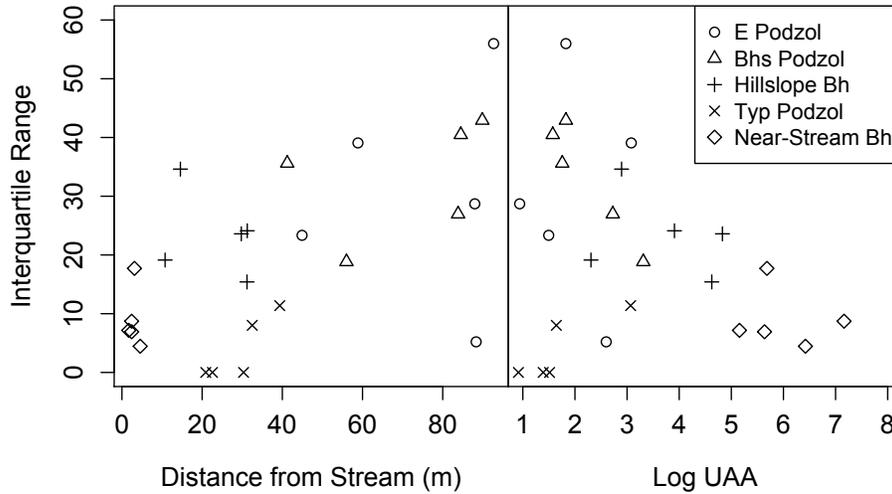


Figure 6. Interquartile range of water table fluctuations in each well plotted against the distance from stream and log upslope accumulated area (UAA). Different symbols indicate the soil unit of each well. With the exception of E and Bhs podzols, soil units separate in this space, illustrating that water table regime is in part related to topographic position.

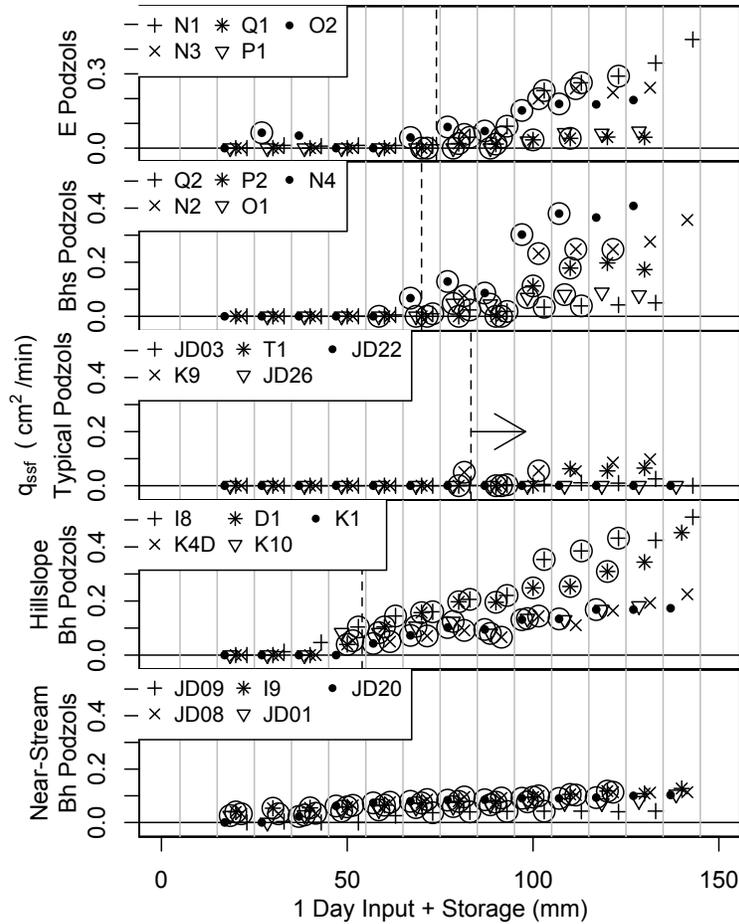


Figure 7. Threshold water table responses for wells in each soil unit. Mean specific discharge (q_{ssf}) is plotted on the y axis in cm^2/min and binned effective storage in mm is plotted on the x axis. Circled symbols denote a statistically significant difference from zero according to a Wilcoxon rank sum test (significance level 0.05). The dashed lines indicate the response threshold for each soil unit, defined as the mean threshold value for all wells in the group. The threshold value for each well was defined as the first storage bin where discharge significantly deviated from zero. The arrow in the typical podzol plot indicates that the mean response threshold for this group is higher than what is plotted because no statistically significant response was detected for two wells in the typical podzol group.

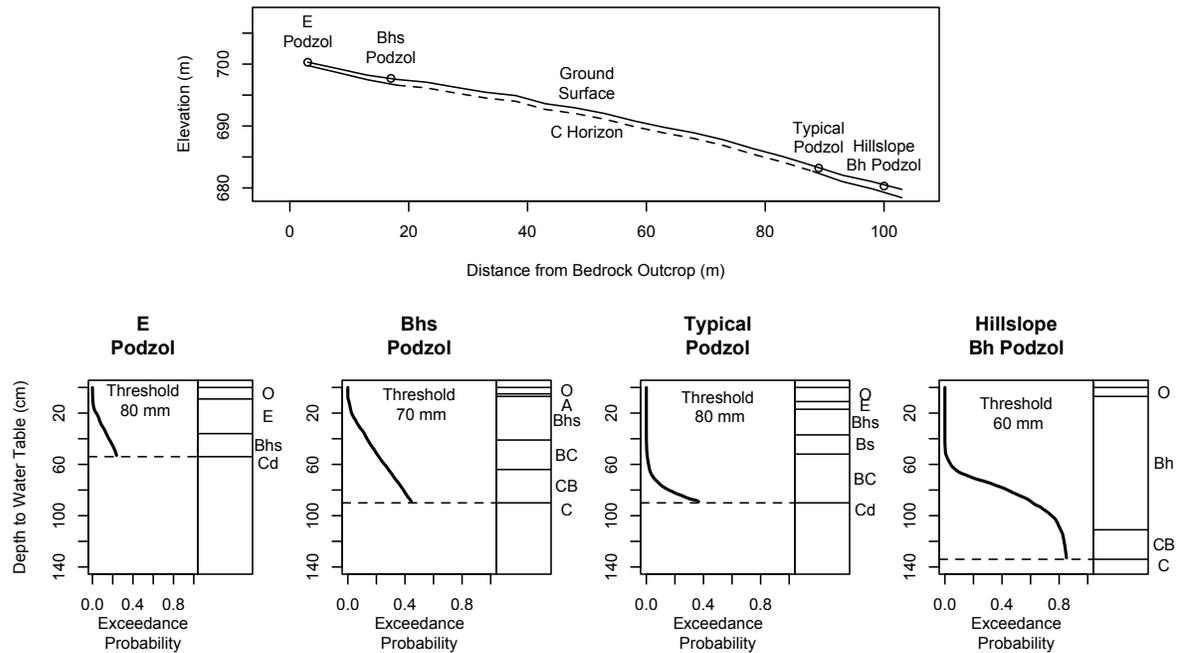


Figure 8. Transect 1 on Figure 1. A transect of wells in soil units along a hillslope beginning at a bedrock outcrop transect in WS3. The top figure shows the ground surface and C horizon as well as the location of the wells. The C horizon depth was interpolated and is dashed where the depth is relatively less certain. The bottom four figures are ECDFs for the wells in the transect with soil horizons shown to the right. The threshold catchment storage for the initiation of water table (corresponding to the beginning of the ECDF line on plot) are shown on each plot.

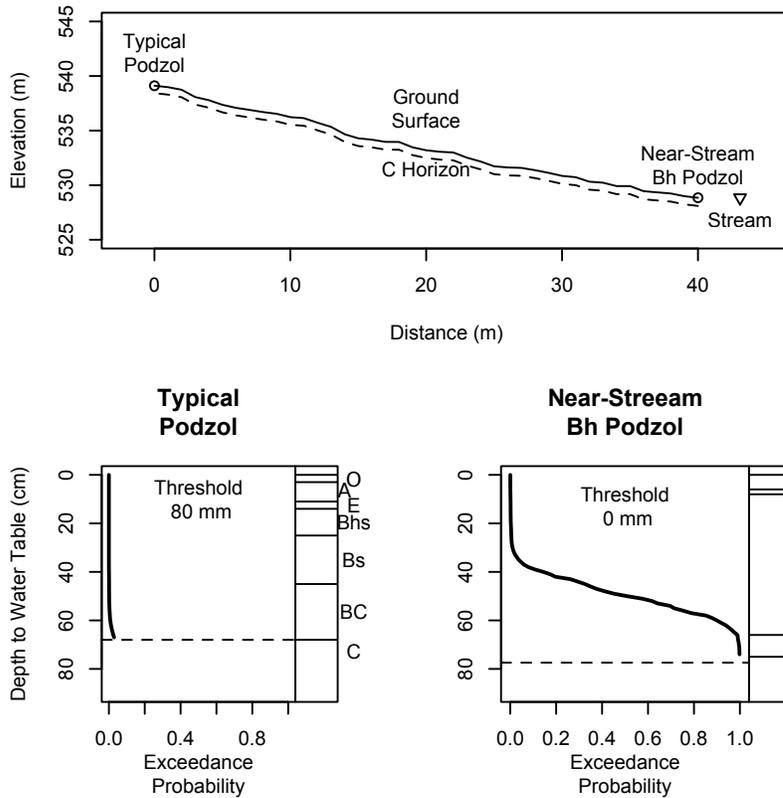


Figure 9. Transect 2 on Figure 1. A near-stream transect of wells in soil units along a hillslope transect in WS3. The top figure shows the ground surface and C horizon as well as the location of the wells. The C horizon depth was interpolated and is dashed where the depth is relatively less certain. The bottom four figures are ECDFs for the wells in the transect with soil horizons shown to the right. The threshold catchment storage for the initiation of water table (corresponding to the beginning of the ECDF line on plot) are shown on each plot.

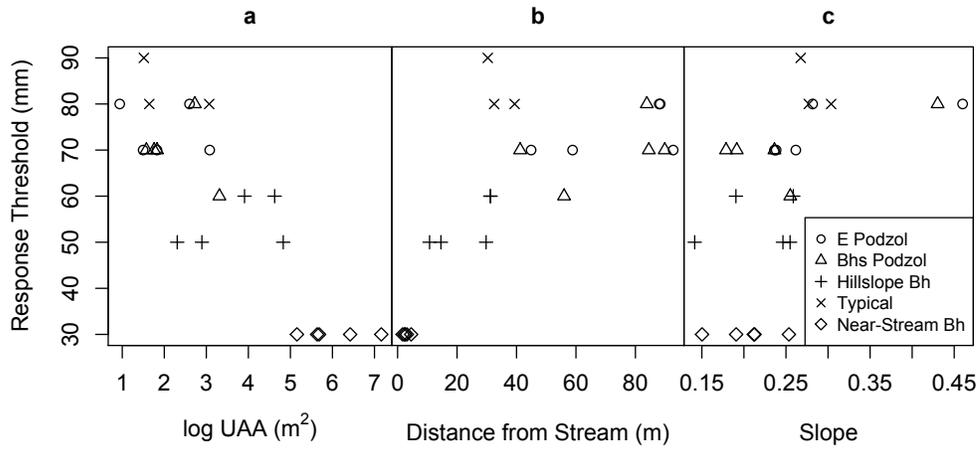


Figure 10. Water table response thresholds plotted against three topographic metrics for the each well. Panel a is log UAA (m²), panel b is distance from the nearest stream (m) and panel c is slope. Different symbols indicate the soil unit of each well.

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Chapter 3: Non-vertical water flux in the unsaturated zone: a mechanism for the formation of spatial soil heterogeneity in a headwater catchment.

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Abstract

Evidence suggests that morphologically distinct variations of podzols in a headwater catchment at the Hubbard Brook Experimental Forest in New Hampshire formed as a result of variations in saturated and unsaturated hydrologic fluxes in the landscape. While saturated flow regimes among these soils have been explained, they do not fully account for the observed variations in soil morphology. Variations in unsaturated fluxes have been hypothesized to explain variations in soil horizon thickness and presence/absence, but have not yet been investigated. We examined tensiometer and shallow groundwater well records to identify differences in unsaturated water fluxes among soils. The lack of unsaturated vertical hydraulic gradients at the study sites suggests that lateral unsaturated flow occurs in several of the soil units. We propose that the variations in soil horizon thickness and presence/absence observed at the site and others are due in part to lateral water flux in the unsaturated zone. This may have implications for the explanation of the distribution of elements on the landscape and, as a consequence, the spatial and temporal variation in water chemistry observed in headwater catchments.

1.0 Introduction

Variations in the thickness and presence/absence of soil horizons along topographic and wetness gradients have been described in a variety of landscapes. In some cases, changes along topographic gradients are consistent with the described soil catena in a location [Dessalegn *et al.*, 2014; Tetzlaff *et al.*, 2014; Vacca *et al.*, 2009]. However, in others the thickness and sequence of soil horizons vary at a smaller spatial scale than recognized landscape level variations [Bailey *et al.*, 2014; Jankowski, 2013; Sommer *et al.*, 2000]. In both cases, specific soils grouped by similar horizon thickness and presence/absence have been shown to be indicative of distinct hydrologic regimes [Gannon *et al.*, in review; Tetzlaff *et al.*, 2014] and biogeochemical processing [Bailey *et al.*, 2014; Laudon *et al.*, 2011; Morse *et al.*, 2014]. These soil groups have been called hydropedological units (HPUs) [Gannon *et al.*, in review; Tetzlaff *et al.*, 2014], a functional classification that defines soil groups relevant to runoff production, biogeochemical processing, and the structure of natural communities.

