An evaluation of surface water sources using spatial and temporal variations in stream chemistry in a headwater catchment

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I. Preface

The goal of this Environmental Studies Honors thesis is to advance understanding of the physical extent and chemical influence of water sources on streams within a small headwater watershed in central New Hampshire. This project stemmed from a summer 2009 internship through the National Science Foundation’s Research Experience for Undergraduates (REU) Program. The program was coordinated through Plymouth State University in Plymouth, New Hampshire. My mentors were Drs. Kevin McGuire (Virginia Polytechnic Institute and State University) and Scott Bailey (United States Forest Service). My research was based at the Hubbard Brook Experimental Forest (HBEF) located in the White Mountain National Forest. Beyond the summer 2009 internship, I spent the following summer, two fall breaks, a spring break and part of a winter term on site working on this particular research project.

This research is of high relevance to the scientific community, specifically to researchers interested in the mechanistic roles of soil evolution and water table dynamics to the solute composition of streams. I have authored three professional presentations and co-authored one professional presentation to date on this work. These include oral presentations at the 2009 and 2010 Hubbard Brook Cooperators’ Annual Meeting, a poster at the American Geophysical Union Fall 2010 Meeting, and an oral presentation at the 2011 New Hampshire Water and Watersheds Conference. Future presentations include the 2011 Hubbard Brook Cooperators’ Annual Meeting and 2011 Catchment Science Gordon Research Conference. The incorporation of my research, including a half page figure, within a National Science Foundation proposal by my co-authors was crucial to its success; the proposal received full funding. The body of this Environmental Studies Honors thesis will be submitted as a co-authored manuscript to the
academic journal, *Hydrological Processes*, this spring. This is a well-respected journal widely read by ecologists, hydrologists and biogeochemists who deal with water issues.

The following overview provides the necessary framework in order for the general reader to understand the broader context as well as the technical information presented in subsequent chapters of this thesis. I establish a comprehensive background for the study site and this project’s research topic as well as provide a historical review of related research leading up to the gap in knowledge my project fills. Finally, I outline the social and environmental importance for this type of scientific knowledge.

**Ia. Site Description and History**

The HBEF was established in 1955 by the United States Forest Service in response to the government’s growing interest in developing a better understanding of sustainable watershed management. Specifically, attention at the time was on understanding the relationship between streamflow, flooding and forestry practices. In 1963, the Hubbard Brook Ecosystem Study (HBES) was initiated by F.H. Bormann, G.E. Likens, N.M. Johnson, and R.S. Pierce. The foundation of HBES expanded the scope of initial research at HBEF to encompass the exploration of a wide set of processes involved in ecosystem and biogeochemical dynamics, by focusing on water and chemical budgets on the watershed scale (Likens and Bormann, 1995). What came to be known as the “watershed approach” to ecological research emerged as a powerful method to assess the integrated response of entire watersheds to disturbance; the volume of streamflow and chemistry of water samples taken from the outlet of each gaged watershed in the HBEF provided an integrated measure of whole ecosystem response. Some termed this a “black box” approach to ecological research in the sense that processes occurring
within the ecosystem were assessed primarily by examining differences between input (e.g. precipitation) and output (e.g. streamflow) at the watershed outlet. Quantifying differences between inputs and outputs allowed researchers to conduct water, energy, and chemical budgets for watersheds, a technique still used today to evaluate ecosystem processes, such as evapotranspiration. This allowed researchers to quantify the impacts of forestry practices, such as logging, on environmental characteristics, such as streamflow and solute concentrations, at the watershed scale.

Since its foundation, HBEF has been at the forefront of developing new scientific methods and providing extensive publically available data sets. Specifically, HBEF has continuously collected data on precipitation, climate, and stream quality at a set of gaged watersheds since its initiation. These public data, coupled with pioneering watershed scale techniques used by its researchers, have made HBEF one of the most valuable long term data sets in the world. HBES has been funded by the National Science Foundation (NSF) since 1963 and in 1988, joined the ranks of 26 Long Term Ecological Research (LTER) sites designated by the NSF funded LTER Network.

HBEF is located in the southern White Mountains of central New Hampshire (43°56’N, 71°45’W). The 3519 hectare (ha) research site is located in a humid, upland, postglacial landscape typical of northern New England. At 450-m elevation, the mean July and January temperatures are 19°C and -9°C, respectively. The mean annual precipitation is 1395 mm with a standard deviation (designated by σ) of 189. Standard deviation is a measure of how widely data is dispersed around the mean value. Snow accounts for 25-33% of the total precipitation. Mean annual streamflow is 869 mm (σ =175) (Bailey et al., 2003). The streams in the Hubbard Brook Valley range from zero to fifth order; the HBEF consists of the entire watershed of the fifth order
Hubbard Brook at the point it leaves the experimental forest. Stream order designates location of tributaries in a stream network, where an unbranched, perennial stream is considered first order. When two first order streams join together, the resulting stream is considered to be a second order stream, and so forth. Zero order refers to ephemeral and intermittent streams, or streams that are not flowing year round.

HBEF has instrumented nine first order headwater watersheds, or catchments, for watershed scale research studies. At each catchment outlet, a weir, or overflow dam, has been installed, which allows researchers to continuously measure stream discharge at the outlet. The catchment used in my research is 41.2 ha Watershed 3 (designated WS3), the hydrologic reference catchment. WS3 has a history of being used as a reference site in paired catchment studies, in which it is compared to another catchment that is manipulated through experiments such as forest harvesting or nutrient additions. Watershed 3 is the largest south facing and most topographically diverse of the gaged catchments at HBEF.

