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Fine scale variations of surface water chemistry in an ephemeral to perennial drainage network

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Abstract:

Although temporal variation in headwater stream chemistry has long been used to document baseline conditions and response to environmental drivers, less attention is paid to fine scale spatial variations that could yield clues to processes controlling stream water sources. We documented spatial and temporal variation in water composition in a headwater catchment (41 ha) at the Hubbard Brook Experimental Forest, NH, USA. We sampled every 50 m along an ephemeral to perennial stream network as well as groundwater from seeps and 35 shallow wells across varying flow conditions. Groundwater influences on surface water in this region have not been considered to be important in past studies as relatively coarse soils were assumed to be well drained in steep catchments with flashy runoff response. However, seeps displayed perennial discharge, upslope accumulated areas (UAA) smaller than those for channel initiation sites and higher pH, Ca and Si concentrations than streams, suggesting relatively long groundwater residence time or long subsurface flow paths not bound by topographic divides. Coupled with a large range in groundwater chemistry seen in wells, these results suggest stream chemistry variation reflects the range of connectivity with, and quality of, groundwater controlled by hillslope hydropedological processes. The magnitude of variations of solute concentrations seen in the first order catchment was as broad as that seen at the fifth order Hubbard Brook Valley (3519 ha). Reduction in variation in solute concentrations with increasing UAA suggested a representative elementary area (REA) value of less than 3 ha in the first order catchment, compared with 100 ha for the fifth order basin. Thus, the REA is not necessarily an elementary catchment property. Rather, the partitioning of variation between highly variable upstream sources and relatively homogenous downstream characteristics may have different physical significance depending on the scale and complexity of the catchment under examination. Copyright © 2012 John Wiley & Sons, Ltd.

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KEY WORDS headwater catchments; surface water chemistry; representative elementary area

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INTRODUCTION

Processes that determine physical, chemical, and biological patterns of forested catchments operate and interact at multiple spatial and temporal scales (Naiman *et al*., 1988; Lowe *et al*., 2006; Leibowitz *et al*., 2008). The interplay of these processes can be seen through spatial variations, or patterns, in stream chemistry (Lawrence and Driscoll, 1990; Fisher *et al*., 2004). However, the mechanistic linkages between the spatial variations in stream water chemistry and the processes that control these patterns are complex and not clearly evident (Turner, 1989; Sivapalan, 2005; Turner, 2005). Further, the scale at which one samples streams affects our perceived understanding of the absolute range of chemical composition across the system as well as the relationship between site-specific composition and influence of local physical, chemical, and biological drivers (Gustafson, 1998).

A priority of catchment research has been to better understand the extent to which headwater regions control downstream water quality (Gomi *et al*., 2002; Alexander *et al*., 2007; Freeman *et al*., 2007; Nadeau and Rains, 2007; Temnerud *et al*., 2010). That said, studies that address spatial and temporal stream chemistry in tributaries as a means of assessing catchment processes and distribution of water sources across a catchment are limited (Temnerud and Bishop, 2005; Likens and Buso, 2006; Asano *et al*., 2009). In such studies, perennial streams are typically emphasized over ephemeral and intermittent channels, which are rarely documented on topographical maps (Bishop *et al*., 2008), or considered in land use management guidelines and regulations (e.g. Blinn and Kilgore, 2004; Dodds and Oakes, 2008). It has been shown, however, that larger catchments, on the scale of fourth and fifth order streams (catchment size of 30–80 km^2) can reflect the range of chemical variation seen within their headwaters (Wolock *et al*., 1997; Temnerud and Bishop, 2005; Temnerud *et al*., 2010). By extension, one may hypothesize that perennial portions of headwater stream networks reflect a range of chemical variation seen within the ephemeral and intermittent channels of smaller catchments yet. Therefore,

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finer scale investigation on the variation in the entire stream network in catchments of zero and first order streams (catchment size of $<1\,\mathrm{km}^2$) is a necessary next step to increase our understanding of the patterns within headwater catchments and processes that dominate the regulation of downstream surface water quality. Here we report a study of chemical variation in an ephemeral, intermittent, and perennial surface water network (zero and first order streams) across a broad range of flow conditions.

A common approach to headwater research is to explain variation of stream chemistry at the catchment scale as controlled by variable proportions of end members of specific water that mix to create the observed stream composition. Studies that have used end member mixing analysis have sampled subsurface water from piezometers and surface water during snowmelt (Kendall *et al.*, 1999; McGlynn *et al.*, 1999), stormflow (Burns *et al.*, 2001), and baseflow (Asano *et al.*, 2009). The assumption that end members of specific water composition are homogeneous in space is imperative for an accurate analysis if sampling a representative location within a larger area. For example, Asano *et al.* (2009) assumed bedrock geology, soil type, and land use were homogeneous within the study catchment, and thus spatial distribution of sampling would not affect end member chemistry. Burns *et al.* (2001) only collected subsurface samples from one hillslope location and one outcrop runoff location and assumed homogeneity across the catchment. McGlynn *et al.* (1999) saw variability within subsurface water chemistry along a 15-piezometer riparian transect, yet assigned sites with variable chemistry as the same source. Although these studies are valuable in understanding broad sources of exported solutes, they may be missing the effects of different hillslope landscape units on subsurface water chemistry. Most analyses to date assume the proposed end members do not vary in space, however, at this point, it is unclear what the effects of spatial heterogeneity of landscape units on water source contribution calculations are and how variability within an end member, such as soil water or hillslope types across a catchment, affects mixing calculations. In our study, we address this uncertainty by sampling subsurface water chemistry at 35 shallow well locations throughout the 41 ha headwater catchment. This high density sampling regime allows us the opportunity to examine if the variability within predictable hillslope units and soil types is low enough to allow for accurate future end member mixing analyses.

Seasonal effects on water sources and subsurface flowpaths play a role in stream chemistry. Johnson *et al.* (2000), Wellington and Driscoll (2004), and Palmer *et al.* (2005) found that stream chemistry at Hubbard Brook Experimental Forest (HBEF) was affected by location of subsurface flowpath within the various soil horizons before entering the stream. These studies concluded high dissolved organic carbon (DOC), aluminium (Al), and low pH in stream chemistry typically occurs because of subsurface water moving through shallow flowpaths (e.g. due to a rain event temporally raising the water table) where it comes into contact with soil having high organic content. High concentrations of silicon (Si), on the other hand, suggested flowpaths that had a longer residence time or contact with Si-rich bedrock. From these studies, we hypothesized spatial variation would be more spatially uniform across stream reaches during periods of high flow conditions (e.g. snowmelt) because the water level will become elevated during such an influx of melt water causing subsurface water to be uniformly driven through shallow flowpaths. In contrast, during low flow conditions, when portions of the stream network more influenced by groundwater contributions would be more prevalent, we hypothesized spatial variability in stream chemistry would be more prominent because groundwater flowpaths will flow through variable end member soil types producing differences in stream chemistry across reaches.