In some cases, the processes driving the formation of HPUs are not well understood. For instance, the HPUs identified in Bailey *et al.* [2014], like the variations in catenas observed in Sommer *et al.* [2001], and Jankowski [2013], are podzol variants. They are the result of the lateral translocation of amorphous organometallic complexes (AOCs) downslope, instead of only vertically in a profile, which is the usual assumption in pedology. The hydrologic processes that drive lateral podzolization are not well understood [Bailey *et al.*, 2014; Jankowski, 2013; Sommer *et al.*, 2000; Sommer *et al.*, 2001]. Hydropedological units have been shown to be indicative of distinct water table regimes, defined by threshold response to catchment storage, and frequency and magnitude of water table response [Gannon *et al.*, in review]. However, soil horizons described as evidence for lateral translocation occurred higher in the soil profiles than water table was observed. Furthermore, similar changes in soil horizonation have been observed where water table is unlikely ever present [Jankowski, 2013]. One potential explanation of the lateral translocation occurring in these soils is lateral (i.e., slope parallel) unsaturated flow, which has been detected in soils in the field [Jackson, 1992; Logsdon, 2007; Torres *et al.*, 1998] and laboratory [Cabral *et al.*, 1992]. Additionally,

lateral unsaturated flow is hypothesized to be responsible for the lateral translocation of spodic components detected in multiple landscapes [*Jankowski, 2013; McDaniel, 1992; Park and Burt, 2002; Sommer et al., 2000; Sommer et al., 2001*]. While it is unlikely that these downslope unsaturated water fluxes contribute much to stormflow [*Anderson and Burt, 1978*], they may be relevant to biogeochemical functions in the catchment if they are important to soil formation.

The purpose of this study was to examine differences in the direction of unsaturated fluxes in forest soils in a steep headwater catchment where lateral podzolization is expected to occur. At three sites representing characteristic transitions between HPUs, soils were described and tensiometers and water level recorders were installed. Using this hydrogeological framework, with detailed soil descriptions and measurements of saturated and unsaturated soil water dynamics, we were able to measure vertical hydraulic gradients and water table fluctuations. We found evidence that HPUs are indicative of specific fluctuations of lateral unsaturated flux that may be partially responsible for the formation of HPUs showing signs of lateral podzolization.

2.0 Site Description

This study took place in watershed 3 (WS3) at the Hubbard Brook Experimental Forest (HBEF) near North Woodstock, NH in the White Mountain National Forest. Watershed 3 is the hydrologic reference watershed for a number of paired watershed studies at HBEF [*Hornbeck, 1973; Hornbeck et al., 1970; Likens et al., 1970*] and has not been experimentally manipulated. HBEF has a humid continental climate. The site receives 1400 mm of precipitation annually, a quarter to a third of which falls as snow. Average temperatures are -9°C and 18°C in January and July, respectively [*Bailey et al., 2003*].

The bedrock in WS3 is the Silurian Rangeley Formation, a sillimanite-grade pelitic schist and calc-silicate granulite. The soil parent materials were deposited during the late Wisconsinan glacial period and are basal and ablation tills of varying thickness, composition, and hydraulic conductivity [*Bailey et al., 2014*]. The major soil type present has been characterized as a well-drained Haplorthod and is a podzol with a sandy loam

texture with 0.5 m average solum thickness [Likens, 2013]. WS3 is steep (20-30%), south-facing, and ranges in elevation from 527-732 m. The catchment is forested with mature, northern hardwood species, American beech (*Fagus grandifolia*), sugar maple (*Acer sacharum*), 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-to-bedrock soils [Likens, 2013].

Despite the previous catchment-wide characterization of soils in WS3 as well-drained Spodosols, Bailey *et al.* [2014] found distinct variations in morphology and a broad range of drainage classes. These variants were found to be indicative of distinct shallow groundwater regimes [Gannon *et al.*, in review] and zones of carbon accumulation [Bailey *et al.*, 2014] in the solum. The solum is defined as the soil from the surface to the base of the B horizon. It is the approximate rooting zone, has varying carbon accumulation depending on the type and thickness of B horizon, and has greater development of soil structure, lower bulk density, and is more weathered than the C horizon. Due to the functional implications of the distinct hydrologic regimes and carbon accumulation in the soil variants, they were classified as HPUs. In WS3, HPUs were named according to their dominant pedogenic horizon [Bailey *et al.*, 2014]. E, Bhs, and Bh podzols are therefore dominated by an E, Bhs, and Bh horizon, respectively. The exceptions to this naming convention are the typical podzol and bimodal podzol. The typical podzol morphology fits the classic concept of a Spodosol, with moderate expression of the B and E horizon. Finally, the bimodal podzol is characterized by an anomalous Bh horizon at the base of the solum in an otherwise typical Spodosol. The anomalous Bh horizon in the bimodal podzol and its location (always between a typical and Bh podzol) suggest it is a transitional soil type, occurring where the processes dominating the formation of typical and Bh podzols intersect.

Of the HPUs identified in WS3, E, Bhs, Bh, and bimodal podzols were hypothesized to be developed at least partly from lateral translocation of AOCs [Bourgault, 2014]. In E podzols, the E horizon is hypothesized to have formed by extensive leaching due to frequent lateral water flux. The Bhs horizon in Bhs podzols is hypothesized to be the

result of the immobilization of AOCs that have been leached from E podzols, which occur directly upslope. Likewise, the Bh horizons in bimodal podzols and Bh podzols are hypothesized to have formed from the immobilization of AOCs from source areas upslope. Typical podzols are hypothesized to be the result of primarily vertical fluxes.

3.0 Methods

3.1 Field methods

This study is based on three intensive instrumentation sites in WS3. Sites were chosen to represent characteristic transitions between soil morphological units in the catchment that we expected were the result of lateral fluxes of water in the solum. The transitions instrumented were E-Bhs podzol, typical-hillslope Bh podzol, and typical-bimodal podzol. At each of the three sites, several small reconnaissance pits were dug in order to locate characteristic HPU on either side of the transition. Once the characteristic soils were located, a pit was excavated to either 10 cm into the C horizon or to bedrock. Pits were characterized based on pedogenic horizons and assigned a podzol type based on horizon type and thickness [Bailey *et al.*, 2014].

After soil profile characterization, eight UMS T4e tensiometers (capable of measuring from -8.7 to 10.2 mH₂O) were installed at each site, with four tensiometers in each of the two pits. In the typical-bimodal and typical-hillslope Bh podzol pits tensiometers were installed into the upslope pit face, while in the E-Bhs podzol pits tensiometers were installed into the pit face orthogonal to the slope, due to a lack of space in the shallower soils. Tensiometers were connected to a Campbell Scientific, Inc. CR1000 datalogger and programmed to record at 10-minute intervals. Each T4e records and subtracts atmospheric pressure with a sensor that is kept above the ground surface.

At the E-Bhs and typical-Bh podzol transitions, wells were installed at each soil pit. Wells were installed 10 cm into the C horizon or on top of bedrock, depending on which was encountered first. Washed, native sand was packed around the well screen and the previously excavated soil was used to backfill the remainder of the pit. The installed wells were constructed of SDR 21 PVC pipe and had a 31 cm screen length with 0.025

cm wide lateral slots spaced 0.32 cm apart. Once installed, the wells were equipped with a 1.5 m Odyssey Water Level Logger, which used capacitance measured along a Teflon coated wire suspended in the well to determine water level. Water level loggers recorded data at 10-minute intervals.

At the bimodal-Bh transition wells were not installed in the soil pits because of proximity to an existing well between the two sites. However, it was found that groundwater regimes often varied greatly between closely spaced wells in different HPUs, necessitating the comparison of water table dynamics at the two pits, not just at the well between them. Therefore, for the two pits at the bimodal-Bh site, a water level time series was created using the positive head measurements from the deepest tensiometer at each site. These water table measurements exclude water table that occurs between that tensiometer and the C horizon, but that distance was small (20.1 cm in the typical podzol and 1.85 cm in the Bh podzol).

The data for this study were collected from 29 July 2011 to 1 April 2012. Data after 1 April 2012 were incomplete due to several equipment malfunctions and were therefore not included in the analysis. Four storms were selected for event-based analysis: a summer storm (8/26/2011), a fall storm (9/29/2011), a winter storm (12/26/2011), and a snowmelt event (3/7/2012). The storms were selected to span a range of antecedent conditions, precipitation intensities/magnitudes, and rainfall/snowmelt combinations. The tensiometer data were used to estimate vertical hydraulic gradients. Water table records were used to compute saturation frequency at different soil depths and to compare water levels to vertical hydraulic gradients.

3.2 Water table regimes

For the purpose of this analysis, water table was always measured as depth to water table within the solum, from the soil surface. Semi-permanent to permanent water tables likely existed deeper in the C horizon in WS3, but for the purposes of examining hydrologic regimes related to soil development, water tables in the C horizon were ignored.

To examine the frequency with which water table exceeded certain depths in each of the study soils, empirical cumulative density functions (ECDFs) were calculated for the data record for each well using R [R Development Core Team, 2013]. ECDFs were plotted along with soil horizon depths in order to examine the frequency of saturation of each horizon.

3.3 Vertical hydraulic gradient

In order to examine the strength and direction of saturated and unsaturated flow through time, vertical hydraulic gradient at each site was calculated as

$$i = - \frac{dh}{dz}$$

where h is hydraulic head at each tensiometer, calculated as the pressure head plus the elevation head relative to a survey benchmark used to determine the relative elevations of the tensiometers. z is the depth of the tensiometers. Positive vertical gradients denote an upward gradient while negative gradients denote a downward gradient.

3.4 Topography

Several topographic measures were calculated for each of the sites in this study to examine relationships with fluctuations of vertical gradients and/or changes in soil chemistry. Topographic measures were calculated from a 5-meter resolution, low-pass filtered, LiDAR derived digital elevation model (DEM). Gillin [2013] found that the DEM used for this analysis produced values for topographic measures most similar to field measurements. Distance from stream was calculated from a stream network mapped from observations of fluvial channel development and streamflow (Figure 1), and Euclidean distance was calculated from each point to the nearest channel. Slope was calculated using the maximum slope algorithm [Travis *et al.*, 1975] and upslope accumulated area (UAA) was calculated with the multiple flow direction algorithm presented in Seibert and McGlynn [2007]. Topographic wetness index (TWId) was calculated using the 5 m downslope index and UAA as described in [Hjerdt *et al.*, 2004]. Site distance was the distance between the two pedons at each of the focus sites and was measured in the field.

4.0 Results

4.1 Topography and Site Locations

Topographic metrics and distant to streams and bedrock outcrops were examined in order to determine their potential influence on hydrologic fluxes. Both the E and Bhs podzol were much closer to exposed bedrock than any other pit in this study, 5 m and 12 m respectively (Table 1), meaning a majority of their upslope accumulated area (UAA) was predominantly bedrock outcrop or shallow bedrock. They were also the farthest from a stream, at 81 m and 74 m, respectively (Table 1). The depth to the C horizon at the site increased downslope from N3 (65 cm) to N4 (80 cm). Slope at the site was 0.24 and the pits were 7 m apart.

The typical-Bh podzol site was much farther from exposed bedrock at 74 and 83 m, and while closer to the stream network at 36 and 31 m, the site was still out of the influence of the riparian zone. Upslope accumulated area increases from 22 m² at K9 to 102 m² at K10, slope decreased from 0.28 to 0.25, and the pits were 7.8 m apart (Table 1).

The bimodal-Bh podzol site was also far from bedrock at 149 and 146 m and closest to the stream network at 36 m and 31 m. The UAA increased downslope from 4.3 m² to 7.6 m², and the slope decreased from 0.33 to 0.29 (Table 1). The two pits at this site were also the closest to one another at 3 m.

4.2 Water table regimes

The ECDFs in Figure 1 were used to examine the frequency with which soil horizons *Bailey et al.* [2014] hypothesized were indicative of lateral translocation were saturated. None of these horizons experienced full saturation during the study period. Water tables were detected within the horizons *Bailey et al.* [2014] hypothesized to be laterally developed to some degree in all wells: 32% of the time in the E podzol, 65% in the Bhs podzol, 73% and 34 % in the two Bh podzols (K10 and H6, respectively), and 10% in the bimodal podzol (Figure 1). However, water table was not detected at the top of any of

these horizons, with the exception of the thin Bh horizon at the bottom of the bimodal podzol. Furthermore, water tables were detected close to the top of the analogous horizons in the E, Bhs, and one of the Bh podzols (H6). However, in the second Bh podzol (K10), water table was not observed during the study period in the top 33 cm of this horizon (Bh horizon, Figure 1).

The typical podzol, a soil developed under unsaturated vertical flow, had the least frequent water table and was dry 60% of the time. The highest recorded water table in the typical podzol was 40 cm from the surface (Figure 1).

4.3 Vertical Gradients

Figure 2 shows the vertical gradient for each site over the entire study period. The E-Bhs transition sites, N3 and N4, had the lowest magnitude vertical gradients, with a median gradient of approximately -0.1 (Figure 2). These two podzols also had gradient values closest to 0. The typical and bimodal podzols had the strongest negative gradients and the whiskers of neither boxplot extend above 0, meaning either 0 gradient or upward gradients were very rare (Figure 2). The Bh podzols in general had less negative gradients, especially in comparison with their upslope pair. H6, a Bh podzol 3 meters downslope of the bimodal podzol H5, had a median vertical gradient around 0.3 and had the widest range of values, with an upper whisker well above 0 and a lower whisker below -0.7 (Figure 2). In contrast, K10 had the most positive (upward) vertical gradient of any of the podzols, with an interquartile range that fell entirely above 0 (Figure 2).