Soils in HBEF catchments are generally Spodosols, which developed in glacial deposits, primarily dense basal till (Likens and Bormann, 1995). These Spodosols are assumed to drain precipitation inputs through the soil too quickly to allow for the buildup of groundwater, and have thus been characterized as well-drained. They are assumed to be underlain by impermeable bedrock (Likens and Bormann, 1995). This has allowed researchers to conduct the water budgets described earlier, with the assumption that there is no groundwater loss or gain, and that the difference between the quantity of precipitation and stream discharge at the weir is due to evapotranspiration.
Recent research at HBEF has revealed a more complex interaction between hydrology and soils than was previously assumed. Studies have begun to take mechanistic approaches to understanding stream inputs and have discovered transient water tables in certain hillslope positions that build up and flush rapidly after storm events and snowmelt (Rosenthal, 1986; Cedarholm, 1994; Detty and McGuire, 2010). Water moving through the unsaturated zone in soils (Johnson et al., 2000; Wellington and Driscoll, 2004) and groundwater moving through hillslopes (April and Newton, 1985; McGlynn et al., 1999) as inputs to streams have been shown to be strongly influenced by the soils they pass through. And while soils influence hydrology and water chemistry, recent work is also indicating that hydrological flow is influencing soil development as well. For example, Detty and McGuire (2010) found persistent water tables at HBEF and Brousseau et al. (in prep.) found that soil profile evolution is related to different landscape positions based on differences in height and duration of water table relative to soil horizons. Brousseau et al. (in prep.) have classified a set of different soil types by distinct water table dynamics with statistically different heights and durations.

As the scientific community progressively recognizes processes within the watersheds are spatially heterogeneous, the question of scale becomes increasingly important. By looking within the catchments at specific stream lengths, or at the reach scale, instead of the watershed scale, it is apparent that streams in similar settings can show remarkably distinct chemical characteristics. For instance, Johnson et al. (1981) was able to show regular gradients in stream chemistry in relation to change in elevation, from first flowing water to the mouth of Falls Brook, a major tributary to Hubbard Brook. Likens and Buso (2006) found disparate spatial patterns in stream chemistry across different perennial tributaries in the HB valley. This study reported that some streams had expansive changes in chemistry along entire stream reaches, while others exhibited
stronger gradients at high or low elevations, and still other streams showed little or no expression of a chemical gradient.

My study takes a logical next step by looking closer at stream chemistry variation over space and time, by focusing on a single headwater catchment and its zero order ephemeral and intermittent stream reaches. I relate this information to physical and chemical controls in the landscape, such as groundwater dynamics and soil type, to mechanistically address gaps in knowledge about variations in stream chemistry.

Ib. Broader Implications

Headwater systems, or zero and first order stream systems, are important components of any landscape, as they regulate regional water quality by setting the natural chemical range of water downstream (Bishop et al., 2008), and are the most abundant stream type worldwide (Lowe and Likens, 2005; Alexander et al., 2007). It has been shown that larger watersheds reflect a regional average of the variation seen within headwaters (Temnerud and Bishop, 2005; Temnerud et al., 2010). These headwater systems offer invaluable ecosystem services, as they provide vital sources of water supply, cycle nutrients, and buffer floodwaters, and the ecosystems that drain to these provide wildlife habitat, and forest products, including lumber, pulp and energy. Although these systems provide many services important to human and natural environments, headwater streams are widely ignored, as the majority of headwaters are not perennial streams, and are thus not documented on typical topographic maps (Bishop et al., 2008). Furthermore, sensitivity to disturbance on headwaters and their ecosystem services is high, making these systems susceptible to damage at low thresholds of environmental, climatic or human impact (Lowe and Likens, 2005). Improper forest management practices have the potential to alter ecological processes in ways that lead to nutrient loss, reductions in forest
productivity and negative effects on processes within the soils that control response and recovery to disturbance (Verry et al., 2000). Thus, it is important to understand the location and extent of the dominant processes and controls within headwaters in order to protect and maintain these sensitive systems.

As headwaters set a natural range of stream chemistry for downstream regions, simply as a result of being the most abundant stream type in landscapes, it is believed a dominant chemical regulation within stream systems occurs in the near stream zone (Dahm et al., 1998), where surface water interacts with groundwater. Riparian zones were considered to be features of lowland streams, with distinctive vegetation and soils. Near stream zones in headwaters on first order streams and headwaters may be distinct as well and perform similar functions as lowland riparian sites do. Riparian zones are typically considered to be found in lowland river systems, with veg and soils. Near stream zones in headwater streams may be distinct as well, and perform functions that lowland riparian sites also perform. However, until this study, there has been little recognition of riparian zones in headwater systems. Riparian zones are the regions at the interface of terrestrial and aquatic ecosystems and are known to be biogeochemically distinct with anomalously high rates of chemical transformations, such as denitrification and mobilization of metals (e.g. mercury and aluminum) (McClain et al., 2003). Riparian buffer strips are used in forest management to mitigate impacts from forest harvest and help sequester nutrients on site, preserve site productivity, and preserve water quality and downstream aquatic habitats by limiting mobilization of metals and excess nutrients associated with eutrophication (Verry et al., 2000).

Current management of riparian buffer strips is generally accomplished through general non-site specific guidelines. The National Forest Management Act of 1976 mandates that
National Forests manage according to plans that specify mitigation methods. Although current
government protocols only establish riparian buffers for perennial streams, recent work, in which
I collaborated at WS3, shows distinct riparian soils along ephemeral stream networks. As a
result, my work has the potential to influence scientists and foresters in how they view the
relationship between landform, soil development, and groundwater contributions to streams.
With information on what landforms influence riparian soil development, foresters can establish
site specific management practices, such as riparian buffer strips, in order to protect not only
headwaters, but the downstream river systems.

As HBEF headwaters drain into the Merrimack River Basin, one of the largest basins in
one of the most densely populated areas in the northeastern United States, scientific
understanding of headwater systems has immense economic and social benefits through
understanding the controls on ecosystem services described earlier. These catchments have a rich
history as subjects of scientific inquiry into watershed scale patterns and processes, widely
available scientific resources and infrastructure, and have been minimally affected by human
activities. Thus, HBEF is a perfect location to push the current understanding of the mechanistic
relationship between landscape and stream hydrology that enable these systems to be so valuable
to society.
II. Introduction

Ecosystem processes that determine physical, chemical, and biological patterns seen across forested catchments operate and interact at multiple spatial and temporal scales (Leibowitz et al., 2008; Lowe et al., 2006; Naiman et al., 1988). Spatial variations in stream chemistry are indicative of variation in processes operating within these landscapes (Lawrence and Driscoll, 1990; Fisher et al., 2004). However, the mechanistic linkages between the spatial patterns seen in stream water chemistry and the processes that control these patterns are complex and not readily apparent (Sivapalan, 2005; Turner, 1989; Turner, 2005). Further, the scale at which we view these chemical variations in streams affects our perceived understanding of the absolute range of stream chemistry that can be seen within the system and the site-specific composition of physical, chemical, and biological drivers (Gustafson, 1998).