Spatial variation in stream chemistry across a catchment reflects the presence of different hillslope processes and thus variable soil chemistry from different hillslope positions. Reach scale studies that relate streamflow generation to hillslope processes can demonstrate how certain portions of catchments represented by distinct hillslope positions, such as topographic spurs and hollows, regulate generation and retention of specific solutes (e.g. Jencso *et al.*, 2010). For example, soil organic matter is critical for the retention and cycling of many elements, including sulfur (S), nitrogen (N), Al, and mercury (Hg). Soil carbon retention, however, can vary between soil types (Oades, 1988) and hotspots (McClain *et al.*, 2003). The distribution of soil types can be located spatially along flowpaths, and therefore, the composition and length of water flowpath may play a role in solute regulation. Furthermore, hotspots, discrete areas that play disproportionately important roles in solute generation (*cf* McClain *et al.*, 2003) may occur in small areas within catchments, such as near-stream zones (Cirmo and McDonnell, 1997; Burt *et al.*, 2010), or groundwater seeps, and are nearly impossible to assess at the catchment outlet because they represent very limited areas within the system and thus may be unrealized in end member mixing analyses. With the use of finer scale studies, we can better understand which hillslope features regulate the retention and mobilization of said elements, thus influencing surface water chemistry.

Research at HBEF has generated extensive knowledge of ecosystem processes at the small catchment scale (11.8–68.4 ha) and thus is an ideal place to study stream chemistry patterns. Several studies have specifically examined variations in stream chemistry in regard to water sources or flowpaths that control the stream water characteristics. Johnson *et al.* (1981) sampled nine sites along a stream channel throughout a 3-year period and concluded that the longitudinal chemistry patterns seen in Falls Brook, a first order tributary at HBEF, were a result of varying lengths of subsurface flowpaths. As flowpath length increased moving downstream, neutralization of acid inputs to the stream, from precipitation, also increased. Hooper and Shoemaker (1986) sampled the stream channel and riparian piezometers at four primary sites along the stream network within watershed 3, our current study site, during baseflow, snowmelt, and rain events during a duration of 4 months and were able to separate 'new' and 'old' water contributions to different portions of the stream network through the use of Si as a conservative tracer. They noted that high concentrations of Si are an indicator of deep water contributions and the concentrations of Si could help pinpoint rates of weathering and thus residence time of the water. Johnson *et al.* (2000) inferred how subsurface water flowpaths vary by altitude in a catchment, through long-term (since 1982) monthly sampling of one soil water and one surface water site across three elevational zones in a headwater catchment at HBEF. Wellington and Driscoll (2004) found episodic acidification of streams within an HBEF watershed during snowmelt and rain events, as a result of the flushing of strongly acidic organic acids and nitrate (NO_3) from the upper soil layers. They also showed that antecedent soil moisture plays a role in the magnitude of solutes exported from the soil during rain events. Palmer *et al.* (2005) examined Al and DOC concentrations at 200–300 m intervals along seven streams (on average 11 samples per stream) in the Hubbard Brook Valley during baseflow conditions. Likens and Buso (2006) sampled surface water at Hubbard Brook tributary junctions and at 100 m intervals until first flowing water along each major tributary twice during intermediate flow conditions (fall and spring). Although these studies have given us a better understanding of the mechanisms controlling stream chemistry, the majority of these studies focused solely on perennial stream sections within the Hubbard Brook Valley (except Hooper and Shoemaker, 1986). The dominant water sources and processes controlling stream chemistry at HBEF have not been studied across the entire ephemeral, intermittent, and perennial stream network, as presumably the mechanisms controlling stream chemistry vary between these different stream types. To address this gap in our knowledge, we compared spatial and temporal stream chemistry variations across the entire ephemeral, intermittent, and perennial stream network in one of the long-term experimental watersheds, with groundwater and seep chemistry, and determined surface and subsurface characteristics, such as upslope accumulated area and soil type, to infer the dominant sources and processes controlling surface water chemistry.

The scale of stream water sampling needed to identify local landscape processes can be difficult to determine, as many catchment properties vary at different scales. The representative elementary area (REA) has been proposed as a metric to describe a threshold in catchment area for which downstream surface water chemistry variation can be predicted based upon upstream ranges (Wolock *et al.*, 1997). Studies have used this threshold in the spatial stream chemistry range to describe the watershed area necessary to differentiate between local processes responsible for chemical variation in headwaters and regional controls on chemistry in larger streams and catchments. Wood *et al.* (1988) and Wolock (1995) suggested the size of an REA was related to topography of a basin as well as soil characteristics. Studies in other regions have found a wide range in REA values between 10 and 1500 ha for upland forested catchments comprised of fourth and fifth order streams (Wolock *et al.*, 1997; Temnerud and Bishop, 2005; Asano *et al.*, 2009). Variation in stream chemistry at HBEF decreases for streams with $>$100 ha drainage area as estimated from Likens and Buso (2006). Sampling density for these previously published surveys was less than 0.2 sampling sites/ha and focused on larger catchments and perennial stream reaches. Fine scale sampling in a headwater catchment, which encompasses zero-order ephemeral and intermittent streams, has not been performed but has the ability to evaluate the applicability of the REA concept to smaller headwater stream systems.

Although studies have examined REA values in larger catchments, Asano *et al.* (2009) suggested that sections of the catchments that are below the critical threshold area will show convergent or asymptotic behaviour in solute concentrations with increasing catchment size, until the critical threshold area has been reached and stream chemistry becomes uniform. They proposed this converging behaviour may be due to subsequent mixing of different water sources as one moves downstream and that asymptotic behaviour may be due to longitudinal changes in landscape units, which cause a masking of water source contribution by landscape processes, such as biological uptake. Because we hypothesized water sources in ephemeral, intermittent, and perennial streams will be based on seasonal contributions of baseflow groundwater and event water, we further hypothesized the REA value will vary with seasonal flow conditions. For example, in high flow conditions, such as snowmelt, the REA value will be smaller, as the water source contributions will be driven by shallow groundwater flowpaths that are in contact with the homogeneous upper layers of organic-rich soils.

We took a fine scale approach to surveying surface water in WS3, a 41 ha headwater catchment in HBEF, in order to

1. Map the full extent of a headwater catchment surface water network, including ephemeral, intermittent, and perennial streams as well as groundwater discharge points (seeps).
2. Characterize spatial and temporal surface water chemistry patterns through high density sampling conducted over a range of seasons and hydrologic conditions.
3. Examine the variation in temporal and spatial stream chemistry patterns in an ephemeral to perennial stream network in relation to catchment area to evaluate the REA concept at a finer scale than had been previously reported.
4. Evaluate spatial groundwater chemistry variation to determine if mixing variation of a groundwater end member might be an appropriate tool to evaluate variation in stream water chemistry.