Vertical gradients were also observed on an event basis. This was done to examine the consistency of saturated and unsaturated responses, to characterize the vertical fluxes during events, and to examine the interplay between water table formation above the C horizon and vertical fluxes. Four events were chosen to span the study timeseries and represent a variety of conditions. Events include a summer storm (8/26/2011), a fall storm (9/29/2011), a winter storm (12/26/2011), and snowmelt (3/7/2012) (Figures 3, 4, and 5).

With the exception of the dry period before snowmelt, all three HPUs hypothesized by *Bailey et al.* [2014] to be indicative of lateral translocation had gradients closest to zero. The E and Bhs podzols had fairly consistent gradients just under zero (Figure 3 E-H, M-P), and the two Bh podzols had gradients just below or alternating between under and over zero (in the case of K10; Figure 4 M-P). The bimodal and typical podzols both had stronger downward vertical gradients, approximately -0.5.

In all HPUs but the E podzol, vertical gradients were observed during precipitation or snowmelt events (Figure 3 E-H). At the Bh, typical, and bimodal podzols, the stronger vertical gradient occurred before the water table increase that was associated with the event (Figure 4, 5). However, in the Bhs podzol the downward gradient became stronger concurrently with water table rise at the site (Figure 3M-P).

5.0 Discussion

5.1 Evidence of unsaturated lateral flow

Unsaturated lateral flow has been hypothesized to occur on hillslopes as a result of anisotropy [*Cabral et al.*, 1992; *McCord et al.*, 1991; *Zaslavsky and Rogowski*, 1969], preferential flow pathways [*Beven and Germann*, 1982; *Bonell*, 1993; *Mosley*, 1979], or from the short term hydrologic effects of decreasing rainfall intensity on steep slopes at the end of a storm [*Jackson*, 1992; *Sinai and Dirksen*, 2006]. As presented by *Weyman* [1973], on a hillslope where unsaturated lateral flow was dominant, equipotential contours would be oriented perpendicular to the ground surface. In this scenario, if one were to measure total potential at two depths at the same slope position, there would be a hydraulic gradient of zero. If measuring total potential from tensiometers installed into a vertical pit face, a hydraulic gradient of zero would indicate a lateral and slightly upward flow direction. Therefore, we considered times when vertical hydraulic gradients were close or equal to zero and the upper tensiometer position was not saturated to be indicative of lateral unsaturated flow downslope through the soil matrix. In other words, these periods suggest that vertical unsaturated flow is less likely. Following this reasoning, the near-zero vertical hydraulic gradients measured in our study (section 4.2) are indicative of periods of lateral unsaturated flow. Therefore, lateral unsaturated flow

frequently occurred in the E-Bhs podzol pair (Figure 2 and 3), the Bh podzol in the typical-Bh pair (Figure 2 and 4) and the Bh podzol in the bimodal-Bh pair (Figure 2 and 5). A conceptual model of lateral unsaturated flow in HPUs on a hillslope is presented in Figure 6.

Other observations from this study are also potentially indicative of unsaturated lateral fluxes in the soil matrix. Soil horizons that are indicative of lateral flow regimes, such as unusually thick E, Bhs, [Bailey *et al.*, 2014; Sommer *et al.*, 2000], and Bh horizons [Bailey *et al.*, 2014; Jankowski, 2013], occur above the extent of water table most of the time at these sites (Figure 1). While infrequent events larger than those observed in this study may saturate these horizons, the lack of frequent lateral saturated fluxes suggests saturated flow regimes are not the only driving force in the formation of these horizons.

Furthermore, in a companion study by Bourgault [2014], scanning electron microscope (SEM) images of soil thin sections and soil extract chemistry were examined for evidence of vertical and lateral translocation within and between HPUs. Soil thin sections revealed that vertically developed horizons had a crumb-like morphology, with AOCs forming pellet-like masses, resulting in higher pore space and higher AOC to mineral ratios. Laterally developed horizons, however, had microstructure that was less defined and more in-filled, with less pore space and lower AOC to mineral ratios. Laterally developed horizons were also found to have lower iron and carbon concentrations but higher concentrations of the more mobile aluminum and manganese than the vertically developed horizons. Bourgault [2014] hypothesized that in the E-Bhs podzol transition, these differences are caused by dissolved organic carbon (DOC) in water solution moving elements downslope in solution. In the typical-bimodal-Bh podzols transition, however, they proposed that either solutional transport or the physical movement of colloidal AOCs was responsible for the changes in soil chemistry and micro-scale morphology. This evidence of lateral translocation provides further support for the occurrence of lateral unsaturated flow, especially in horizons where water table was not detected.

It is important to recognize the possibility that morphological differences in soils that correlate well with our unsaturated lateral flow hypotheses do not necessarily confirm lateral soil development is currently taking place. It is possible that the soil morphological patterns we observed are relicts of previous conditions where differences in hydrologic flow regime and/or other factors such as vegetation differences may have led to their development. Despite this possibility, even the correlation of current flow regimes and dominant flux directions with HPUs may prove useful to examining runoff generation processes and patterns in spatial and temporal stream chemistry.

5.2 Implications of unsaturated lateral flow: Soil development

Unsaturated lateral flow provides a mechanism for the variations in soil formation observed in WS3. *Sommer et al.* [2000] identified similar patterns in soil formation, where podzol formation occurs laterally along a hillslope instead of vertically, calling it lateral podzolization. The proposed mechanism for this was mobilization of spodic material by unsaturated water flux, and subsequent downslope immobilization [*Sommer et al.*, 2000]. However, *Sommer et al.* [2000] did not measure this lateral movement of water in the unsaturated zone. *Bailey et al.* [2014] identified the same patterns in WS3 and identified differences in water table regime that were consistent with some HPUs experiencing greater and more frequent water flux. These differences were also found to be consistent among podzols in *Gannon et al.* [in review]. However, as shown in Figure 1, water tables did not occur high enough in soil profiles during this study to explain all observed variations. Observations of unsaturated lateral flow provide a way to link the hypotheses of *Sommer et al.* [2000] with the observations of *Bailey et al.* [2014] and *Bourgault* [2014] to describe the process by which AOCs may be mobilized throughout the profile and translocated downslope.

In the E-Bhs podzol pair, lateral unsaturated fluxes may be responsible for mobilizing AOCs from the O horizon and upslope of the E podzol in bedrock areas overlain by thin organic horizons in solution as DOC and translocating it downslope to the Bhs podzol. Amorphous organometallic complexes (AOCs) may then be immobilized in the Bhs podzol as the intensity of water flux drops due to the increasing thickness of the solum

and C horizon (Figure 1). In the bimodal-Bh and typical-Bh podzol pair, lateral unsaturated flow from water draining from upslope typical or bimodal podzols may translocate soluble or solid phase AOCs to Bh podzols (Figure 1, Table 1).

As mentioned in section 5.1, it is possible that the current water table regime in WS3 is different from that which formed the HPUs. A previous climate in which higher, more frequent water tables dominated may offer one alternative explanation. However, similar downslope translocation of AOCs was observed by *Jankowski* [2013] in a sand dune landscape where water table was even less likely to have played a role, providing further evidence that these processes can occur in the absence of saturation. Therefore, if these soil-forming processes can occur without the presence of water table, it is possible that they are occurring above the periodic water tables we observed in the current hydrologic regimes of HPUs in WS3.

5.3 Implications of unsaturated lateral flow: stream water chemistry

Unsaturated lateral flow is not identified as contributing to stormflow generation due to the much lower hydraulic conductivities of soils during unsaturated conditions [*Anderson and Burt*, 1978]. While these flow rates may be unimportant to water transport to the stream network, they may be critical in explaining the spatial distribution of stream water chemistry. *Bishop et al.* [2004] described how solutes can be quickly mobilized to the stream network by water tables rising into the unsaturated zone, mobilizing the water and solutes therein. If unsaturated lateral flows are translocating AOCs downslope to zones of accumulation, they may be translocating material to regions that become source areas with the addition of water from event-timescale water table rise. Furthermore, if lateral translocation moves solutes downslope to pedons or horizons that infrequently experience water table, it may be an important mechanism for the storage of elements in the landscape.

These soil-forming processes may offer an explanation for the patterns in stream water chemistry observed in *Zimmer et al.* [2013]. Unsaturated fluxes may contribute to the translocation of AOCs into zones of accumulation: Bhs and Bh podzols. Once catchment

storage exceeds the threshold necessary to create water table in these podzols, the areas close enough to stream channels or in connection with streams through preferential flowpaths in the C horizon will contribute to streamflow while mobilizing unsaturated zone solutes. The contribution of HPUs that are zones of accumulation could then aid in explaining the varying longitudinal patterns in stream water chemistry in WS3 and sites where such gradients in soils are present.

6.0 Conclusions

In this study, we examined pressure head records for three sites containing five different hydropedological units (HPUs) in watershed 3 at the Hubbard Brook Experimental Forest. We detected both persistent and event-based unsaturated lateral flow in four of five HPUs. We propose that these unsaturated lateral flows are at least partially responsible for soil development above the highest detected water tables in these HPUs, potentially in conjunction with infrequent high water tables. Furthermore, we propose that these unsaturated lateral flows may be responsible for concentrating elements in HPUs that act as zones of accumulation. Saturation of these zones may create hotspots that deliver water with unique chemistry to the stream, whereas lack of saturation of these zones may result in long-term storage of elements in some HPUs.

Figures and Tables

Table 1. Topographic metrics for each of the profiles at the focus sites. Pairs of sites are alternately shaded and unshaded. UAA is upslope accumulated area, TWId is downslope topographic wetness index, and HPU stands for hydrogeological unit.

Site	ID	HPU	Dist between pits (m)	UAA (m ²)	Slope (-)	TWId ln(m ²)	Dist to Stream (m)	Dist to Bedrock (m)
E-Bhs	N3	E	7.1	6.2	0.24	6.7	80.8	5.0
	N4	Bhs	7.1	20.2	0.24	7.9	73.9	12.1
Bimodal-Bh	H5	Bimodal	2.9	4.3	0.33	5.8	15.0	149.2
	H6	Bh	2.9	7.6	0.29	6.5	10.0	146.0
Typical-Bh	K09	Typical	7.8	21.5	0.28	7.6	36.1	74.3
	K10	Bh	7.8	102.0	0.25	9.2	31.6	83.8

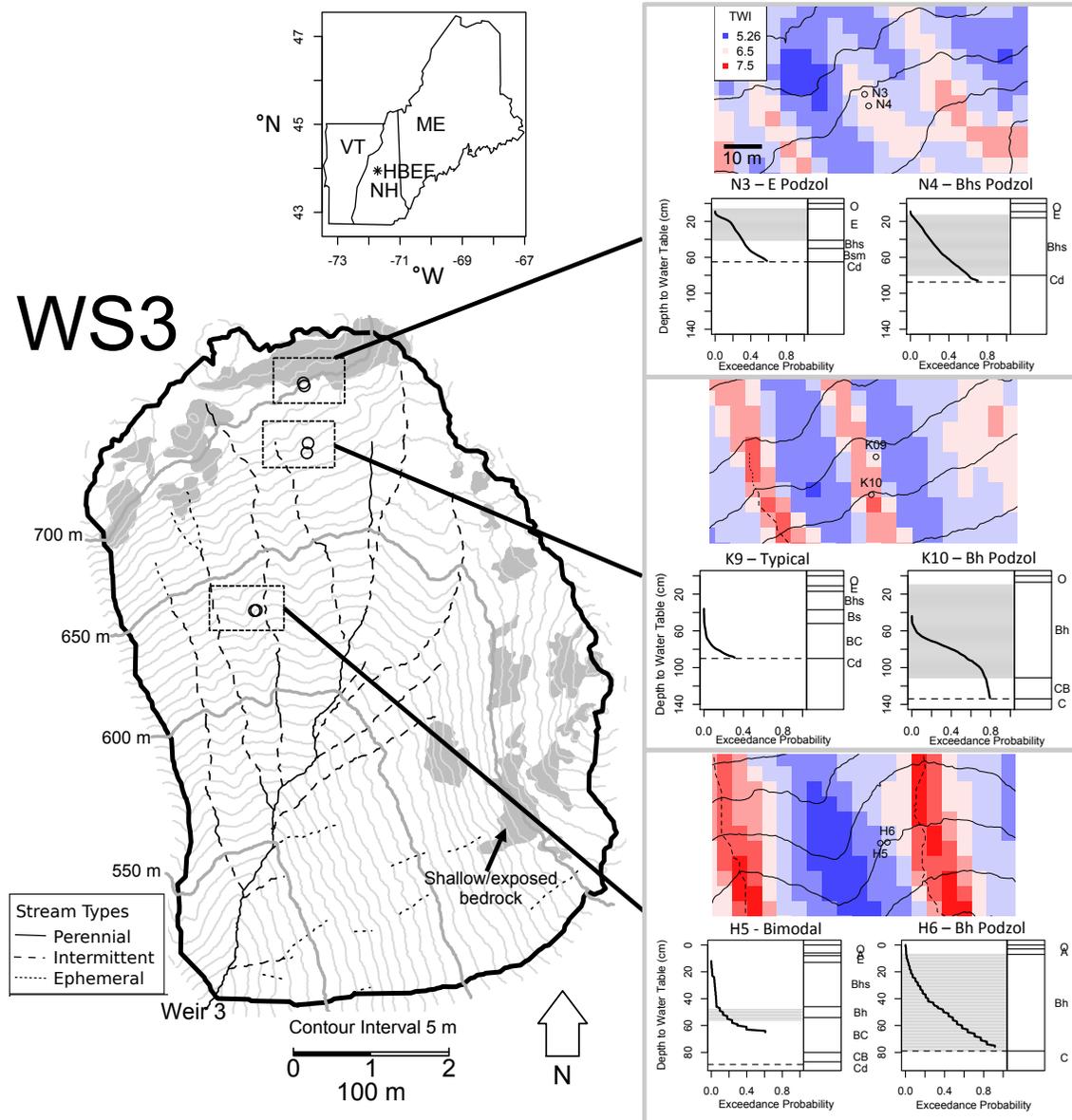


Figure 1. Map of Watershed 3 (WS3), maps of study sites, study well empirical cumulative density functions (ECDFs), and soil horizons at study sites. An inset map of the location of Hubbard Brook Experimental Forest in northern New England is also included. In WS3 perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. Areas with bedrock outcrops or shallow to bedrock areas are indicated by shaded grey areas. Study sites are indicated by circles on the map. Each of the study areas is shown in detail to the right of the WS3 map. The detailed maps include 5 m contour intervals and topographic wetness index (TWI). Below each of the detailed maps are ECDFs for the water level measurements at each site showing the

exceedance probability of water levels at the site. The grey shaded portion of the ECDF corresponds with the horizon hypothesized by *Bailey et al.* [2014] to be indicative of lateral translocation. Attached to the right of each of the ECDFs is the soil horization at the corresponding site.