A priority of hydrologic research has been to better understand the extent to which headwater regions control stream water quality to downstream systems (Freeman et al., 2007; Gomi et al., 2002; Alexander et al., 2007; Temnerud et al., 2010). A fine scale approach is necessary to increase our understanding of patterns and processes seen within the streams in headwater watersheds. Prior to our study, the “watershed approach,” a powerful and widely used method, focused on assessing the integrated processes of an entire watershed by focusing primarily outside the watershed. Some termed this a “black box” approach to ecological research in the sense that processes occurring within the ecosystem were assessed by examining differences between inputs (e.g. precipitation) and outputs (e.g. streamflow). For instance, research at the small watershed scale at Hubbard Brook Experimental Forest (HBEF), New Hampshire, assumes the outlet of a defined watershed represents an overall signature for water chemistry throughout the upstream reaches (Bormann and Likens, 1967; Likens et al.,
This approach, however, ignores possible insights from spatial patterns of variation within the watershed and will miss the location and extent of hotspots, areas that play disproportionately important roles in intrawatershed solute generation. These biogeochemical hotspots may occur in small areas within watersheds (McClain et al., 2003), such as riparian zones (Cirmo and McDonnell, 1997; Burt et al., 2010), and are nearly impossible to assess at the watershed scale, since they represent very limited areas within the system and may not be reflected at the outlet.

Intrawatershed studies at multiple scales have the potential to fill in gaps in our knowledge of the nutrient cycling process that are inherent in the watershed approach. For example, nitrogen (N) inputs (e.g. nitrogen deposition) in forested watersheds greatly exceed N outputs (e.g. stream nitrogen export), although there is little evidence that nitrogen pools are accumulating at rates that account for this difference (Campbell et al., 2004). Land use, vegetation, and hydrology greatly influence rates of N loss and retention (Campbell et al., 2004). Identification and focus on specific hotspots with unique vegetation, soil, or hydrologic characteristics could account for the missing storage or fluxes of N needed to balance the N budget. McClain et al. (2003) concluded that although biogeochemical hotspots actively process and retain N, it is difficult to quantify the extent of their influence at the watershed scale. Further, researchers have argued that coupled biogeochemical research in both terrestrial and aquatic systems is needed to better understand N processing, as in-stream processes can play important roles in the N budget (Bernhardt et al., 2005; Lowe and Likens, 2005).

Finer scale studies that relate stream flow generation to hillslope processes can help scientists understand if certain portions of catchments represented by hillslope sequences regulate generation and retention of specific solutes. For example, mercury (Hg) deposition to forested watersheds has risen over the last 100 years due to industrialization; up to 90% of the
Hg deposited on the landscape is believed to be retained (Scherbatskoy et al., 1998; Kamman and Engstrom, 2002). Soil organic matter characteristics largely control the fate and bioavailability of toxic Hg in forested watersheds (Dittman et al., 2009; Haitzer et al., 2002; Skyllberg et al., 2003). However, soil carbon retention varies between soil types (Oades, 1988) and hotspots (McClain et al., 2003). Through finer scale studies, we can have a better understanding of which hillslope sequences regulate the retention and mobilization of Hg, through the generation and release of dissolved organic carbon (DOC).

Many studies have focused on the chemistry at a watershed outlet to identify water sources upstream. These studies have assumed there is no groundwater in headwaters, or that groundwater could be neatly differentiated between the hillslope and the riparian area. For example, many studies have divided “old water,” or water stored in the watershed before an event, and “new water,” or precipitation inputs during events, as an explanation for temporal variations in stream chemistry seen at the outlet of a catchment (Kirchner, 2003; McGlynn and McDonnell, 2003; Swistock et al., 1989). Burns et al. (2001) derived an explanation of streamflow in a headwater catchment in Panola Mountain, GA as a mixture of overland runoff from bedrock outcrops, hillslope groundwater and riparian groundwater. Asano et al. (2009) argued that stream chemistry was generated from a conservative mixture of water from fractured bedrock and shallow soil water.

Studies that address spatial and temporal stream chemistry of tributaries as a means of assessing processes and water sources occurring within the catchment are limited (Likens and Buso, 2006; Asano et al., 2009; Temnerud and Bishop, 2005). One of the earliest explorations of stream chemistry variation was by Johnson et al. (1981). They concluded the longitudinal chemistry patterns seen in Falls Brook, a tributary in HBEF, were a result of varying subsurface
flowpaths. As flowpath length increased moving downstream, neutralization of acid inputs to the stream also increased.

Research at HBEF has generated extensive knowledge of ecosystem ecology at the watershed scale, and thus is an ideal place to study stream chemistry patterns. However, the dominant water sources and processes controlling stream chemistry at HBEF have not been studied in detail. Until recently, as seen in the previous studies, groundwater was not considered to be an important source of stream flow. These headwater streams have a flashy response to precipitation events and become dry during summer and extended periods with no precipitation (Likens and Bormann, 1995). As a result, shallow, coarse textured soils in these steep upland catchments are considered to be well drained (Likens and Bormann, 1995), with no water table development. Recently, however, Detty and McGuire (2010) showed persistent shallow water table development in the hillslopes in Watershed 3 (WS3), the hydrologic reference watershed for HBEF and the catchment we used for our study. Brousseau et al. (in prep.) identified several distinct soil types distributed along hillslopes according to differences in depth and duration of water table development.