METHODS

Setting

This study took place in watershed 3 (WS3), a 41 ha reference catchment of HBEF, located within the southern White Mountains of central New Hampshire (43°56′N, 71°45′W). The climate of HBEF is humid continental with average January and July temperatures of −9 and 18 °C, respectively. Roughly 25–33% of the 1400 mm of annual precipitation occurs as snow, and almost 50% of the 870 mm of annual runoff occurs during the spring snowmelt period (Bailey *et al.*, 2003). Elevation ranges from 229 to 1015 m in the HBEF and 527 to 732 m in WS3. The experimental catchments are steep (20–30%) and are south facing (Likens and Bormann, 1995). WS3 comprises the headwaters of Paradise Brook (PB), a first order stream within WS3 and 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*) at lower to middle elevations. 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 catchment divide (Likens and Bormann, 1995).

The catchment is underlain by mica schist bedrock of the Silurian Rangeley Formation with a foliation striking north to northeast, reflecting regional metamorphism (Barton *et al.*, 1997). Bedrock is exposed along the upper boundaries of the watershed and in a few locations along the stream network. Spodosols of sandy loam texture developed in the shallow granitoid glacial till parent material are the main soil type present. Detty and McGuire (2010a) divided WS3 into three regions on the basis of drainage network organization (Figure 1): 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. The main stem of PB runs southwesterly through the central part of the watershed. We identified ephemeral stream channels in the field and used the field survey to extend a light detection and ranging (LiDAR) digital elevation model (DEM) generated drainage map of the watershed (Figure 1).

Topographic characteristics

In order to evaluate the role of surficial processes in streamflow generation and spatial chemical patterns, we resampled a 1 m airborne LiDAR DEM derived from data acquired in November 2009 to create a 5 m DEM and to determine upslope accumulated area (UAA) for each water sampling site. All sampling points were georeferenced using a Trimble Geoexplorer XT GPS unit with an external antenna and real time correction to achieve a precision of approximately 1 m. UAA for each sampling point was calculated using a triangular multiple flow direction algorithm (Seibert and McGlynn, 2007).

Surface water survey

The tributaries were categorized into stream types based on Hansen (2001). Sites were characterized as having perennial (permanent flow), intermittent (seasonal

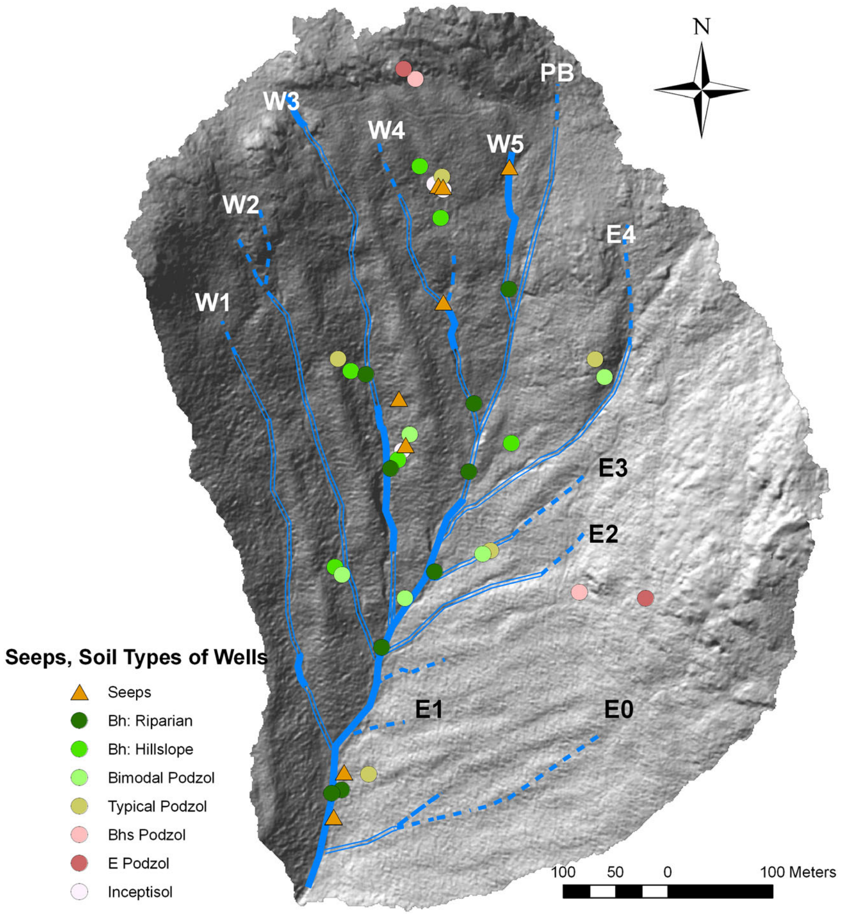

Figure 1. Watershed 3, shown with a hillshade representation of a 1 m digital elevation model. Circles represent groundwater sampling wells with soil type designation. Orange triangles represent locations of seeps. Each tributary is labelled at its head with the subwatershed designation. Stream reaches are classified by flow regime as ephemeral (dashed line), intermittent (double line), or perennial (solid line)

flow primarily during the non-growing season), or ephemeral flow (flow for hours or days only after large storm events). Channel initiation for each tributary was delineated in the field as locations with first sign of ephemeral flow with displacement of leaves and organic matter. Transitions between stream types were quantified by repeated field surveys of the stream network during a range of flow conditions. Seeps or natural groundwater discharge points located outside the stream channel were also mapped. There were nine seeps sampled during each survey if visible flow was observed (90% of the time). Surface water samples were taken approximately every 50 m along the main 800 m perennial PB and its ten seasonal tributaries (ranging in length from 50 to 600 m; Figure 1) when flowing water was present. Streams were sampled six times during a broad range of flow conditions (Table I). 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 in order to minimize collection of sediment (<10% of all samples were collected with syringes). Seeps required syringe sampling as well, as there were no defined channels in the mucky organic soils in seeps. Samples were filtered in the field with a 0.45 μM glass microfiber filter. Samples were collected within a 6-hour period on each survey date, refrigerated, and shipped monthly to the analytical lab for chemical analysis. Water samples were analysed for all major solutes as well as a few trace solutes (iron (Fe), manganese (Mn)). pH was measured potentiometrically with a Broadley James rain probe within a day of sample collection at the field lab. Dissolved metals, including Ca, Al, Na, Mg, Si, and K, were analysed on a Varian Vista axial inductively coupled plasma spectrometer at the Forestry Sciences Laboratory (FSL), Durham, NH, USA. Trace metals including Mn and Fe were analysed by Perkin Elmer Elan 6000 ICP-MS at the US Geological Survey, Menlo Park, CA, USA. Precision is estimated to be better than 3% for these elements. Other analyses made at the FSL included the anions Cl, NO_3, and SO_4 on a Metrohm-Peak 761 compact ion chromatograph, DOC on a Shimadzu TOC-5000A, and total dissolved nitrogen on an Antek nitrogen detector.