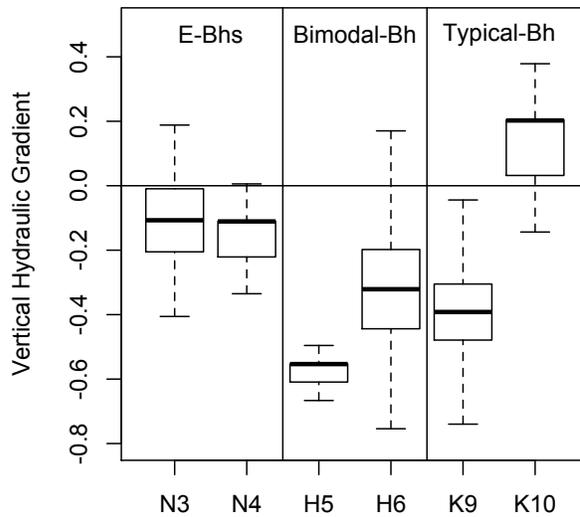


Figure 2. Boxplots of vertical hydraulic gradient measurements from the duration of the study period (29 July 2011 to 1 April 2012). Negative gradients are downward and positive gradients are upward. Each boxplot is the data from one pit (named on the x axis) and the grouped boxes are the three study sites. 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 quartile plus or minus 1.5 times the IQR, and points are outliers beyond the range of the whiskers. Vertical lines divide study sites, which are labeled at the top of the plot.

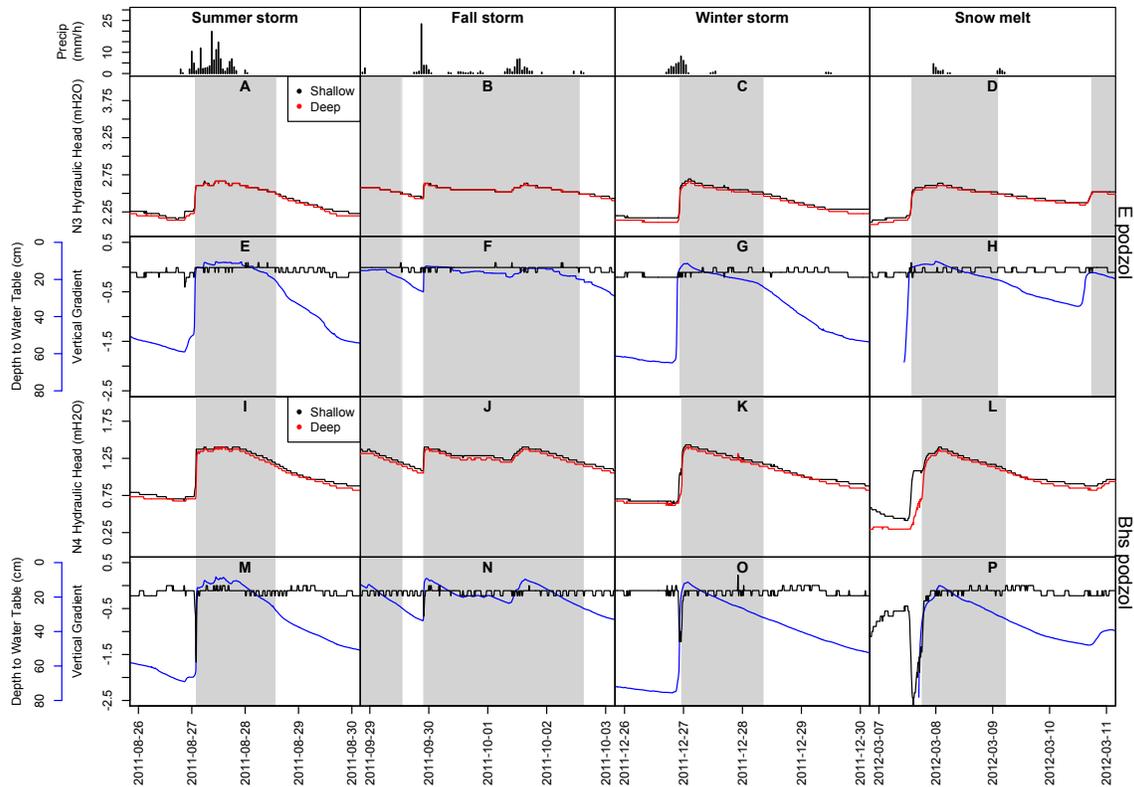


Figure 3. Precipitation, total head from tensiometers, vertical hydraulic gradient from tensiometers, and depth to water table are shown for the E (N3) – Bhs (N4) transition site for 4 events: a summer storm (8/26/2011), a fall storm (9/29/2011), a winter storm (12/26/2011) and snow melt (3/7/2012). The shaded times indicate that the upper tensiometer recorded saturation. In plots showing hydraulic gradient (A-D and I-L) the shallow and deep tensiometer records are colored black and red, respectively. In the plots showing water table and hydraulic gradient (E-H and M-P) the blue line is water table and the black line is vertical gradient.

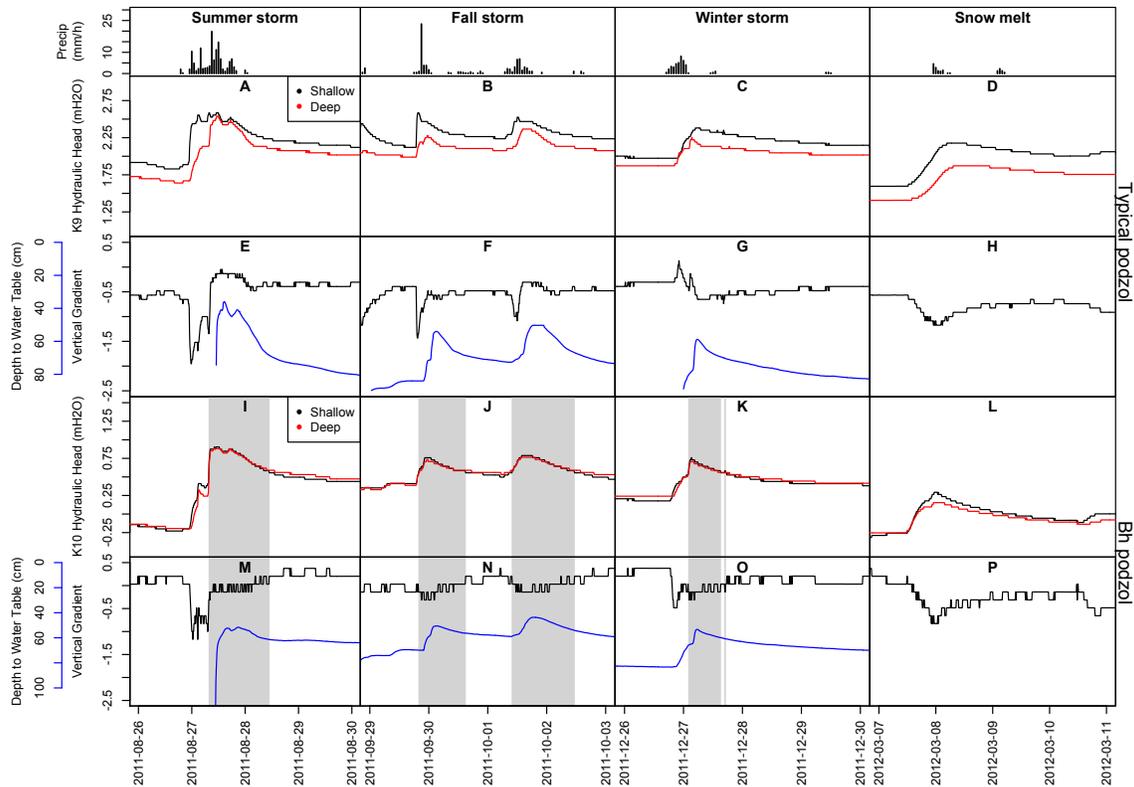


Figure 4. Precipitation, total head from tensiometers, vertical hydraulic gradient from tensiometers, and depth to water table are shown for the Typical (K9) to Bh (K10) transition site for 4 events: a summer storm (8/26/2011), a fall storm (9/29/2011), a winter storm (12/26/2011) and snow melt (3/7/2012). The shaded times indicate that the upper tensiometer recorded saturation. In plots showing hydraulic gradient (A-D and I-L) the shallow and deep tensiometer records are colored black and red, respectively. In the plots showing water table and hydraulic gradient (E-H and M-P) the blue line is water table and the black line is vertical gradient.

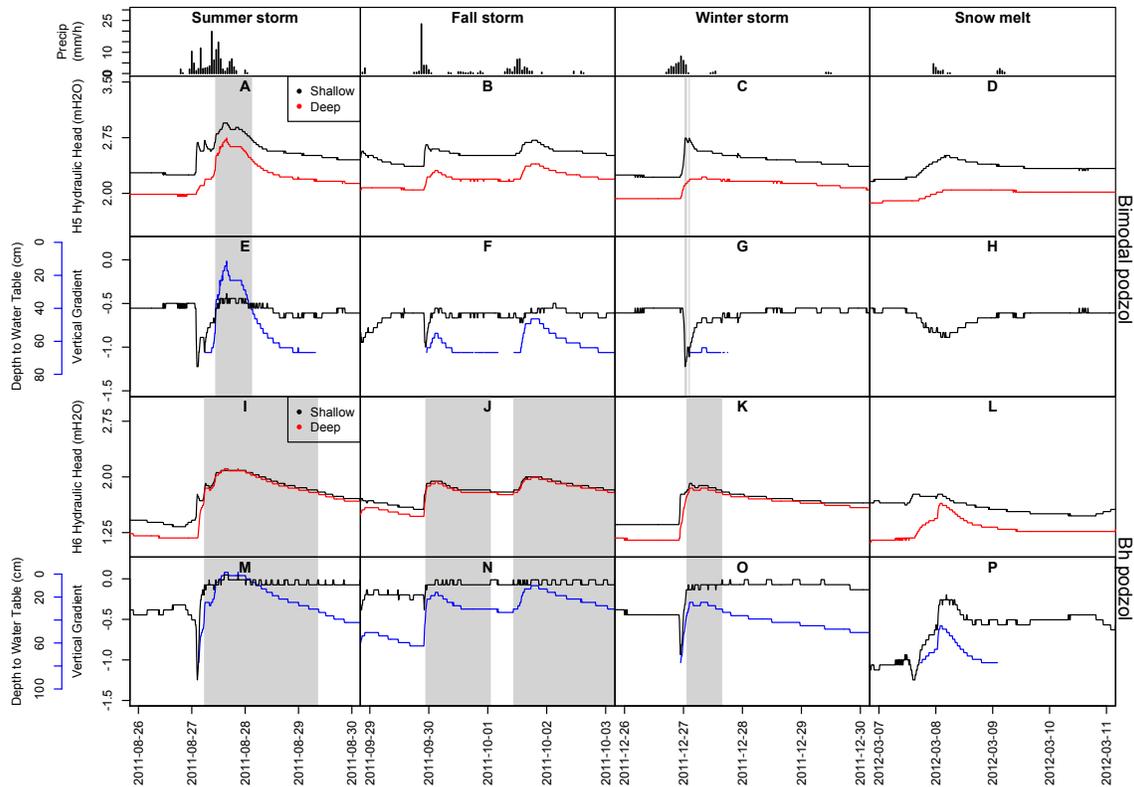


Figure 5. Precipitation, total head from tensiometers, vertical hydraulic gradient from tensiometers, and depth to water table (calculated from positive pressure head at tensiometers at this site) are shown for the Bimodal (H5) to Bh (H6) transition site for 4 events: a summer storm (8/26/2011), a fall storm (9/29/2011), a winter storm (12/26/2011) and snow melt (3/7/2012). The shaded times indicate that the upper tensiometer recorded saturation. In plots showing hydraulic gradient (A-D and I-L) the shallow and deep tensiometer records are colored black and red, respectively. In the plots showing water table and hydraulic gradient (E-H and M-P) the blue line is water table and the black line is vertical gradient.