Soil types can vary across very small scales, however, and scale of stream water sampling in order to capture local landscape processes can be difficult to determine. The representative elementary area (REA) is a proposed metric to describe a threshold in watershed area for which downstream stream chemistry variation can be predicted based upon upstream ranges (Wolock et al., 1997). Studies have used thresholds in spatial chemistry in streams to describe the watershed area necessary to differentiate between local processes responsible for chemistry variation of headwaters and regional controls on chemistry of larger streams (Asano et al., 2009; Temnerud and Bishop, 2005). These studies have found a wide range in REA values between 10 and 1500
ha for upland forested catchments comprised of fourth and fifth order streams. The sampling densities for these surveys were less than 0.2 sampling sites/ha and focused on perennial stream networks. Fine scale sampling in a headwater catchment, which encompasses zero order ephemeral and intermittent streams, has the ability to test if the REA concept is robust.

This study takes a fine scale approach to sampling variations in spatial and temporal stream chemistry in WS3, a 41.2 ha headwater catchment in HBEF in order to link landform processes with stream characteristics. We begin by sampling ephemeral, intermittent and perennial surface water sites (zero and first order streams) across a broad range of hydrologic conditions. The sampling density of similar studies ranged from 0.007 – 0.22 surface water sample sites/ha, while our sampling density was 2.7 sites/ha. Concurrently, we sampled seeps, or groundwater discharge sites, as well as groundwater wells in distinct soil types across the catchment. We then compared the spatial and temporal stream chemistry variations to surface and subsurface characteristics, such as upslope accumulated area, soil type, and groundwater and seep chemistry to generate a mechanistic hypothesis for the dominant sources and processes controlling surface water chemistry.

III. Methods

Setting

This study took place in Watershed 3 (WS3), the 41.2 ha hydrologic reference watershed of the Hubbard Brook Experimental Forest, which is set within the southern White Mountains of central New Hampshire (Figure 1) (43°56’N, 71°45’W). The climate of HBEF is humid continental with average January and July temperatures of −9°C and 18°C, respectively. Roughly 25-33 percent of the 1400 mm of annual precipitation occurs as snow, and almost 50
percent of the 870 mm of annual runoff occurs during the spring snowmelt period (Bailey et al., 2003). Elevation ranges from 229 to 1,015 m in the Hubbard Brook Valley and 500 to 800 m in the gaged headwater catchments. These catchments are steep (20-30%) and are south facing (Likens and Bormann, 1995). WS3 comprises the headwaters of Paradise Brook, a second order tributary of Hubbard Brook. The catchment is covered by a mature hardwood forest, primarily American beech (Fagus grandifolia), sugar maple (Acer sacharum), and yellow birch (Betula alleghaniensis). Balsam fir (Abies balsamea), red spruce (Picea rubens), and white birch (Betula papyrifera var. cordifolia) dominate in the shallow soil of bedrock controlled ridges along the watershed divide (U.S. Department of Agriculture Forest Service, 1996). Spodosols of sandy loam texture developed in the shallow glacial till parent material are the main soil type present.

The catchment is underlain by mica schist bedrock (Barton et al., 1997), which is exposed along the upper boundaries of the watershed and in a few locations along the stream network. Detty and McGuire (2010) divided WS3 into three regions determined by stream channel network organization: parallel drainage separated by spurs in the western portion (tributaries W1-W5), convergent drainage in the northeastern portion (tributaries E1-E4), and limited expression of surface drainage in the southeastern portion of the watershed (Figure 2).
Figure 1. Shaded relief map of HBEF with instrumented research catchments. The study site, W3, is located in northeastern corner. Elevation ranges from 222 m (purple) to 1015 m (red).

The main stem of Paradise Brook (PB) runs southwesterly through the central part of the watershed. We surveyed additional ephemeral stream channels not inventoried by Detty and McGuire (2010) to generate a complete drainage map of the watershed (Figure 2).

Five soil types have been identified in WS3 (Brousseau et al., in prep.). Typical Spodosols are the most common soil type present. Vertical percolation processes of unsaturated flow promote acidic leaching that allows typical Spodosols to form. They are characterized by moderate podzolization, with a thin O, thin E, thin Bhs over Bs, and underlain by Cd. They are located on backslopes in moderately deep to deep (1-2 m) drift. They are moderately well to well drained and have a water table that rarely extends above the B/C interface. Bimodal Spodosols are similar to typical Spodosols, but have an anomalous Bh horizon where organic carbon accumulates at the B/C interface.
Figure 2. Watershed 3, shown with a hillshade representation of a 1m Digital Elevation Model (DEM). Circles represent soil pit sample sites with soil type designation. Pink triangles represent locations of seeps and each tributary is labeled at its head with the watershed designation. Stream types are marked with a solid line (perennial reaches), dotted line (intermittent), or double solid line (ephemeral).

They are developed by both vertical percolation in the upper profile and horizontal illuviation where water table frequently rises into the lower B horizon. Umbrepts are found along concave hillslopes, on benches, as well as in the riparian zone, where transient water tables frequently inundate the B horizon. Umbrepts have thick A horizons that grade into Bh horizons, which are thought to form from lateral illuviation. Lateral Spodosols are located where bedrock outcrops are interspersed with shallow soils along the watershed divide. The soils have the horizon
sequence of typical Spodosols, except that soil horizons are arranged along the hillslope, rather than vertically in the classical sense of a pedon. Riparian soils are typically Umbrepts, but have less of a water table expression in the B horizon due to high hydraulic conductivity of streamside lag deposits (Detty and McGuire, 2010). In addition to the 5 soil types identified by Brousseau et al. (in prep.), we found Aquepts, typified by Bw horizons and permanent shallow water tables in the vicinity of several of the larger seeps.

**IIIa. Water Sample Type**

The tributaries were categorized into stream types based on the categories by Hansen (2001). Sites were characterized as having perennial (permanent flow), intermittent flow (seasonal flow primarily during the non-growing season), or ephemeral flow (flow for hours or days only after large storm events). Seeps defined as groundwater discharge points located outside the stream channel, were also studied and considered as a separate water sample type (Figure 2).