Groundwater survey

We sampled groundwater across WS3 from a suite of wells installed during the work described by Detty and McGuire (2010a,b). Installation focused on near stream areas (concave footslopes), hillslopes (planar backslopes), and topographic divides (convex shoulders). Each well was constructed of SDR 21 PVC pipe (3.18 cm outer diameter) with a 31 cm screen length consisting of 0.025 cm width lateral slots with 0.32 cm spacing between slots (Detty and McGuire, 2010a,b). The wells were installed so the base of the screen was in the upper C horizon, between 40 and 100 cm deep. Additional wells were installed during the present study around two of the larger seeps as well as in soil types underrepresented by earlier installations. For the purpose of comparing groundwater chemistry, wells were stratified into soil groups on the basis of the assumption that soil morphology reflects differences in groundwater conditions (this assumption is being tested with on-going studies) (Table II; Figure 1). A battery-operated peristaltic pump was used to purge the wells and collect water samples for chemical analyses. Groundwater samples were analysed for the same parameters as surface water samples.

RESULTS

Drainage network characteristics

By overlaying a grid of UAA on the stream network map, we determined the UAA associated with the locations of stream type transitions. On average, channel initiation occurred at a UAA of 0.25 ha and transitions from ephemeral to intermittent streamflow occurred on average at 0.83 ha. The transition from intermittent to perennial flow occurred at an average UAA of 17.8 ha. A break from the normal pattern of increasing prevalence of flow with accumulating subcatchment area was observed with the transition from perennial back to intermittent flow at several sites. This transition was most variable with average UAA of 1.42 ha with a range of 0.43–3.64 ha (Figure 2). Groundwater seeps had substantially smaller UAAs than channel initiation sites, with a mean of 0.08 ha. 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. These perennial sites had an average UAA of 0.18 ha. Despite the perennial flow

Table I. Dates, conditions, and number of samples collected for the six surveys of surface water chemistry of watershed 3

Survey date	Stream sites sampled	Seeps sampled	Streamflow (mm/h)	Exceedance probability (%)	Seasonal conditions
9 July 2009	119	7	0.177	14.2	Early summer, relatively wet
1 April 2010	98	9	0.278	12.8	Immediate post-snow melt
18 June 2010	53	8	0.027	63.8	Late spring, low flow
6 August 2010	34	8	0.014	77.1	Late summer, baseflow
21 August 2010	17	5	0.005	87.5	Extremely low flow
1 October 2010	103	9	3.207	0.2	First large storm of the autumn

Exceedance probability refers to the percentage of the streamflow record (years 2000–2010) at the gauged outlet that exceeds the streamflow conditions during the survey period.

Table II. Morphology of soil units defined by Brousseau *et al.* (in prep) and general setting of groundwater monitoring wells

Soil Description	Number of wells	General setting
E podzol: shallow soils dominated by an eluvial horizon (E – mineral particles stripped of organic matter, Fe, and Al)	2	Within and immediately downslope of areas of interspersed bedrock outcrops
Bhs podzol: shallow soils dominated by an illuvial horizon (Bhs – depositon of organic–Fe–Al complexes on mineral surfaces)	2	Immediately downslope of E podzols, near bedrock outcrops
Typical podzols: deeper soils with thin E and Bhs horizons	5	Dominant in the portions of the catchment with deeper glacial drift; typical of backslopes
Bimodal podzols: deeper soils with a typical (thin E and Bhs) upper sequence and a zone of organic matter illuviation at the B/C interface	4	At breaks of slope (concave hillslope positions) and footslopes.
Bh podzols: dominated by Bh horizons (generally lacking E and Bhs horizons)	6	Toeslopes and streamside locations
Inceptisols (lacking E, Bhs, and Bh horizons)	5	Seeps

at these initiation points, these sites led to downstream tributaries with intermittent flow (Figure 1). Tukey's honestly significant difference criterion ($\alpha = 0.05$) demonstrated that the UAA values of seep sites and channel initiation sites were significantly different from all other channel transition sites (Figure 2).

Seeps

Distinct solute concentrations compared with surface water, distinct vegetation, and persistent water flow in nine isolated seeps suggest these sites represent upwelling of groundwater. During initial surveys, we located and sampled 30 sites of groundwater discharge, mostly occurring in stream bank locations. All but nine of these groundwater discharge sites showed similar solute concentrations to the adjacent stream channel and had variable flow conditions mimicking fluctuations in streamflow. These were considered to represent hyporheic exchange and not sampled further. Of the nine groundwater discharge points with distinct chemistry, four of these sites were on benches away from the near-stream zone, two were channel initiation sites of western tributaries, and three were small saturated areas on the stream bank-adjacent mid-portions of stream reaches. Together these nine sites, considered to represent distinct sources of groundwater to the stream network, were included in the subsequent sample surveys.

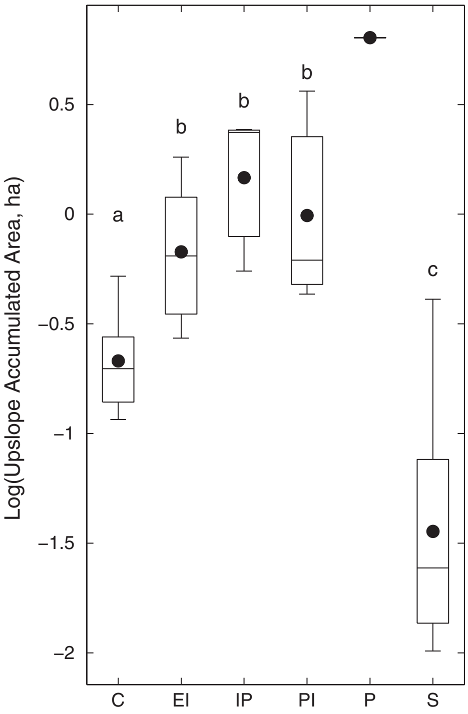

Figure 2. Mean and standard error for upslope accumulated area for stream channel initiation points (C; $n = 15$), transition from ephemeral to intermittent flow (EI; $n = 9$), transition from intermittent to perennial flow (IP; $n = 3$), transition from perennial to intermittent flow (PI; $n = 5$), first perennial site on Paradise Brook (P, $n = 1$), and seeps (S; $n = 9$). P represents the only site in WS3 that is continuously perennial downstream from the site. Lower case letters above each boxplot indicate a statistically significant difference in means ($p < 0.05$)

The seeps had perennial flow that was relatively invariant compared with stream channel flow across all seasonal conditions. Observations of the direction of flow in the field confirmed that the near-stream seeps were recharged from upslope and not from riparian exchange from the adjacent channel. Seeps had higher pH, Na, Si, and Ca and lower Al than perennial stream sites (Figure 3). Seeps were located along various portions of the western tributaries and along PB near the outlet of the watershed, but no seeps were found along the eastern tributaries (Figure 1). Smaller seeps were characterized by active discharge through perennially saturated organic soils. Larger seeps were further characterized by distinct vegetation, including species diagnostic of perennial groundwater discharge, such as golden saxifrage (*Chrysosplenium americanum* Schwein. ex Hook), and species generally associated with enriched northern hardwood forests (Sperduto and Kimball, 2011), such as zigzag goldenrod (*Solidago flexicaulis* L.) and silvery glade fern (*Deparia acrostichoides* (Sw.) M. Kato). These species are indicative of higher pH or Ca concentrations and are otherwise absent from the typical acidic northern hardwood forest at HBEF.