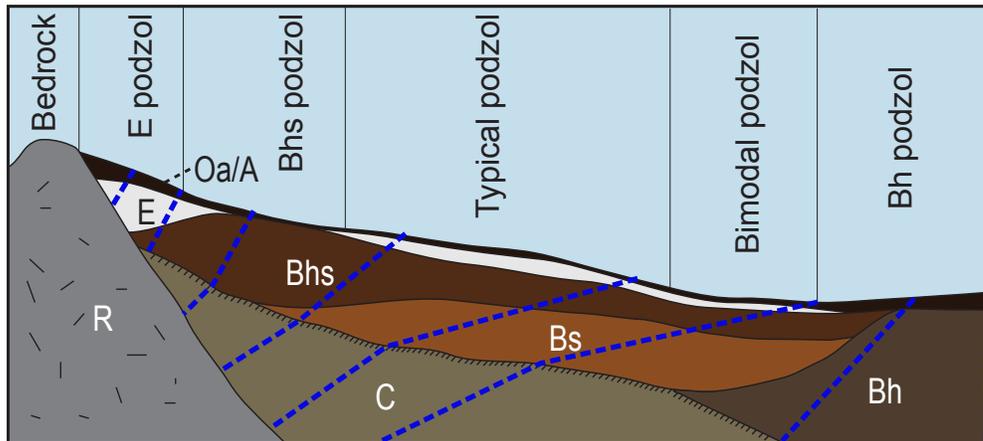


Figure 6. Soil schematic conceptual diagram from *Bailey et al.* [2014] showing soil horization along a typical HPU sequence in WS3. Theoretical unsaturated flow equipotential lines are shown by blue, dashed lines. Moving down the slope the lines of equipotential move from a condition with entirely lateral flow in the E and Bhs podzols to a primarily vertical flow in the typical podzol and then back to entirely lateral flow in the Bh podzol.

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Chapter 4: DOC sources in upland soils in a headwater catchment.

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Abstract

In order to investigate potential source areas to help explain patterns of dissolved organic carbon (DOC) in streamwater in watershed 3 (WS3) at the Hubbard Brook Experimental Forest (HBEF), we examined shallow groundwater level records, in-situ fluorescent dissolved organic matter (FDOM) concentrations at the catchment outlet, and DOC concentrations in soil water, groundwater, and streamwater sampled throughout the catchment. While near-stream soils are generally considered a DOC source in forested catchments, we found DOC concentrations in near-stream groundwater were no higher than other hillslope wells and water tables in near-stream soils did not rise into the shallow B or O horizons even during events. In contrast, DOC concentrations in groundwater in shallow upland soils derived from runoff from bedrock outcrops covered by leaf litter and shallow organic matter had elevated DOC concentrations (5-15 mg/L). Streamwater samples in channel heads sourced in part by these soils had the highest DOC concentrations in the catchment. Finally, FDOM fluctuations at the catchment outlet followed groundwater fluctuations in these shallow upland soils. We show that shallow upland soils receiving runoff from organic matter-covered bedrock outcrops and hydrologically connected to the stream may be source for DOC in WS3. The patterns of groundwater and streamwater chemistry observed in this study may aid in describing event-scale as well as long-term patterns in DOC export from headwater catchments.

1.0 Introduction

One of the ways carbon is moved through the landscape in headwater catchments is as dissolved organic carbon (DOC) in soil water, groundwater, and streamwater. In addition to the role of DOC as a component of carbon export from ecosystems, DOC in surface water is ecologically important [Laudon *et al.*, 2005], is a key component to nutrient cycling [Brookshire *et al.*, 2005; Neff *et al.*, 2003; Perakis and Hedin, 2002] and facilitates the transport of metals in the environment [Driscoll *et al.*, 1994; Shafer *et al.*, 1997]. Understanding how DOC moves through the landscape is therefore important for understanding carbon fluxes/export and ecosystem and biogeochemical processes in catchments [Roulet and Moore, 2006]. Additionally, trends of increasing DOC export have been observed in catchments around the world and are poorly understood [Evans *et al.*, 2006; Hudson *et al.*, 2003; Oni *et al.*, 2013]. A better understanding of DOC source areas in headwater catchments may help explain variations in catchment carbon output as well as the spatial distribution of carbon in headwater catchments.

The primary source for DOC in streamwater in catchments without wetlands has been identified as near-stream areas [Bishop *et al.*, 2004; Laudon *et al.*, 2011; Palmer *et al.*, 2005]. Using observations from water levels and soil water DOC concentrations, several authors have suggested that high near-stream water tables mobilize DOC from shallow organic soil horizons, thereby delivering water with elevated DOC concentrations to streams [Boyer *et al.*, 1997; Easthouse *et al.*, 1992; Inamdar *et al.*, 2004; Winterdahl *et al.*, 2011]. Upland soils have also been identified as DOC sources in cases where water tables extend into their organic horizons, albeit to a lesser extent than more frequently saturated near-stream soils [Ågren *et al.*, 2014; McGlynn and McDonnell, 2003; Terajima and Moriizumi, 2013].

The delivery of DOC from near-stream soils 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. In this scenario, it is reasonable that hillslope groundwater with low DOC would acquire

DOC as it passes through the shallow soil horizons in the near-stream zone, where soil organic matter content is high [Laudon *et al.*, 2011]. However, several studies have identified frequent water table occurrence in areas outside the near-stream zone that were not simply continuations of a saturated area extending up a hillslope [Dhakal and Sullivan, 2014; Gannon *et al.*, in review; Penna *et al.*, 2014]. In cases where the spatial extent of these water tables intersects a stream, they may be actively contributing to streamflow. These observations suggest that if frequent water table fluctuations in areas outside the near-stream zone intersect organic horizons, they could be sources of DOC to streamwater.

Furthermore, it has been shown that near-stream soils are not always DOC sources. Grabs *et al.* [2012] observed near-stream groundwater levels and soil water chemistry at the Krycklan catchment in Sweden and found that in some near-stream soils where water tables did not rise close to the surface, total organic carbon (TOC) in soil water did not increase during events. These soils were therefore found to not be sources of TOC to the stream. Additionally, in a study of network spatial patterns in streamwater chemistry at the Hubbard Brook Experimental Forest (HBEF), DOC concentrations decreased moving downstream and zones of higher concentrations occurred in patches along the stream network [McGuire *et al.*, 2014; Zimmer *et al.*, 2013]. The observation of decreasing DOC concentrations downstream has been made at other sites [Laudon *et al.*, 2011; Temnerud and Bishop, 2005], and is not consistent with a uniform near-stream DOC source. Zimmer *et al.* [2013] also found DOC concentrations in groundwater were no higher in near-stream soils than any other hillslope soil. In fact, the highest DOC concentrations observed in groundwater were from shallow soils near channel heads [Zimmer *et al.*, 2013].

Several authors have identified the importance of understanding the spatial distribution and hydrologic connectivity of DOC sources in order to understand DOC output from headwater catchments [Ågren *et al.*, 2014; Laudon *et al.*, 2011; McGlynn and McDonnell, 2003]. Previously observed DOC patterns in groundwater and the stream network in WS3 [McGuire *et al.*, 2014; Zimmer *et al.*, 2013] suggest that developing a conceptual model

of DOC generation at this site may be useful in providing further insights into DOC source areas in headwater catchments in general. Therefore, we investigated spatial patterns observed in streamwater DOC in WS3 at HBEF using shallow groundwater fluctuations, the spatial distribution of soils in the catchment as modeled by *Gillin et al.* [in review], DOC in groundwater and soil water, and in-stream fluorescent dissolved organic matter (FDOM) [*Pellerin et al.*, 2012] records at the catchment outlet. To do this we characterized DOC concentrations in soil and groundwater in different soils in the catchment. We then mapped the probable spatial extent of water table in these soils throughout the catchment along with DOC concentrations throughout the stream network from *Zimmer et al.* [2013]. Finally, we compared FDOM fluctuations at the outlet of WS3 to water level fluctuations in different soils in the catchment. Through this combination of analyses at varying spatial and temporal scales, we addressed the following two primary research questions:

1. What source areas in the catchment drive patterns of DOC concentrations observed in the WS3 stream network?
2. Can the patterns in DOC concentrations in the WS3 stream network help explain DOC concentrations at the catchment outlet?

2.0 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), which acted as the hydrologic reference watershed for several paired watershed studies [*Hornbeck*, 1973; *Hornbeck et al.*, 1970; *Likens et al.*, 1970] and thus has not been experimentally manipulated. HBEF has a humid continental climate, with average temperatures of -9°C and 18°C in January and July, respectively [*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 a Silurian sillimanite-grade pelitic schist and calc-silicate granulite called the Rangeley formation. The soil parent materials are basal and ablation

tills of varying thickness, composition, and hydraulic conductivity and were deposited during the late Wisconsinan glacial period [Bailey *et al.*, 2014]. The range of slopes in WS3 is about 20-30%, it is south facing, and ranges in elevation from 527-732 m. The catchment is forested with mature 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].

While soils in the WS3 have been broadly characterized as podzols, Bailey *et al.* [2014] found distinct variations in the characteristic morphology and a broader range of drainage classes. These variants were found to be indicative of distinct zones of carbon accumulation [Bailey *et al.*, 2014] and shallow groundwater regimes [Gannon *et al.*, in review] in the solum. The solum is defined as the more weathered soil from the surface to the base of the B horizon. It is the approximate rooting zone and with respect to the parent material it is a zone with greater development of soil structure, lower bulk density, and varying carbon accumulation depending on the type and thickness of B horizon. These soil variants were classified as hydropedological units (HPUs) [Gannon *et al.*, in review] due to the functional implications of the distinct hydrologic regimes and zones of carbon accumulation. Each HPU was named after the dominant pedogenic horizon in the profile [Bailey *et al.*, 2014]. Therefore, E, Bhs, and Bh podzols are dominated by an E, Bhs, and Bh horizon, respectively. The bimodal and typical podzols are the exceptions to this naming convention. The horizonation in typical podzols is like that of the classic concept of a Spodosol, with moderate expression of the B and E horizon. Bimodal podzols are characterized by an anomalous Bh horizon at the base of the solum. Bimodal podzols were always found in small transitional zones between typical and Bh podzols. Because these soils were not always present as a transition between typical and Bh podzols, occurred over a range of topographic variables, and have a small spatial footprint, they were not included in the predictive soil model from Gillin *et al.* [in review] or water table characterizations in Gannon *et al.* [in review], and were therefore excluded from this analysis as well.

3.0 Methods

3.1 Well Records and Samples

Water table data for this study is from a spatially distributed shallow groundwater well network throughout WS3. The well network was designed to monitor water table dynamics across different HPUs throughout the catchment, and was established by three different studies. *Detty and McGuire* [2010a; b] installed 28 wells, seven of which were used for this study. These wells had soil morphology characterized in adjacent soil pits by *Bailey et al.* [2014]. In order to have three wells in each HPU identified in WS3, an additional seven wells with detailed soil characterization were installed by *Bailey et al.* [2014]. Finally, 11 more wells were installed and soils were characterized by *Gannon et al.* [in review], to bring the total number of wells in each HPU considered in this study to five (25 total wells).

Wells were either installed with a 10 cm hand auger or in a backfilled soil pit and were constructed of (standard dimension ratio) SDR 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. In order to get the base of the well screen into the C horizon, the auger was used to bore 10 cm beyond the solum. In cases where a C horizon was not present, wells were installed on top of bedrock. Augered holes were backfilled 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-minute intervals.

Water table was measured as height of water table within the solum relative to the C horizon for the purpose of this analysis. Semi-permanent to permanent water tables likely exist deeper in the C horizon in WS3, but for the purposes of examining hydrologic regimes related to DOC movement these were ignored.

Several wells and Prenart soil suction lysimeters 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 2-3 sites for each HPU. They were all installed adjacent to the characterized pit. Lysimeters were installed near the top and bottom of the dominant pedogenic horizon in Bhs (3 sites, 5 lysimeters total) and hillslope Bh podzols (3 sites, 8 lysimeters total) and near the top and bottom of the B horizon in typical podzols (3 sites, 4 lysimeters total). Due to the thin solum of E podzols only one lysimeter was installed in the middle of the E horizon (2 sites, 2 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 hours or 12 hours if predicted nighttime temperatures would freeze the collected water. Samples were collected at the end of this period. The wells recording water level 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 5 wells in E podzols, 66 samples from 6 wells in Bhs podzols, 77 samples from 6 wells in hillslope Bh podzols, 11 samples from 3 wells in near-stream Bh podzols, and 17 samples from 3 wells in typical podzols. Groundwater and soil solution samples were not filtered prior to analysis. Analysis of the samples for DOC concentrations was carried out at the Forestry Sciences Laboratory in Durham, NH, USA with a Shimadzu TOC-5000A. The groundwater samples used in this analysis were taken on 55 dates from 5 March 2010 to 28 June 2013, including samples from *Zimmer et al.* [2013]. Lysimeter 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. Not all wells and lysimeters were sampled on each date, as some did not yield sufficient sample volume.

3.2 Spatial extent of water table development

In order to examine the potential contributing area to streamflow, the probable extent of water table in the catchment was mapped for two dates where spatial stream chemistry was available from *Zimmer et al.* [2013], 9 July 2010 and 6 August 2010. 9 July 2010 was chosen to be representative of a higher flow in the stream: streamflow on that date

had a 14% exceedance probability [Zimmer *et al.*, 2013]. A low flow date was also examined, on 6 August 2010 streamflow had a 77% exceedance probability [Zimmer *et al.*, 2013], indicating conditions were near baseflow. The spatial extent of each HPU was derived from the soil predictive model in Gillin *et al.* [in review]. For each cell in a 5 m grid of WS3, the HPU with a probability of 0.5 or higher according to the model was considered to be the HPU in that cell. 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.* [in review] 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.* [in review] plus measured rainfall on the sampling date was over the threshold needed to elicit a water table response in that HPU according to Gannon *et al.* [in review].