**IIIb. Surface Water**

Surface water samples were taken approximately every 50 m along the main 800 m perennial Paradise Brook and its ten seasonal tributaries (ranging in length from 50 m to 600 m; Figure 2) when flowing water was present. Six surveys were conducted during a broad range of flow conditions (Table 1). Samples were taken in 125 mL HDPE bottles at small cascades, or fast moving water. In dry conditions, syringes were used to obtain sample from trickling sections where flow was minimal. Seeps required syringe sampling as well, as there were no defined channels in the mucky organic soils in seeps. The entire sample suite was collected within a six-hour period on each survey date. Water samples were analyzed for pH with a Broadley James
Rain probe. Dissolved metals, including Ca, Al, Na, Mg, Si, and K, were analyzed on a Varian Vista axial ICP at the Forestry Sciences Laboratory (FSL), Durham, NH. Trace metals including Mn, Fe, Zn, Rb, Sr, Ba, and Pb were analyzed by Perkin Elmer Elan 6000 ICP-MS at the US Geological Survey, Menlo Park, CA. Other analyses made at the FSL included the anions Cl, NO$_3$, and SO$_4$ on a Metrohm-Peak 761 Compact Ion Chromatograph, non-particulate organic carbon (NPOC) on a Shimadzu TOC-5000A, and total dissolved nitrogen (TDN) on an Antek Nitrogen Detector.

<table>
<thead>
<tr>
<th>Survey Date</th>
<th>Number of Samples</th>
<th>Streamflow mm/hr</th>
<th>Seasonal Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-Jul-09</td>
<td>93</td>
<td>0.177</td>
<td>early summer, relatively wet</td>
</tr>
<tr>
<td>1-Apr-10</td>
<td>107</td>
<td>0.278</td>
<td>immediate post-snow melt</td>
</tr>
<tr>
<td>18-Jun-10</td>
<td>61</td>
<td>0.027</td>
<td>late spring, low flow</td>
</tr>
<tr>
<td>6-Aug-10</td>
<td>42</td>
<td>0.014</td>
<td>late summer, baseflow</td>
</tr>
<tr>
<td>21-Aug-10</td>
<td>22</td>
<td>0.005</td>
<td>extremely low flow</td>
</tr>
<tr>
<td>1-Oct-10</td>
<td>112</td>
<td>3.207</td>
<td>first large storm of the autumn</td>
</tr>
</tbody>
</table>

### IIIc. Soil and Groundwater

We sampled groundwater across WS3 from a suite of piezometers installed by Detty and McGuire (2010) and from additional piezometers installed during our study period. Detty and McGuire (2010) installed a spatially distributed piezometer network throughout the catchment in order to capture hydrometric responses of different landscape positions. Installation focused on near stream areas (concave footslopes), hillslopes (planar blackslopes), and topographic divides (convex shoulders). Each well was constructed of SDR 21 PVC pipe (3.18 cm OD) with a 31 cm screen length consisting of 0.025 cm width lateral slots with 0.32 cm spacing between slots (Detty and McGuire, 2010). The wells were installed so the base of the screen was in the upper C horizon, between 50 cm to 175 cm deep. Additional piezometers were installed during the
present study around two of the larger seeps as well as in soil types underrepresented by earlier installations throughout the watershed in order to have similar numbers of wells in each soil type identified by Brousseau et al. (in prep). In total, there were five wells in Aquepts, four wells in bimodal Spodosols, two wells in lower lateral Spodosols, two wells in upper lateral Spodosols, nine wells in riparian soils, one well in the perennial stream, five wells in typical Spodosols, and six wells in Umbrepts (Figure 2). A battery operated peristaltic pump was used to collect water samples for chemical analyses. Groundwater samples were analyzed for the same parameters as surface water samples. Water levels were monitored at ten minute intervals using Odyssey water level loggers, which use a capacitance measurement to determine the wetted length of flexible Teflon®-coated wire that is suspended freely in the pipe. Water level recorder data will be considered in a subsequent paper and are not presented here.

IIIId. Topographic Characteristics

In order to evaluate the role of surficial processes in stream flow generation and spatial chemical patterns, we used Light Detection and Ranging (LiDAR) based Digital Elevation Model (DEM) to determine upslope accumulated area for each water sampling site. On average, channel initiation occurred at an UAA of 2655 m² (σ =437 m²) and transitions from ephemeral to intermittent stream flow occurred on average at 3792 m² (σ=824 m²). The transition from intermittent to perennial flow was most variable with an average of 17,358 m² (σ =4498 m²) with a range of 1159 m² to 26,527 m² (Figure 9). The seeps had substantially smaller UAAs than channel initiation sites, with a mean of 803 m² (σ =433 m²). Seeps at the heads of some of the western tributaries, such as W3 and W5, were associated with anomalous perennial flow conditions at channel initiation points. Despite the perennial flow at these initiation points, these sites led to downstream tributaries with intermittent flow (Figure 2).
IV. Results

IVa. Spatial Patterns

On each of the six sampling dates, we saw pronounced spatial variation in surface water chemistry across 41.2 ha WS3, with ranges in solute concentrations similar to those found across the entire 3519 ha HBEF (Table 2). For instance, all median concentrations were similar (within ~50%) between WS3 and all of HBEF, with the exception of Al, which was two times higher in WS3. Within WS3, the concentration range of Al and NO\textsubscript{3} spanned two orders of magnitude, while DOC, K, Mg, and Ca spanned one order of magnitude, and Na, SO\textsubscript{4}, Cl and Si spanned less than one order of magnitude. The pH ranged more than two units for WS3, with a median of 5.0. Across HBEF, the concentration range of K and NO\textsubscript{3} spanned more than two orders of magnitude difference and all other parameters spanned within one to two orders of magnitude. The pH ranged more than three units, with a median of 5.4.