Spatial patterns

This section of results will focus on our comparison of ranges in stream chemistry across WS3 and HBEF as well as our assessment of spatial patterns in surface water chemistry

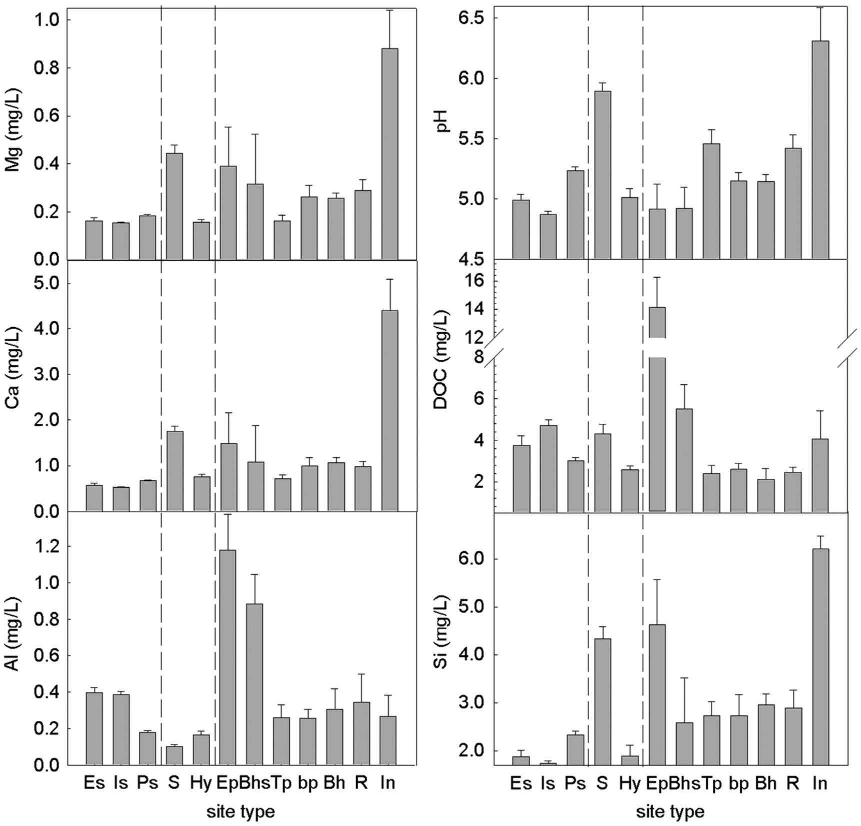

Figure 3. Mean and standard error of ion concentrations and pH in surface water by streamflow regime (left of first dashed line), groundwater discharge type (central section), and groundwater from wells in distinct soil types (right of second dashed line) including: ephemeral streamflow (Es; $n = 39$), intermittent streamflow (Is; $n = 236$), perennial streamflow (Ps; $n = 136$), seeps (S; $n = 49$), hyporheic (Hy; $n = 16$), E podzol (Ep; $n = 7$), Bhs podzol (Bhs; $n = 6$), typical podzol (Tp; $n = 8$), bimodal podzol (bp; $n = 11$), Bh podzol (Bh; $n = 15$), riparian Bh podzol (R; $n = 22$), and inceptisol (In; $n = 10$)

as controlled by UAA. It also examines, how eastern and western tributaries differentiate themselves on the basis of spatial stream chemistry patterns and how stream type (perennial, intermittent and ephemeral) is a control on stream chemistry. Spatial patterns of groups of solutes that respond similarly are shown with a subset of solutes that best represent the general patterns we observed. A complete collection of solute maps is provided in the Supporting Information.

In order to examine spatial patterns in surface water chemistry, we first looked at the ranges in stream chemistry across 41 ha WS3 with those found across the entire 3519 ha HBEF. On each of the six sampling dates, we saw pronounced spatial variation in surface water chemistry across WS3, with the range of variations in solute concentrations similar to those found across HBEF (Table III). 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_3 spanned two orders of magnitude, whereas DOC, K, Mg, and Ca spanned one order of magnitude, and Na, SO_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_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.

We examined how spatial patterns in surface water chemistry are related to UAA. In WS3, most of the variability in solute concentrations occurred at sampling sites that had less than 0.6–3.0 ha UAA (Figure 4), with noticeable reductions in variation occurring at both of these values. Concentrations were relatively invariant with UAA above values of 0.6–3.0 ha within sampling dates. However, between sampling dates, some solute concentrations vary between 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 Si concentrations at sites with UAA above 0.6 ha were relatively invariant in both space and time (Figure 5a). 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 5b). 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.

Table III. 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

	Watershed 3			HBEF		
Ion	Median	Minimum	Maximum	Median	Minimum	Maximum
Calcium	0.56	0.15	3.53	0.89	0.16	8.47
Magnesium	0.16	0.02	1.02	0.28	0.05	2.31
Potassium	0.10	0.03	0.58	0.14	0.01	1.86
Sodium	0.66	0.33	2.48	0.76	0.11	7.68
Aluminium	0.23	0.01	2.27	0.10	0.01	0.71
pH	5.00	4.07	6.42	5.42	4.00	7.47
Sulfate	2.46	1.50	4.48	3.96	0.45	5.40
Nitrate	0.01	0.00	1.28	0.09	0.01	0.91
Chloride	0.26	0.16	1.13	0.31	0.04	0.53
Silicon	1.89	0.98	4.86	2.33	0.14	6.59
DOC	2.38	0.83	13.28	3.82	0.38	25.16

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.