3.3 FDOM

A flow through FDOM fluorometer (WETLabs, Philomath, OR) was installed in WS3 just upstream of the v-notch weir. The fluorometer estimated the quantity of fluorescent, humic-like DOM using a single excitation/emission pair (370/460 nm; with 10 and 120 nm full width at half maximum excitation/emission bandpass filters, respectively).

Every 30 minutes a sample was pumped into the fluorometer after a 2-minute sample flush and warm up period. Data were collected for 30 seconds at 1Hz to a Campbell Scientific CR1000 datalogger (Campbell Scientific, Logan, UT). The last 10 seconds of each sampling period was then averaged to one mean and standard deviation value. The blank corrected output sample voltage was then multiplied by an instrument-specific conversion factor supplied by the manufacturer to convert from to ppb quinine sulfate equivalents (QSE, fluorescence of 1 ppb quinine sulfate dehydrate in 0.1 N H₂SO₄). The sensor had a confirmed linear response ($r^2 > 0.99$) up to 167 ppb QSE.

4.0 Results

4.1 Groundwater

The percent 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 2). Figure 2 shows that wells in E and hillslope Bh podzols recorded the most frequent incursions into the upper portions of the soil profile where soil organic matter is generally higher. Wells in Bhs podzols recorded incursions into these horizons, but less than 5% of the time. Wells in near-stream Bh podzols and typical podzols did not record water tables in upper portions of the soil profile as defined here.

DOC in the groundwater of E and Bhs podzols was highest, with a mean of 14.5 mg/L in E podzols and 5.5 mg/L in Bhs podzols (Figure 3A). DOC concentrations in near-stream soils were no higher than hillslope Bh podzols or typical podzols. Mean DOC concentration in groundwater in typical, hillslope Bh, and near-stream Bh podzols were all less than 3 mg/L (Figure 3A).

In typical and hillslope Bh podzols water sampled from suction lysimeters had higher DOC than that in the groundwater (Figure 3). However, in E and Bhs podzols an opposite contrast was observed; groundwater in these soils had higher DOC than water sampled from suction lysimeters (Figure 3A).

4.2 Spatial patterns in DOC

Potential area contributing to streamflow was examined by producing maps of the probable extent of water table in the catchment for high and low flow: 9 July 2010 and 6 August 2010, respectively. On 9 July, the date with higher flow, the storage plus precipitation level according to modeled storage from *Gannon et al.* [in review] was 85 mm. This meant E, Bhs, hillslope Bh, and near-stream Bh podzols would be expected to have water table in their solum (Figure 4). While two of five typical podzols responded in the 80-90 mm storage range in *Gannon et al.* [in review], the mean response threshold for the group was over 85 mm and therefore they were not mapped as having water table. On 6 August 2010, near baseflow conditions, the storage plus precipitation level was 55.7 mm [*Gannon et al.*, in review], meaning only Bh podzols would be expected to have

water table in their solum based on the model. Therefore, only Bh podzols were mapped for this date in Figure 4.

Stream samples on 9 July 2010 from *Zimmer et al.* [2013] with the highest DOC generally occurred at channel heads (Figure 4). Furthermore, on a reach basis, DOC decreased downstream as the source area made up of near-stream Bh and hillslope Bh podzols increased (Figure 4). Finally, spatially expansive water tables were observed near channel heads in the catchment in E and Bhs soils (Figure 4). While only a portion of this area was likely contributing directly to stormflow, there were several sampling sites on the stream network where most of the soils in their catchment area were E and Bhs podzols (Figure 4). It should be noted, however, that this soil predictive map should not be treated as a completely accurate representation of soil spatial distribution in the catchment. There are several places in the catchment, specifically near channel heads in the western tributaries to WS3, that E and Bhs podzols may have been over predicted because of the limited accuracy of the shallow bedrock area map used in the model [*Gillin et al.*, in review].

On 6 August 2010, under lower flow and with water table only in Bh podzols, stream DOC concentrations were consistently low. The only exceptions were the two sampling points high on a western tributary (W3) with primarily bedrock contributing area. These two points had higher streamwater DOC concentrations than anywhere else in the catchment on that sampling date.

Streamwater 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 6 sampling dates in *Zimmer et al.* [2013] are also shown in Figure 3B. Paradise Brook had slightly higher DOC than near-stream Bh, hillslope Bh, and typical podzols. Similarly, the western tributary outlets all had similar DOC concentrations compared to near-stream Bh, hillslope Bh, and typical podzols. The eastern tributary outlets, however, had streamwater DOC concentrations that were consistently higher than hillslope Bh,

near-stream Bh, and typical podzols. Only E and Bhs podzols had higher DOC concentrations than the outlets of the eastern tributaries.

4.3 Temporal patterns in DOC

The timing of the FDOM response at the outlet of WS3 was compared to water table fluctuations in HPUs to examine how outlet FDOM varied with potential source areas as suggested by water table records in the solum of soils distributed throughout the catchment (Figures 5, 6). Recorded water tables in all wells that responded to the events on 2 October 2011 and 20 April 2012 (Figures 5, 6) peaked before FDOM at the outlet. The primary observable contrast in the response of HPUs in relation to outlet FDOM was on the recession limb of the FDOM and water table responses. Water tables in E and Bhs podzols continued receding throughout the FDOM recession during both events (Figures 5, 6). Water tables in hillslope Bh podzols receded with FDOM during the October storm (Figure 5) but during the April storm water tables stayed high throughout the FDOM recession (Figure 6). Very little water table fluctuation was observed in near-stream Bh podzols during either event, resulting in generally flat relationships between FDOM and water table levels (Figures 5, 6). The minimal response of near-stream Bh podzols was especially evident during the April event. Figure 6 shows FDOM at the outlet had a defined peak while water table in the near-stream Bh podzols increased no more than 10 cm and in one case was not observed. Therefore, wells in the HPUs with the highest DOC concentrations in groundwater, E and Bhs podzols, had water table responses that were most closely correlated with FDOM fluctuations at the outlet.

5.0 Discussion

5.1 DOC sources

DOC concentrations in streamwater in WS3 decreased down the stream network toward the outlet on 9 July 2010 (Figure 4). The same pattern has been observed in other watersheds at Hubbard Brook [*Likens and Buso, 2006; McGuire et al., 2014*] and in the Krycklan catchment in Sweden [*Laudon et al., 2011*]. The pattern is likely not uncommon; however, as noted by *Laudon et al. [2011]*, few studies have the spatial resolution of stream chemistry to observe longitudinal patterns. The pattern observed at

Hubbard Brook has been attributed primarily to areas with shallower soils and thicker organic horizons in higher elevation coniferous zones contributing more DOC to streamwater [Johnson *et al.*, 2010; Lawrence *et al.*, 1986; Likens and Buso, 2006]. Water in O horizons at Hubbard Brook has indeed been shown to have much higher DOC than in B horizons in studies using suction lysimeters [McDowell and Wood, 1984; McDowell and Likens, 1988] and zero-tension lysimeters [Dittman *et al.*, 2007], but a flowpath for the delivery of this water to the stream has not been identified. Furthermore, McDowell and Wood [1984] suggested specifically that streamflow is generated from B horizons due to the similarity of streamwater and B horizon DOC concentrations.

Our results reaffirm that high elevation coniferous zones are DOC sources to streamflow. The HPU's with high DOC (Figure 3) in groundwater, E and Bhs podzols, coincided with the coniferous zones at higher elevation in the catchment. Furthermore, the probable extent of water table predicted in the catchment suggests there were expansive event water tables in the channel heads of WS3 on the high flow date (Figure 4, 9 July 2010). These channel head areas, with the highest percentage of E/Bhs podzol contributing area, also had the highest streamwater DOC concentrations according to the spatial streamwater chemistry from Zimmer *et al.* [2013] (Figure 4). Additionally, DOC at the outlets of eastern tributaries, which have more E and Bhs podzol area in their channel heads, was higher than at the outlets of western tributaries. The contribution of water from E and Bhs podzols was also consistent with the FDOM fluctuations observed at the catchment outlet (Figure 5, 6). FDOM fluctuations at the outlet matched well with the water table fluctuations in E and Bhs podzols. This was especially the case on the recession limb, where FDOM decreased until E and Bhs water tables subsided. While the rapid rate of in-stream DOC removal at HBEF may cast doubt on how DOC from channel heads could be responsible for fluctuations at the catchment outlet, these removal rates were determined during low flow conditions [McDowell, 1985]. Therefore, while still a factor in determining longitudinal patterns in DOC, removal rates are likely less of a factor during higher flow conditions when landscape factors more strongly influence DOC patterns [Tiwari *et al.*, 2014].

E and Bhs podzols appear to be sourcing DOC to channel heads in WS3; however, the high DOC in groundwater in these soils may not be completely explained by groundwater rising into shallow soil horizons. While water tables in these soils responded quickly to events, rising high into the soil profile, they were infrequently in the very top of the solum, where DOC is highest (Figure 2). Furthermore, Figure 2 shows that water tables were in the upper portion of the solum just as often in hillslope Bh podzols as E podzols and more often than Bhs podzols, and yet groundwater in both E and Bhs podzols was higher than that of hillslope Bh podzols. This is especially unexpected for E podzols because E horizons typically have much lower carbon content than the B horizons that dominate Bh and Bhs podzols [Bailey *et al.*, 2014]. A process that may explain these differences is illustrated in Figure 7. The upslope area of E and Bhs podzols is mostly bedrock covered with a thin layer of organic material [Bailey *et al.*, 2014]. Furthermore, evidence suggests the frequent water tables observed in E and Bhs podzols were due to rainwater flushing directly off the bedrock into these shallow soils [Gannon *et al.*, in review]. This offers an explanation for the high DOC concentrations in groundwater in E and Bhs podzols. As shown in Figure 7, water falls on bedrock contributing areas, possibly obtaining high DOC concentrations from the thin forest floor material that covers most of these areas. It is therefore likely that the DOC in E and Bhs podzol groundwater is coming from runoff delivered directly to the water table from generally impervious and low storage capacity upslope bedrock contributing areas covered in a thin layer of organic material.

We did not observe evidence that water flow through near-stream soils increased DOC concentrations. Water tables were not observed in the O horizon or shallow B horizon in near-stream soils (Figure 2). Furthermore, DOC concentrations in the groundwater of near-stream soils in WS3 were no higher than those of hillslope soils, apart from E and Bhs podzols (Figure 3A). Finally, DOC concentrations at several tributary outlets in the catchment were higher than that of groundwater in near-stream soils (Figure 3B). DOC concentrations that are higher in streamwater than in near-stream soils suggests this DOC is coming from elsewhere in the catchment. This is consistent with the findings of Grabs *et al.* [2012], who observed that fluctuations of water table in near-stream soils in a drier,

till derived portion of their study site at the Krycklan catchment did not result in much change in total organic carbon (TOC) concentrations in soil water.

It is difficult to say how applicable these findings are to other sites, partially due to the lack of high spatial resolution stream chemistry at most sites. However, at sites with similarly well-drained, post-glacial soils and bedrock outcrops, the same bedrock-area DOC generation and limited near-stream water table rise are likely present. Additionally, the DOC concentrations at the outlet of WS3 were much lower than those observed in catchments where high near-stream water tables and/or wetlands have been shown to contribute DOC to the stream [Boyer *et al.*, 2000; Laudon *et al.*, 2011; McGlynn and McDonnell, 2003]. Low background concentrations, due to the lack of contribution from wetlands or near-stream soils, allowed detection of the signal from shallow upland bedrock sourced soils. In catchments with more prolific sources of DOC it may be difficult to detect the contributions of these soils. The identification of this DOC source, however, offers an additional tool for explaining spatial extent of DOC source areas and catchment outlet DOC fluctuations in WS3 at Hubbard Brook.

5.2 Implications for carbon storage

While near-stream soils did not contribute high levels of DOC to the stream network in WS3, Bailey *et al.* [2014] identified higher carbon concentrations in Bh podzols than other soils in WS3. This suggests that these soils are not atypical near-stream soils with regard to carbon content. Therefore, the primary reason they were not large DOC sources is most likely that they did not experience the necessary high water tables observed in other studies [Boyer *et al.*, 2000; McGlynn and McDonnell, 2003], not because of a lack of carbon in the soil. If these soils are not exporting this carbon as DOC, they may be storing carbon in the catchment in more recalcitrant form. The amount of precipitation in the northeastern United States, however, has been increasing and is predicted to continue to increase with changing climate [Campbell *et al.*, 2011; Hayhoe *et al.*, 2007]. These increases in precipitation, as well as a shift in seasonality to more winter storms [Hayhoe *et al.*, 2007] may lead to higher near-stream water tables, which could mobilized carbon that is currently being stored.

5.3 Implications for runoff generation

The identification of upland soils in the channel head region of the catchment (i.e., E and Bhs podzols) as a source of streamwater DOC also implies they are important to streamflow generation. If contributing areas are considered to be some portion of the spatial extent of water table in the catchment, water table mapped in Figure 4 indicates that E and Bhs podzols contribute to streamflow when the catchment is wet. The presence of frequent water tables in the solum in these areas is corroborated by *Gannon et al.* [in review], who examined water level records from several wells in each HPU in WS3 and found frequent water tables in E and Bhs podzols that rose nearly to the ground surface. Furthermore, the water table in near-stream areas does not extend very far up the hillslope (Figure 4) as near-stream areas are very efficient at transmitting hillslope water to the stream due to their higher hydraulic conductivities [*Detty and McGuire, 2010*]. This suggests a different conceptual model of streamflow generation than the classic idea of a variable source area [*Hewlett and Hibbert, 1967*]. While water tables expand and contract in the near-stream zone, they are limited by topography and high hydraulic conductivity. However, spatially expansive water tables that occur in shallow soils near channel heads may also contribute to streamflow during events while imparting different chemical signatures to streamwater.