Table 2. Comparison of mean concentration and range of ions from entire 3519 ha Hubbard Brook Valley conducted by Likens and Buso (2006) and 41 ha Watershed 3. Hubbard Brook Valley wide surveys of 625 sites along stream network conducted during moderate flow conditions during spring and fall of 2001. Watershed 3 surveys conducted during similar moderate flow conditions in July 2009 and April 2010.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Median</th>
<th>Watershed 3 Minimum</th>
<th>Maximum</th>
<th>Median</th>
<th>HBEF Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>0.56</td>
<td>0.15</td>
<td>3.53</td>
<td>0.89</td>
<td>0.16</td>
<td>8.47</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.16</td>
<td>0.02</td>
<td>1.02</td>
<td>0.28</td>
<td>0.05</td>
<td>2.31</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.10</td>
<td>0.03</td>
<td>0.58</td>
<td>0.14</td>
<td>0.01</td>
<td>1.86</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.66</td>
<td>0.33</td>
<td>2.48</td>
<td>0.76</td>
<td>0.11</td>
<td>7.68</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.23</td>
<td>0.01</td>
<td>2.27</td>
<td>0.10</td>
<td>0.01</td>
<td>0.71</td>
</tr>
<tr>
<td>pH</td>
<td>5.00</td>
<td>4.07</td>
<td>6.42</td>
<td>5.42</td>
<td>4.00</td>
<td>7.47</td>
</tr>
<tr>
<td>Sulfate</td>
<td>2.46</td>
<td>1.50</td>
<td>4.48</td>
<td>3.96</td>
<td>0.45</td>
<td>5.40</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.01</td>
<td>0.00</td>
<td>1.28</td>
<td>0.09</td>
<td>0.01</td>
<td>0.91</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.26</td>
<td>0.16</td>
<td>1.13</td>
<td>0.31</td>
<td>0.04</td>
<td>0.53</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.89</td>
<td>0.98</td>
<td>4.86</td>
<td>2.33</td>
<td>0.14</td>
<td>6.59</td>
</tr>
<tr>
<td>DOC</td>
<td>2.38</td>
<td>0.83</td>
<td>13.28</td>
<td>3.82</td>
<td>0.38</td>
<td>25.16</td>
</tr>
</tbody>
</table>
In WS3, most of the variability in solute concentrations occurred at sampling sites that had less than 0.6 ha upslope accumulated area (UAA) (Figure 3). Concentrations are relatively invariant with UAA above values of 0.6 ha (6000 m²) within sampling dates. However, between sampling dates, concentrations vary with lowest concentration at highest flow in October and highest concentration at lowest flow in late August. For example, Si concentrations at sample sites with UAA less than 0.6 ha were highly dependent on flow conditions, whereas sites with UAA above 0.6 ha were relatively invariant in both space and time (Figure 3a). During low flow conditions in August 2010, Si ranged from 3.5 to 9.2 mg/L at sample sites with UAA less than 0.6 ha. The same sites during the highest flow conditions in April and October 2010 ranged from less than 1.0 to 3.0 mg/L in Si. From 0.6 to 41.2 ha, Si concentrations were relatively invariant within sample dates; concentrations did not rise above 2.0 mg/L in October, or above 4.0 mg/L in August. Values for pH varied inversely with UAA for baseflow conditions during the August surveys at sites with UAA less than 0.6 ha (Figure 3b). During other flow conditions, pH showed a converging trend at sites with smaller UAA. For sites with UAA greater than 0.6 ha, pH increased to slightly greater than 6 in baseflow conditions, but was constant at 5.2 during higher flow conditions.

Contrasting spatial patterns in solute concentrations between individual stream reaches were similar across sampling dates. The strongest gradients in pH, Ca, and Na were in tributaries W1-3 and PB, where all parameters increased in concentration in a downstream direction (Figure 4). W4 and W5 had the highest pH, Ca, and Na, with variable longitudinal gradients and highest concentrations at the sites closest to seeps. In contrast, the eastern tributaries had the lowest pH, Ca and Na concentrations with minimal increase downstream. Compared to the streams, seeps had the highest pH values and Ca and Na concentrations in the catchment (Figure 4). Spatial
patterns in Al and DOC concentrations were opposite to those shown by pH, Ca, and Na; Al and DOC decreased downstream in tributaries W1-3 and PB and had higher concentrations in the eastern tributaries.

Figure 3 (a). Si versus UAA of sampling sites for all survey dates. Concentrations are relatively invariant with UAA above values of 6000 m^2 within sampling dates. Between sampling dates, concentrations vary with lowest concentration at highest flow in October and high concentration at lowest flow in late August.
Figure 3 (b). pH versus UAA of sampling sites for all survey dates.

DOC concentrations, however, were uniformly low in W1 and W2. Seeps were consistently low in Al, but were variable in DOC content.

Mg and Si showed similar spatial patterns to pH, Ca, and Na, but had weaker gradients. Concentrations generally increased downstream in all tributaries. However, most variability in Mg and Si concentrations were seen in stream and seep comparisons. Higher concentrations of Mg and Si in the seeps are not reflected in the adjacent stream sites, except during the lowest flow conditions (Figure 5). This contrasts with the patterns found for pH, Ca, Na, and Al, where seeps appeared to have an influence on adjacent stream sites during all flow conditions (Figure 6).

NO$_3$, K, SO$_4$, and Cl showed less consistent patterns across space or time compared to those already discussed. NO$_3$ concentrations decreased downstream in W1-4. The eastern tributaries showed no gradients in NO$_3$, but showed differences between tributaries. E2 and E3
had high concentrations of NO$_3^-$, while E4 and PB were uniformly low. Seep concentrations were equal to or lower than stream concentrations. K did not display any consistent spatial patterns. For example, W1 showed concentrations of K decreasing downstream during April and July surveys, but concentrations increased downstream during the October survey. Seeps had higher K concentrations than streams in June and both August surveys, but lower than streams in the October survey. SO$_4^{2-}$ and Cl, which had among the lowest range of variation in concentration amongst the major ions, showed no consistent spatial patterns or differences between seeps and streams. Overall, concentrations of some, but not all, ions are spatially variable, but that variability is not consistent. The inconsistent ions show random variations across space and time.