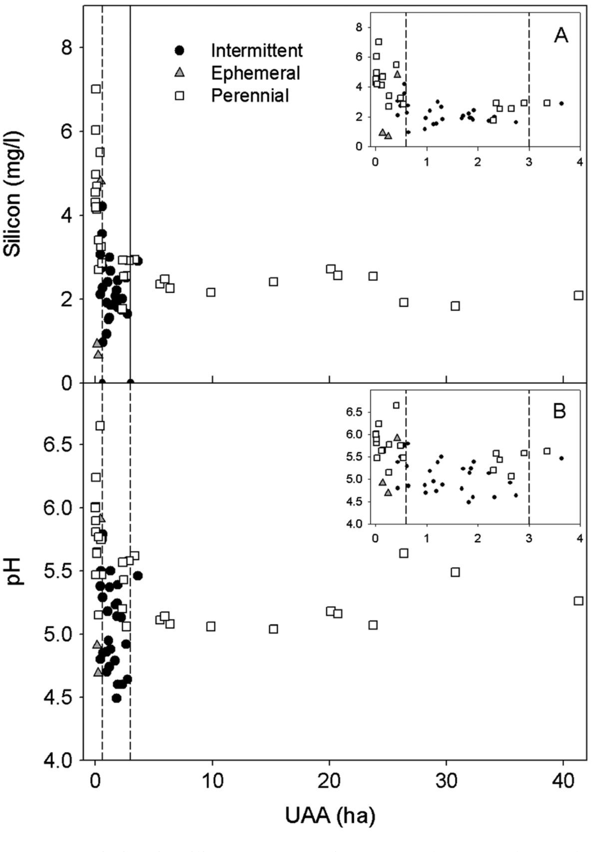

Figure 4. Variation in silicon concentration (A) and pH (B) by upslope accumulated area (UAA) of surface water sampling sites on 18 June 2010. The inset expands the *x*-axis to focus on variation less than 4 ha. The vertical dashed lines indicate UAA values of 0.6 and 3.0 ha where noticeable reduction in solute variation occurs

We investigated how tributaries within the catchment differentiated in spatial patterns in specific solute concentrations. We discovered the spatial patterns in solute concentrations within individual stream reaches were persistent across sampling dates. The strongest gradients in concentration over distance in pH, Ca, and Na were in tributaries W1, W2, W3, and PB, where all parameters increased in concentration in a downstream direction (e.g. Figure 6). W4 and W5 had the highest pH, Ca, and Na observed in streams, with variable longitudinal gradients and highest concentrations at the sites closest to seeps (see supporting information). In contrast, the eastern tributaries had the lowest pH, Ca, and Na concentrations with minimal increase downstream. Compared with the streams, seeps had the highest pH values and Ca and Na concentrations in the catchment (Figure 3). 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, W2, W3, and PB and had higher concentrations in the eastern tributaries. DOC concentrations, however, were uniformly low in W1 and W2. Seeps were consistently low in Al but were variable in DOC content (Figure 8; Supporting Information).

Mg and Si showed similar spatial patterns to pH, Ca, and Na, but had weaker gradients or overall spatial changes in concentration. Concentrations generally increased downstream in all tributaries, however, the largest variability in Mg and Si concentrations were seen in stream and seep comparisons. Higher concentrations of Mg and Si were typical in the seeps and were seen in stream sites downstream of seeps during the low flow conditions (see Figure 7 for Si; other parameters in Supporting Information). 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 8 for Al). That is, adjacent stream sites have elevated concentrations of these parameters across all dates, whereas the tributaries that are not directly connected to seep discharge have lower concentrations that seem to fluctuate as varying flow conditions affect the connectivity of the adjacent hillslopes to the streams.

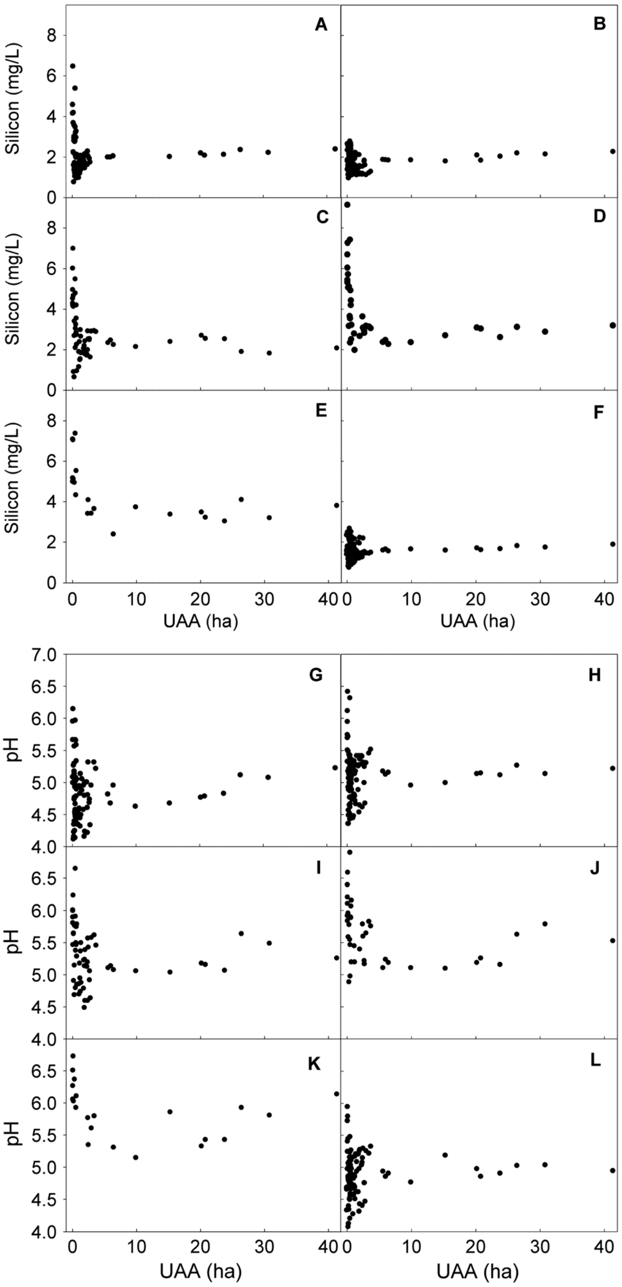

Figure 5. (a) Concentration of silicon *versus* upslope accumulated area (UAA) of sampling sites for survey dates: (A) 9 July 2009, (B) 1 April 2010, (C) 18 June 2010, (D) 6 August 2010, (E) 21 August 2010, and (F) 1 October 2010. (b) pH *versus* UAA of sampling sites for all survey dates: (G) 9 July 2009, (H) 1 April 2010, (I) 18 June 2010, (J) 6 August 2010, (K) 21 August 2010, and (L) 1 October 2010

Nitrate, K, SO_4, and Cl showed less consistent patterns across space or time compared with those already discussed. Nitrate concentrations decreased downstream in W1, W2, W3, and W4. The eastern tributaries showed no gradients in NO_3 but showed differences between tributaries. E2 and E3 had high concentrations of NO_3, whereas E4 and PB were uniformly low. Seep concentrations were equal to or lower than stream concentrations. Potassium 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. Sulfate 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.