6.0 Conclusions

In this study we presented evidence from shallow groundwater level fluctuations; groundwater, soil water, and streamwater dissolved organic carbon (DOC) concentrations; spatial patterns in streamwater DOC concentrations; and fluorescent dissolved organic matter (FDOM) fluctuations at the catchment outlet that help explain the general pattern of DOC sources in watershed 3 (WS3) at the Hubbard Brook Experimental Forest (HBEF). We presented a new conceptual model where DOC was delivered to the stream in channel head areas where bedrock outcrops covered in a thin layer of organic material were sources of DOC to groundwater in the soils downslope. We found that the process generally described as responsible for DOC generation in headwater streams, where near-stream water tables intersect shallow, high DOC soil

horizons, transmitting that DOC to the stream, was not a major driver in WS3. DOC concentrations in near-stream groundwater were not higher than other hillslope soils and water tables were not observed in the upper horizons of these soils. Rather, soils in channel head areas with primarily bedrock contributing areas had the highest DOC concentrations in soil water and groundwater. These soils were found to have spatially expansive water tables during events, likely indicating they contribute water to channel heads, where the highest DOC in streamwater was observed. Furthermore, water table fluctuations in these soils matched fluorescent dissolved organic matter (FDOM) observations 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 suggests that the variable source area in WS3 is both an expansion of water table from the near-stream zone and in channel head areas.

Figures

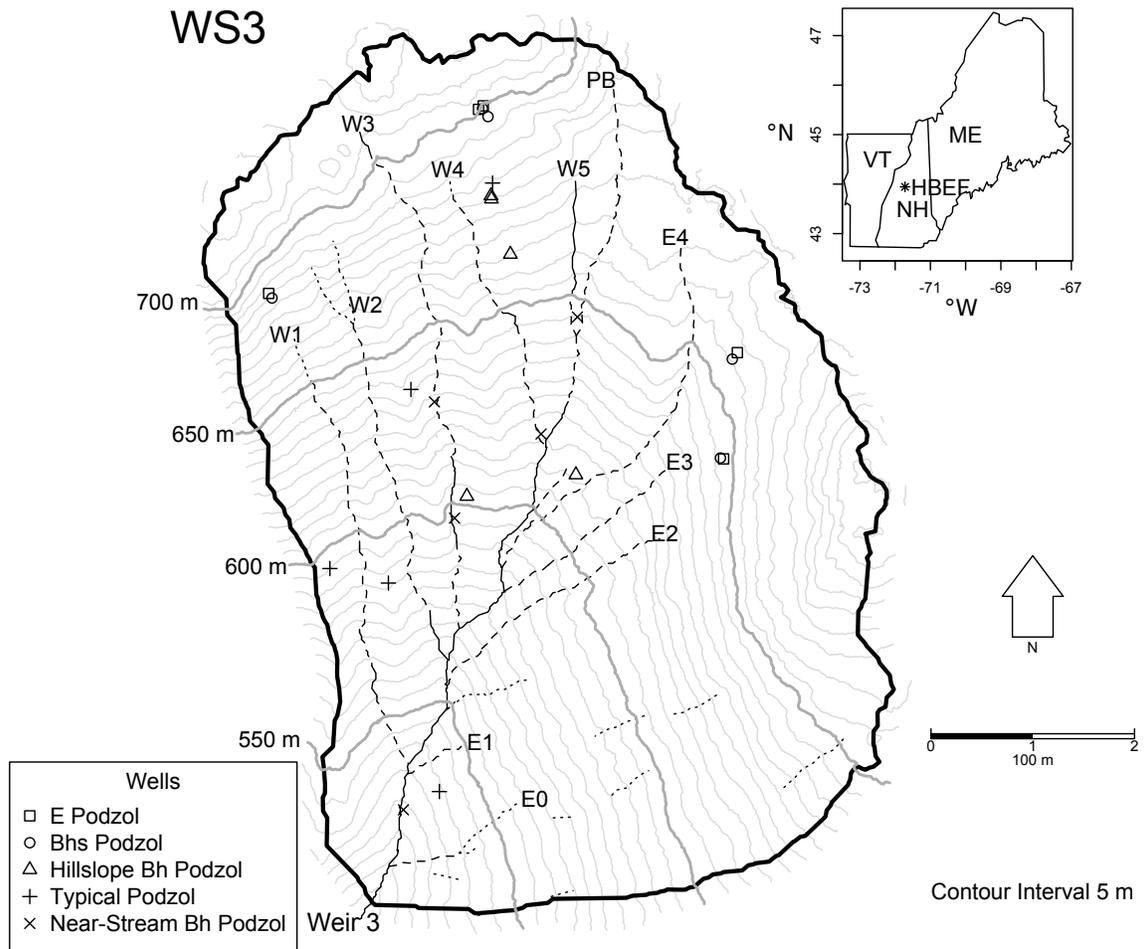


Figure 1. Map of Watershed 3. The inset map indicates the location of HBEF in northern New England. Perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. Shallow groundwater wells are indicated by symbols on the map. Soil morphological units are indicated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

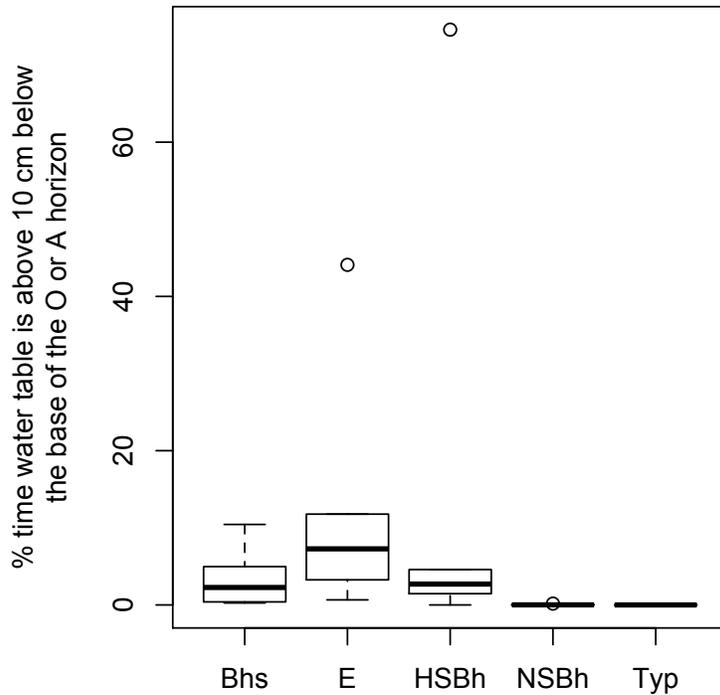


Figure 2. Percent time in 2 years that wells in each HPU recorded water table above 10 cm below the O horizon or A horizon if present (n = 5 per group). HPUs shown are Bhs podzols (Bhs), E podzols (E), hillslope Bh podzols (HSBh), near-stream Bh podzols (NSBh) and typical podzols (Typ). The middle line 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 quartile plus or minus 1.5 times the IQR, and points are outliers beyond the range of the whiskers.

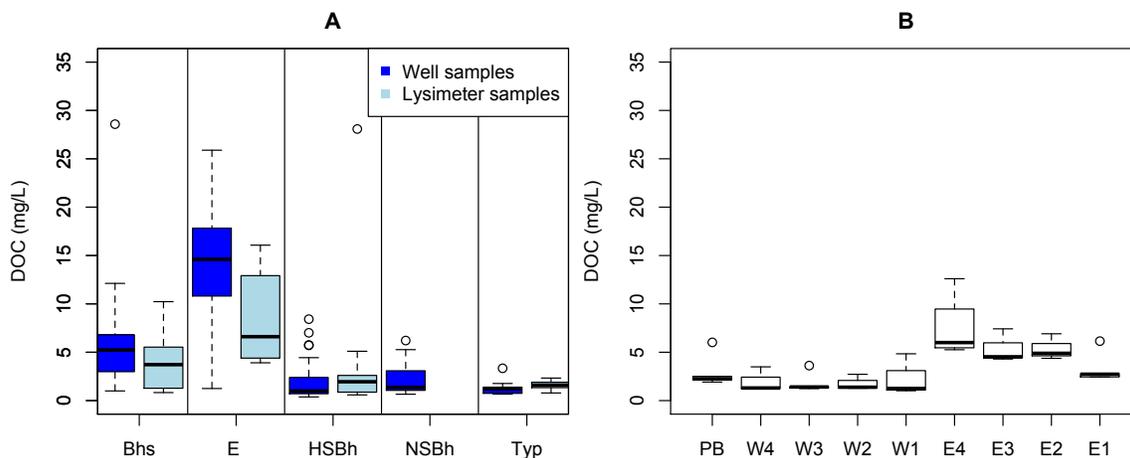


Figure 3. DOC (mg/L) of groundwater and lysimeter samples in HPUs (A) and at the outlets of WS3 and 8 tributaries within WS3. Panel A shows groundwater and lysimeter water for each HPU except near-stream Bh podzols (NSBh), as no lysimeter samples were available. For Bhs podzols (Bhs) $n = 66$ for groundwater (6 wells) and 28 for lysimeter samples (3 sites: 5 lysimeters total). For E podzols (E) $n = 45$ for groundwater (5 wells) and 12 for lysimeter samples (2 sites: 2 lysimeters total). For hillslope Bh podzols (HSBh) $n = 77$ for groundwater (6 wells) and 31 for lysimeter samples (3 sites: 8 lysimeters total). For near-stream Bh podzols $n = 11$ for groundwater (3 wells). Finally, for typical podzols (Typ) $n = 17$ for groundwater (3 wells) and 16 for soil water (3 sites: 4 lysimeters total). Panel B shows DOC in streamwater at the outlet of WS3 (Paradise Brook, PB), 4 tributaries on the western side of the catchment (W1, W2, W3, W4) and 4 tributaries on the eastern side of the catchment (E1, E2, E3, E4). 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 quartile plus or minus 1.5 times the IQR, and points are outliers beyond the range of the whiskers.

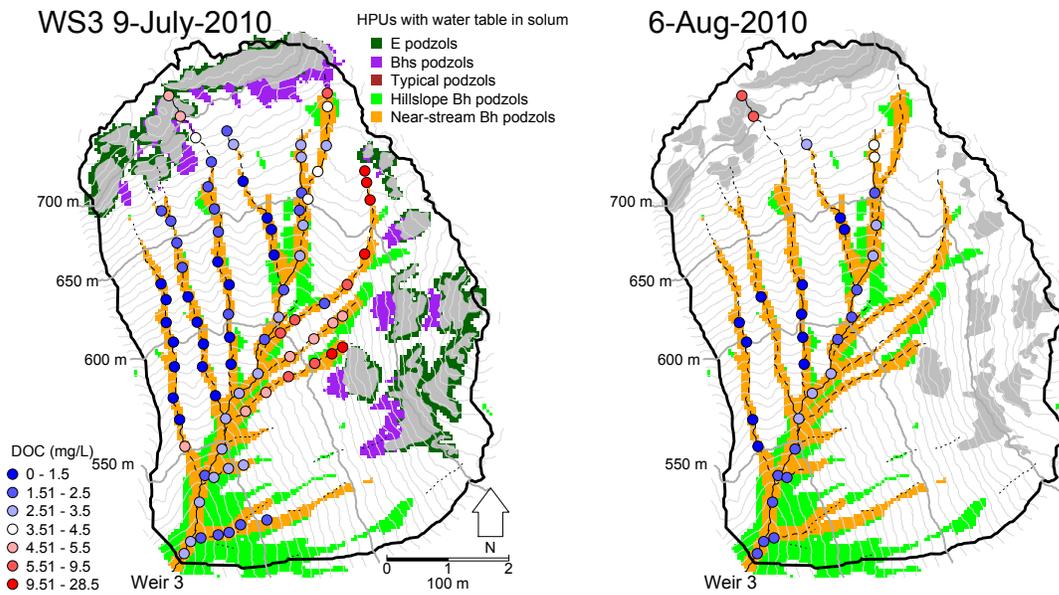


Figure 4. Map of HPUs with water table in their solum according to the modeled storage value and threshold of water table response from *Gannon et al.* [in review] and predicted HPU locations from *Gillin et al.* [in review] and spatial streamwater DOC (mg/L) from 9 July 2010 and 6 August 2010 from *Zimmer et al.* [2013]. Grey areas on the maps denote areas with exposed or shallow bedrock as mapped by *Gillin et al.* [in review]. Perennial, intermittent, and ephemeral streams are shown by solid, dashed, and dotted lines, respectively. The contour interval is 5 m.