**IVb. Seeps**

Unusual patterns in solute concentrations, distinct vegetation, and persistent water flow in nine isolated seeps suggest these sites represent distinct water sources. During the first survey in July 2009, we located and sampled 30 sites of groundwater discharge. All but nine of these sites showed similar solute concentrations to the adjacent stream channel (Figure 8). These nine outliers were classified as seeps and were sampled in all six survey dates, while the rest of the groundwater discharge sites were considered to be locations of near stream hyporheic exchange and were not sampled in the remaining surveys. The seeps had low, steady flow rates that did not increase during storms or dry up during extended periods without precipitation. The majority of these sites are not immediately adjacent to the channel. Seven seeps were between 5 m and 100 m from the stream. Two seeps were less than 5 m away from the stream channel, but unlike the hyporheic flow sites that had similar chemistry to the adjacent channel, they appeared to represent a distinct water composition. Seeps had higher pH, Na, Si, and Ca and lower Al than perennial stream sites (Figure 7). Seeps were located along various portions of the western
tributaries and along Paradise Brook at the outlet of the watershed, but no seeps were found along the eastern tributaries (Figure 2). Smaller seeps were characterized by active discharge through organic, wet soils. Larger seeps were also characterized by active discharge but also had distinct vegetation, including species diagnostic of perennial groundwater discharge, such as golden saxifrage (Chrysosplenium americanum Schwein. ex Hook), and species generally associated with rich northern hardwood forests, such as zig-zag goldenrod (Solidago flexicaulis L.) and glade fern (Diplazium pycnocarpon (Spreng.) Broun). These species are indicative of higher Ca concentrations and are absent from the typical acidic northern hardwood forest at HBEF.
Figure 8. Graphs of groundwater concentrations versus the concentrations seen at stream sampling sites most adjacent to seeps, for Ca, Si, Al and pH. All values plotted are potential seep sites, however, actual seep sites (S) considered to be distinct sources were off 1:1 line for at least three parameters shown. Discharge points with water chemistry similar to the adjacent channel were considered to represent hyporheic exchange (H).
IVc. Stream Type and Flow Regime

We examined the relationship between stream chemistry and stream type at each sampling site to differentiate patterns in solute concentrations in perennial, ephemeral and intermittent streams.
Figure 4. Longitudinal stream chemistry graphs for representative eastern and western zero order tributaries, E4 and W3. Seeps located in the W3 sub-catchment are also shown. Samples measured from confluence with first order stream, Paradise Brook.

Figure 5. Maps of low flow August and high flow April surveys for Si concentrations. Circles represent stream sample sites and triangles represent seep sites. Stream type is perennial (solid line), ephemeral (dotted line), and intermittent (double line).

Perennial stream reaches had higher pH, Na, and Si and lower Al, NO₃, and DOC compared to ephemeral and intermittent sampling sites (Figure 7). The intermittent western tributaries included isolated perennial segments, whereas the eastern tributaries were intermittent from first flowing water to the junction with Paradise Brook (Figure 2). In eastern tributaries, there were higher concentrations of Al, NO₃, and DOC and lower pH, Na, and Si. The gradients of these particular ion concentrations in western tributaries were strong, even in intermittent segments. In particular, Ca concentrations showed strong longitudinal gradients in western tributaries (Figure
4), even though there was no consistent difference in Ca concentrations between ephemeral, intermittent, and perennial sites (Figure 7).

Although consistent spatial patterns were seen across tributaries on different survey dates, changes in overall solute concentrations fluctuated according to flow regime. The lowest flow surveys during June and August 2010 showed higher concentrations for Si, SO₄, and Na. The highest flow survey during October 2010 had somewhat lower concentrations for Na, Mg, and Si, and higher concentrations for K, Cl, and DOC. During the snowmelt period in April, Cl concentrations were lowest and NO₃ concentrations were the highest. In contrast, pH was lowest
during the moderate flow July 2009 survey, highest during the low flow August 2010 surveys, and low with minimal spatial variation during high flow in October.
IVd. Groundwater Chemistry

Solute that showed distinct spatial variation in surface water concentrations also varied in the groundwater found between soil groups. Lateral Spodosols with shallow bedrock, which are common in upper eastern portions of the watershed, displayed high concentrations of Al, Fe, DOC, NO₃, and Mn, with low values in pH, Ca and Na (Figure 7). Typical Spodosols, which are the dominant soil type and common in planar and backslopes throughout the watershed, had moderate concentrations for all parameters measured. Bimodal Spodosols and Umbrepts are found in benches and toe slopes and are more common along the western tributaries at the bases of spurs and at lower hillslope areas near the seeps. These had high concentrations of Na, Si and
high pH. Aquepts, found only in the larger seeps, had high concentrations of Mn, Fe, Si, Ca, Na, and NO₃ and had high pH (Figure 7).
V. Discussion

Marked variations in solute concentrations between reaches in WS3 suggest that individual tributaries within a small first order headwater catchment are controlled by varying inputs of groundwater from different soil types and seeps. Soil types are represented by water table dynamics with variable chemistry and water table saturation patterns. Seeps have distinct groundwater dynamics with high, perennial water tables, and have distinct hydric vegetation unique within the HBEF headwater catchments.

The representative elementary area (REA) concept, or the scale where chemical variability within a catchment drastically diminishes, has the potential to partition catchment areas in such a way as to differentiate between local processes and regional controls dominating stream chemistry. Although Temnerud and Bishop (2005) argued for a REA of 1500 ha and Asano et al. (2009) suggested 10 to 150 ha, our research found all solute concentrations become fairly constant when upslope accumulated area was greater than 0.6 ha. We further found that the range in variation in stream chemistry in 3219 ha HBEF (Likens and Buso, 2006) was matched by the chemical range seen in 42 ha WS3. These similarities between Likens and Buso (2006) and our study suggest spatial stream chemistry is behaving as a fractal with chemical variation independent of scale at the watershed level. The dissimilarities between REA values in the literature and the chemistry seen across WS3 and HB suggest sampling density and the inclusion of hotspots, such as seeps, play a large role in the determination of an appropriate REA. The REA value depends upon the type of watershed. We found, by looking at the ephemeral and intermittent streams in a headwater catchment, a REA value much smaller than those reported in literature that focused on medium sized perennial stream networks of fourth to fifth order catchments. An REA value calculated at the hillslope or headwater scale compared to an REA
calculated across a river basin will describe different physical and chemical controls on stream chemistry. For our study, REA represented the extent of soil types and fractured bedrock in the catchment. However, a regional watershed is controlled by processes bigger than soil variability along a hillslope, and instead could be controlled by a combination of distinct landscape components. Thus, we believe REA as an elementary area is questionable.