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. Perennial stream reaches had higher pH, Na, and Si and lower Al, NO3, and DOC compared with ephemeral and intermittent sampling sites (Figure 3). The intermittent western tributaries included isolated perennial segments, whereas the eastern tributaries had ephemeral headwaters that transitioned to intermittent between 5 and 250 m from the junction with perennial PB (Figure 1). 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, Na concentrations showed strong longitudinal gradients in western tributaries (Figure 6), even though there was no consistent difference in Na concentrations between ephemeral, intermittent, and perennial sites (Figure 3).

Although consistent patterns in relative differences in solute concentrations along reaches were seen on all the survey dates, changes in overall solute concentrations fluctuated according to flow regime. The lowest flow surveys during June and August 2010 showed higher concentrations of Si, SO_4, and Na, compared with concentrations seen in higher flow surveys. The highest flow survey during October 2010 had somewhat lower concentrations of Na, Mg, and Si, and higher concentrations of K, Cl, and DOC, compared with concentrations seen in lower flow surveys. During the snowmelt period in April, Cl concentrations were lowest and NO_3 concentrations were the highest of the sampling surveys. 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 October 2010 survey.

Groundwater chemistry

Solutes that showed distinct spatial variation in surface water concentrations also varied in the groundwater found between soil groups. Water sampled from E and Bhs podzols with shallow bedrock, which are common in upper eastern portions of the watershed (Table II), displayed high concentrations of Al, Fe, DOC, NO_3, and Mn, with low values in pH, Ca, and Na (Figure 3). Water sampled from typical podzols, which are the dominant soil type and common on planar slopes and backslopes throughout the watershed (Table II), had moderate concentrations for all parameters measured. Bimodal podzols and Bh podzols were found in benches and toe slopes and are more common along the western tributaries at the bases of

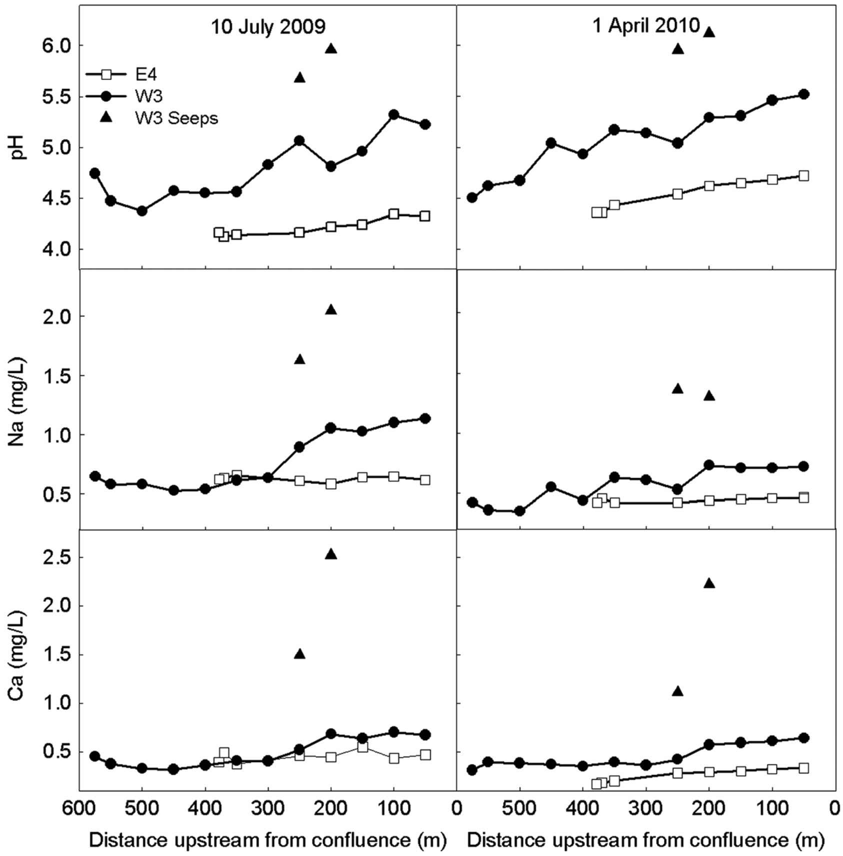

Figure 6. Longitudinal stream chemistry graphs for representative eastern and western zero order tributaries, E4 and W3. Seeps located in the W3 subcatchment are also shown. Samples sites are plotted by distance measured upstream from the confluence with first order stream, Paradise Brook

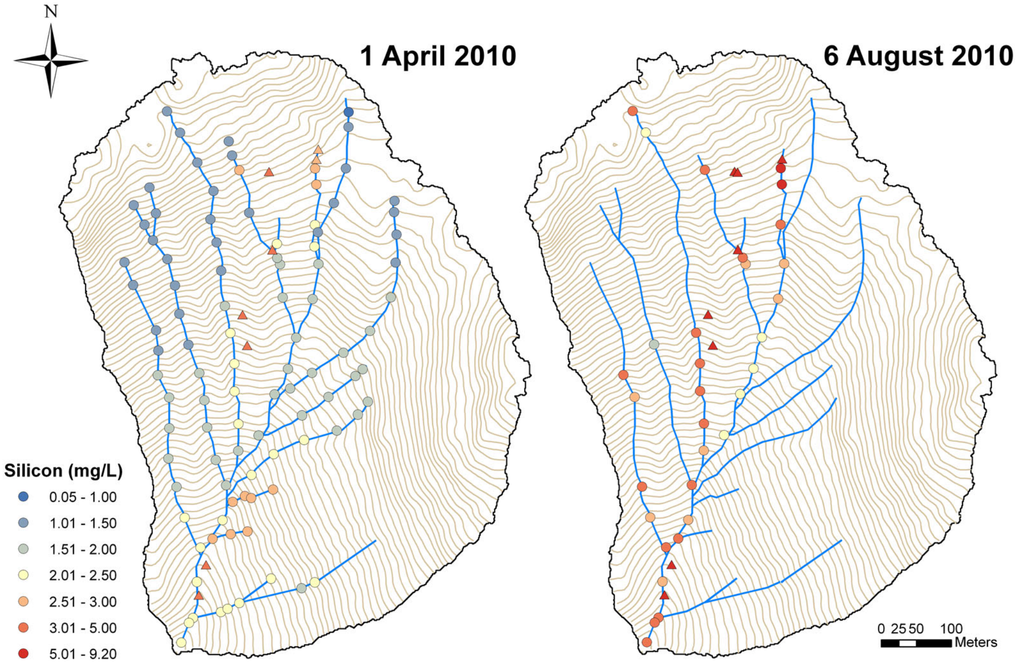

Figure 7. Maps of high flow (1 April 2010) and low flow (6 August 2010) surveys for silicon concentrations. Circles represent stream sample sites and triangles represent seep sites. The same colour ramp designates solute concentrations in both streams and seeps

spurs and at lower hillslope areas near the seeps (Table II). Water sampled from these soils had high concentrations of Na and Si and high pH. Water sampled from Inceptisols, found only in the larger seeps (Table II), had high concentrations of Mn, Fe, Si, Ca, Na, and NO_3, and had high pH (Figure 3).