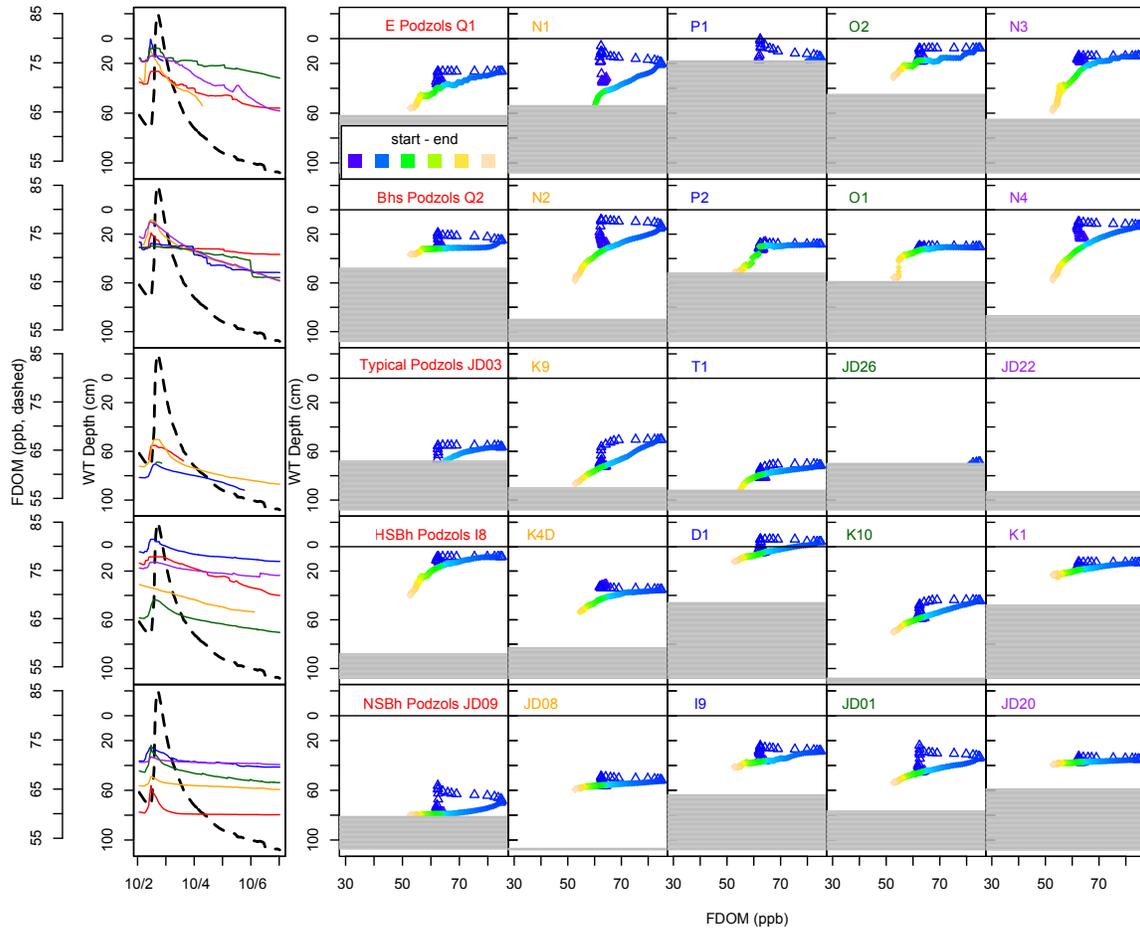


Figure 5. FDOM at the catchment outlet and water table at an example well in each HPU are shown for an event starting on 2 October 2010. FDOM is indicated by a dashed line in the plots on the left, water table is indicated by the solid line, the color of each line corresponds to the well name of the same color in the plots on the right. Plots on the right are water table (y axis) plotted against FDOM (x axis), the color of the plots goes from red at start to beige at the end of the event shown in the plots on the right. Points on the rising limb of the FDOM timeseries 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.

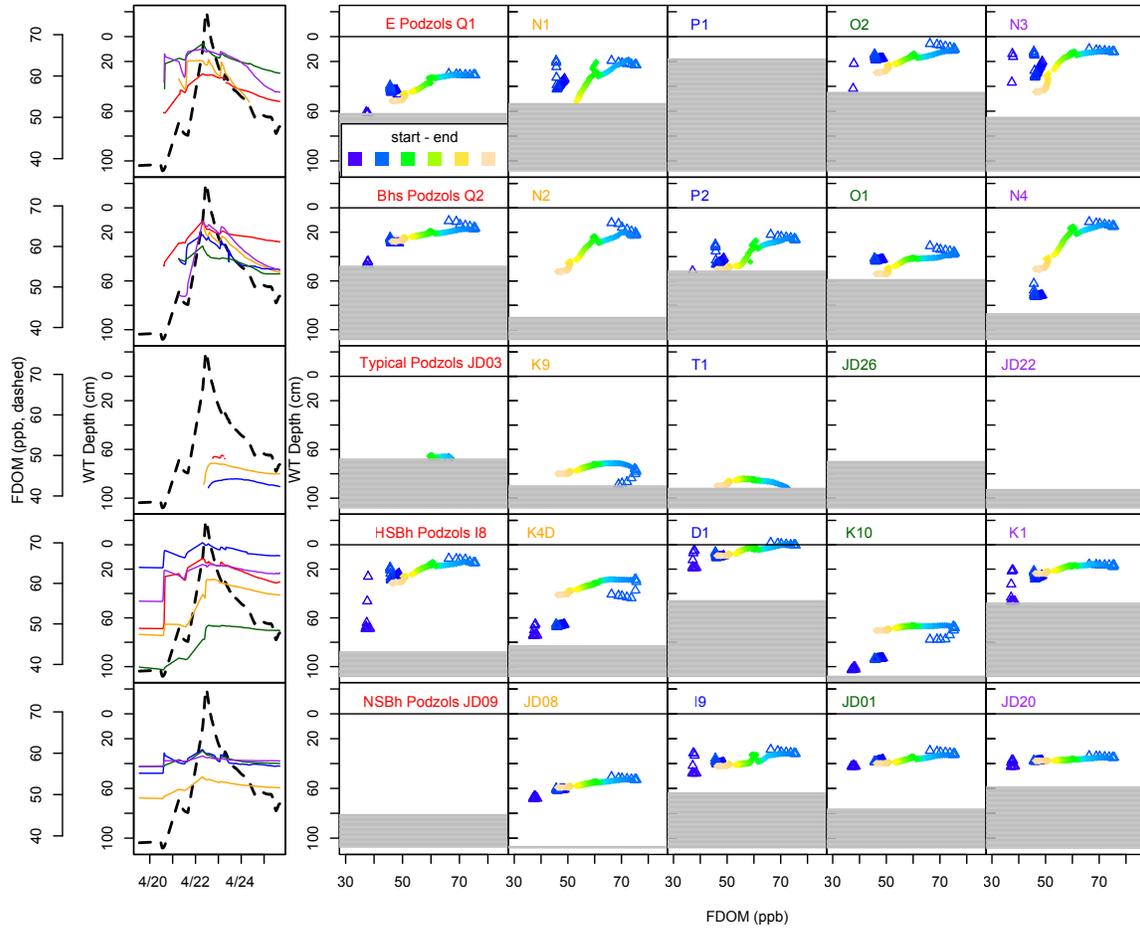


Figure 6. FDOM at the catchment outlet and water table at an example well in each HPU are shown for an event starting on 20 April 2010. FDOM is indicated by a dashed line in the plots on the left, water table is indicated by the solid line, the color of each line corresponds to the well name of the same color in the plots on the right. Plots on the right are water table (y axis) plotted against FDOM (x axis), the color of the plots goes from red at the start to beige at the end of the event shown in the plots on the right. Points on the rising limb of the FDOM timeseries 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.

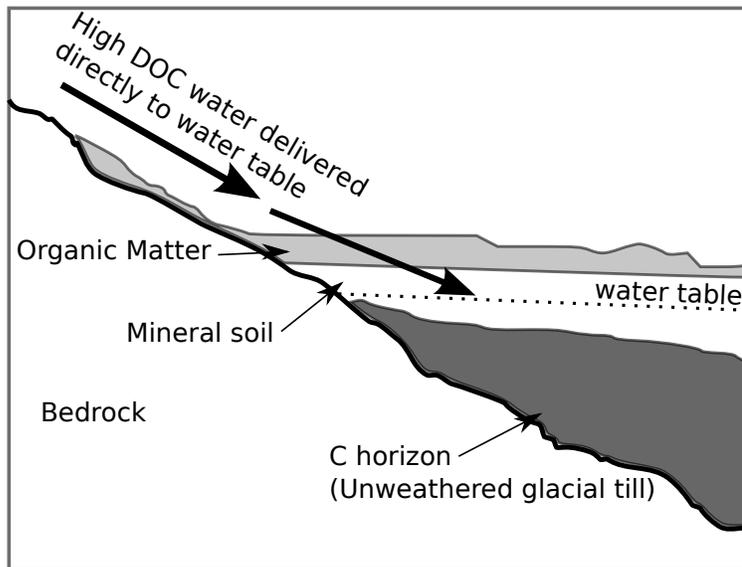


Figure 7. Conceptual model of DOC delivery to shallow groundwater in E and Bh podzols. Precipitation is shown to flow down the impervious bedrock surface through a shallow forest floor layer, obtaining high DOC. This bedrock runoff then flows directly into the shallow soils immediately below

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Conclusions

Headwater streams are important natural resources to understand and protect. While larger rivers, lakes, and reservoirs are generally used as municipal water supplies, over 50% of total stream length in the contiguous United States is made up of headwater streams [Nadeau and Rains, 2007]. Despite the importance of these small streams, they are still largely unknown in terms of understanding the processes that lead to their streamflow generation and water quality [Bishop *et al.*, 2008]. It is crucial to understand how headwater streams work if we are to begin to understand how water supplies will be affected by land use changes and/or changes in climate. One potential way to expand our understanding of headwater catchments is to examine soils in tandem with hydrology to identify the flow paths and soil forming processes that cause patterns in soil heterogeneity. This could provide valuable insights into the spatial distribution of the processes that control streamflow generation and water quality in headwater catchments.

For these reasons, this dissertation focused on better explaining runoff generation mechanisms, soil formation, and spatial and temporal patterns in streamwater chemistry in a headwater catchment. In order to address these questions in a novel way, a hydropedological approach was taken, where soil development and hydrological processes are inextricably linked and must be considered holistically. At Hubbard Brook Experimental Forest (HBEF), soils are generally podzolic and illustrate this linkage well because changes in horizonation as a result of hydrologic flowpaths are easily detected.

The first study in this dissertation aimed to explore the relationship between soil horizonation and hydrologic flowpaths by examining water table fluctuations in different morphologically defined soil units, called hydropedological units (HPUs), in watershed 3 (WS3) of the HBEF. The principle hypothesis of this study was that HPUs had distinct, quantifiable water table regimes.

Next, measurements of the vertical flux of water in HPUs were used to detect differences in unsaturated flow directions to explain patterns in soil development in the catchment.

The primary objective of this study was to determine if variations in soil horizonation above the maximum height of observed water table fluctuations could have been caused by lateral unsaturated flow.

Finally, dissolved organic carbon (DOC) concentrations in soil water, groundwater, and streamwater were used to investigate whether or not the spatial distribution of HPU's in the catchment could be used to interpret spatial and temporal patterns of DOC in streamwater in headwater catchments.

These investigations yielded the following conclusions:

1. Hydropedological units in WS3 have unique water table regimes characterized by the frequency and magnitude of water table fluctuations, percent time water tables were detected in the solum of the soils, and at what level of catchment storage water tables rose into the shallow soil.
2. Water tables do not uniformly extend up from the near-stream zone. The spatial extent of water table in the catchment depends on which HPU's in the catchment are responding at the current level of catchment storage. This results in a spatial patchwork of water table in the catchment in which some water tables are likely connected to the stream and contributing runoff and some are not.
3. Lateral unsaturated flow occurs above water tables in HPU's. This is likely responsible, in part, for the lateral translocation of amorphous organometallic complexes, resulting in lateral podzolization.
4. E and Bhs podzols, located near channel heads in the catchment, are sources of DOC for streamwater. This helps explain the trend of decreasing DOC concentrations moving downstream in streams at HBEF.

These conclusions illustrate the usefulness of a hydropedological approach to characterizing processes that generate streamflow and affect streamwater chemistry in headwater catchments. The findings of this work also implicitly bring up a host of

continuing research questions related to the applicability of these findings across spatial scales and at sites with different soils. For example, future work should examine whether or not similar spatial patterns in soil morphology related to the magnitude and direction of water flux can be detected in landscapes where the primary soil type is not a Spodosol. Furthermore, spatial patterns in streamwater chemistry should be investigated further. First, the process that leads to high DOC concentrations in E and Bhs podzols should be investigated along with where and how these HPUs contribute water to streams, whether on event or longer timescales. Additionally, the spatial distribution of HPUs should be examined in relation to the spatial patterns of solutes other than DOC in WS3. This would be very useful in determining which patterns in water chemistry are related to different shallow flow paths through HPUs and which are more dependent on a deeper flow system or variations in deeper flowpaths in the catchment.

Additionally, water table fluctuations in the solum of HPUs were found to be consistent among HPUs and related to overall catchment wetness. These findings were used to hypothesize the relationship of certain HPUs to runoff generation, but these hypotheses have not been tested. If the role of HPUs in runoff generation can be better understood in terms of when and how they contribute to streamflow, it may be of great utility to catchment hydrologic modeling efforts, e.g., developing process-based spatially explicit models or better parameterization of soils in models. It is therefore an important area of future research to begin investigating the relationship between transient water tables in channel heads and disparate hillslopes and runoff generation. If this relationship can be substantiated, it would offer a valuable tool for investigating the effects of climate change to catchment runoff generation by highlighting catchment areas that are simultaneously the most relevant to runoff generation and sensitive to changes in precipitation regimes.

This study may therefore be very useful to investigations of how headwater catchments will respond to land use and climate change. A framework was presented in this dissertation where catchment runoff generation and biogeochemical processes can be grouped by similar, predictable soil units. The hope is that this can be utilized in the future to make better predictions about how catchment discharge and chemical output

will change due to changes in land use or climate and that it may be of great utility to managers dealing with complex systems and multiple management objectives.

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