Before this study, groundwater contributions to streams were not considered to be responsible for variation in stream chemistry at HBEF. Likens and Buso (2006) surveyed stream chemistry across the entire HB Valley, but did not consider groundwater as a major chemical driver in the headwater streams. Johnson et al. (1981) suggested chemical variations were driven by varying flowpath lengths of water in the subsurface, but did not specify groundwater as a source. They spoke of below ground flowpaths but didn’t distinguish between unsaturated and saturated flow processes. Johnson et al. (2000) compared stream chemistry and vadose zone soil water chemistry from high, mid, and low elevations. They explained stream chemistry by the unsaturated zone in soils of different vegetation/elevation zones, and did not recognize groundwater in HBEF catchments. This is the first paper to recognize groundwater as an important aspect in determining stream chemistry. It is apparent local topography and hydrologic positioning cause the development of distinct soil types. Groundwater processes in these soil types are controlling chemical transformations and thus dictating ground and stream water chemistry. We believe the presence of groundwater in different soil types can partially, if not fully, explain the variation in solute composition seen across the catchment.

Western tributaries show stronger gradients in solute chemistry and higher pH and concentrations in Ca, Si, and Na. The presence of bimodal Spodosols and Umbrepts in benches and toe slopes along spurs throughout the western tributaries show elevated levels of pH, Si, and
Na, compared to transient groundwater developed in other soil types (Figure 7). In contrast, eastern tributaries are dominated by high concentrations of Al, Fe, DOC, NO3, Mn, Si, low values in pH, and low concentrations of Ca and Na. These high concentrations mirror the chemistry seen in the transient water tables of lateral Spodosols along the upper portions of the watershed. This is due to shallow flowpaths that interact with high levels of organic matter.

The distinct groundwater chemistry in Umbrepts and bimodal Spodosols may not be enough to explain the steeper gradients in solute concentrations or the anomalous perennial flow found in select portions of western tributaries. Aquepts, however, represent a different, non-transient type of groundwater development and were only found in seeps, as described earlier. These soils have groundwater with high pH and concentrations of Ca, Si, and Na, which are reflected in the adjacent stream reaches. These high levels indicate a contribution from mineral weathering and suggest long-term exposure of weatherable minerals due to a long residence time of groundwater, potentially caused by water moving through deeper flowpaths in deep glacial till or fractured bedrock.

These seeps have two to five times higher concentrations of Si, Ca, and Na, and have higher pH than stream sites (Figure 5) and play a large role in the overall chemistry of the catchment. Western tributaries have perennial stream segments unique to the western portion of the watershed where seeps are present and these tributaries mirror chemical concentrations found in the seeps. In contrast, eastern tributaries are dominated by intermittent and ephemeral stream reaches, have no seeps, and have contrasting solute concentration patterns to what is found in seeps. Seeps have perennial flow and the chemical and physical influence of them is best seen in low flow conditions when groundwater contributions from seeps and near-stream Umbrepts elevate Si and Na at the watershed outlet (Figure 5). Previous studies of watershed-scale mass
balance have seen but not understood these variations of stream chemistry at the watershed outlet. These isolated hotspots explain temporal variation of solute composition at the outlet, especially at low flow conditions. During higher flow conditions, seep contributions become diluted from a larger contribution by the drainage of transient water tables in typical and lateral Spodosols, which dominate the landscape.

Along with distinct seep chemistry, unique subsurface characteristics suggest the possibilities for subsurface flow in the seeps could be from a deep glacial till aquifer or fractured bedrock. For instance, the placement of seeps falls in a linear, northeastern trend, spanning from the base of the watershed to the upper portions of the western tributaries (Figure 6). This local lineation coincides with the regional foliation in metamorphic bedrock (Barton et al., 1997), suggesting fractures could be more dominant on this lineation plane. The upslope accumulated area at these perennial seeps (803 m$^2$) is smaller than that found in the initiation sites of ephemeral stream channels (2655 m$^2$). This suggests subsurface flow boundaries extend beyond topographic drainage divides, since groundwater contributions to seeps cover much smaller areas of the watershed than the perennial seep discharge insinuates. These sites may represent drainage from a deeper till reservoir over a larger area, or fractured bedrock not bound by a topographic divides. Topographic divides could be spurs within the watershed, or the watershed divide itself.
VI. Conclusion

Based on fine scale sampling of surface water in a small headwater catchment, stream chemistry has been found to be more variable across space than time than previously thought. Comparing these variations to groundwater and seep chemical analyses, it is apparent two discrete types of water sources throughout the catchment are regulating the spatial pattern in stream chemistry. We conclude groundwater flowing through distinct soil types based on hillslope position and water table dynamics provide one important mechanisms for controlling stream chemistry. This conclusion contrasts with those of previous studies on water sources at HBEF that have assumed that groundwater is non-existent and that soil water controls stream chemistry. The second stream chemistry source is groundwater discharge from perennial seeps that we believe could be originating from a deep glacial till aquifer or fractured bedrock. It is apparent from our data that the perennial seeps within the catchment act as local hotspots that control the chemical signature of water at the outlet of the catchment at low flow conditions. We believe stream water chemistry at the watershed scale behaves as a fractal and that a potential REA value for a headwater catchment is 0.5 ha. This value is much lower than other REAs calculated using different sampling intervals on larger streams, and so we believe REA is not a robust concept as it depends on scale of sampling and type of watershed.
VII. References Cited


Lawrence GB, Driscoll CT. 1990. Longitudinal patterns of concentration-discharge relationships