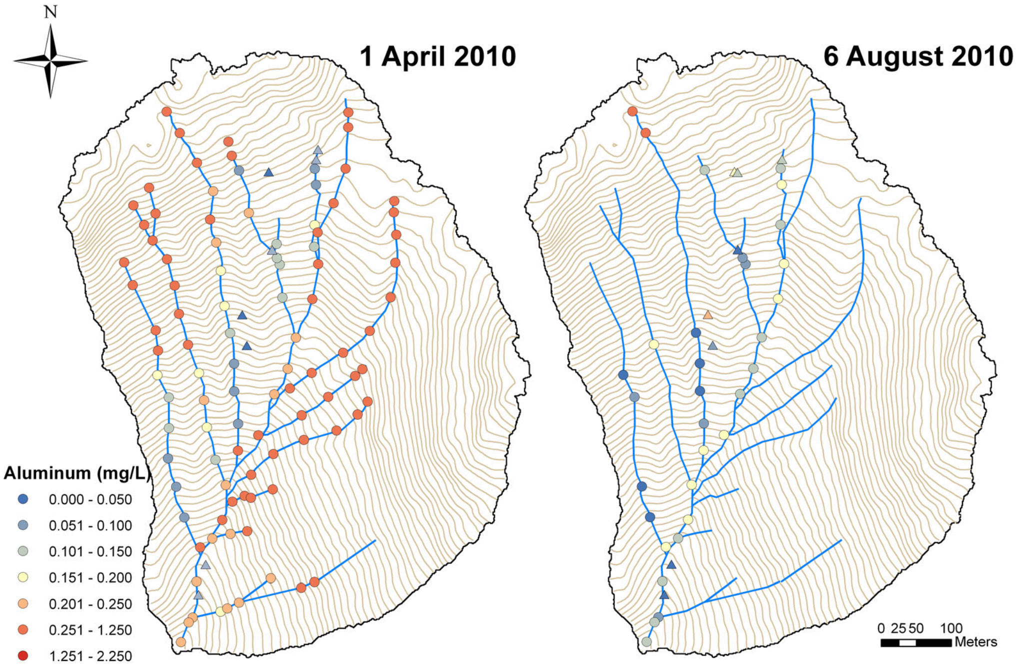

Figure 8. Maps of high flow (1 April 2010) and low flow (6 August 2010) surveys for aluminium concentrations

DISCUSSION

We found that the range of variation in most of the stream solute concentrations in 3219 ha HBEF (Likens and Buso, 2006) was similar to the chemical range seen in 41 ha WS3. These similarities between the study of the larger HBEF by 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. This contradicts our initial hypothesis based on the literature (e.g. Asano *et al.*, 2009) that stream chemistry would be relatively uniform within a subwatershed, but variable between subwatersheds, due to such changes as bedrock geology and soil type, providing much more variation in chemistry through the aggregation of individual subwatersheds, up to the valley scale.

Marked variations in solute concentrations that are persistent across varying flow conditions within reaches in WS3 suggest that individual tributaries within a small first order headwater catchment are controlled locally by varying inputs of groundwater from different soil types and seeps. Seeps have two to five times higher concentrations of Si, Ca, and Na, have higher pH than stream sites (Figure 3), and have a large influence on spatial and temporal variations in streamwater chemistry. Western tributaries have perennial stream segments unique to the western portion of the watershed where seeps are present and these tributaries reflect influence of the chemical composition of the seeps. In contrast, eastern tributaries are dominated by intermittent and ephemeral stream reaches, have no seeps, and do not show the spatial variation in pH, Si, Ca, and Na seen near seeps along the western tributaries. Seeps have perennial flow and their chemical and physical influence is best seen in low flow conditions when groundwater contributions from seeps and near-stream Bh podzols are the primary cause of elevated Si and Na at the watershed outlet (Figure 7). Previous studies of watershed-scale mass balance have seen but may not have understood these variations of stream chemistry at the watershed outlet. Seeps as isolated hotspots of hydrological transport (Vidon *et al.*, 2010) 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 of drainage of transient water tables in typical podzols and lateral podzols, which dominate the landscape. However, even with the seep contributions diluted, spatial patterns influenced by these seeps across individual tributaries are persistent across varying flow conditions.

Along with distinct seep chemistry, unique subsurface characteristics suggest the possibilities that subsurface flow to the seeps could be from a deep glacial till aquifer or fractured bedrock. For instance, the location of seeps falls in a linear, northeastern trend, spanning from the base of the watershed to the upper portions of the western tributaries (Figures 1, 7). 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 UAA at these perennial seeps (0.08 ha) is smaller than that found in the initiation sites of ephemeral stream channels (0.25 ha). This suggests subsurface flow boundaries extend beyond topographic drainage divides, because upslope groundwater contributions to seeps cover much smaller areas of the watershed than the amount of perennial seep discharge insinuates. These sites may represent drainage from a deeper till reservoir over a larger area, or fractured bedrock not bound by topographic divides. Topographic divides could be spurs within the watershed, or the watershed divide itself.

The 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, Asano *et al.* (2009) suggested 10–150 ha, and the entire HBEF has an REA of 100 ha (Likens and Buso, 2006; Doogan, 2010). In contrast, our research found all solute concentrations become fairly constant when UAA was greater than 0.6–3.0 ha. We believe the dissimilarities between REA values in the literature, as well as the similar chemistry ranges seen across WS3 and HBEF, are due to differences in sampling density and to the inclusion of hot spots of biogeochemical processing and hydrological transport in the sampling regime. For example, the sampling density of previous studies ranged from 0.007 to 0.22 surface water sample sites/ha, whereas our sampling density is 2.7 sites/ha. Further, we believe that the REA values vary with general catchment size and location in the landscape, which suggests that the REA is not an elementary catchment property. Rather, we believe the partitioning of variation between highly variable upstream sources and relatively homogenous downstream characteristics may have different physical significance depending on the scale and land type of the catchment under examination. For example, at the headwater scale, hillslope topography and soil sequences may influence how groundwater flowpaths interact with the stream network, driving variation in ephemeral to first order streams. At the basin scale, the aggregation of these hillslope characters may matter less than broader variations in geologic substrate or land use. Although stream chemistry variability may collapse at a certain area threshold, creating self-similar, or fractal stream chemistry characteristics, the REA concept does have the ability to record the processes producing the self-similar behaviour in spatial surface water chemistry. In our study, for example, REA seems consistent with the extent of soil types and deep groundwater contribution (e.g. fractured bedrock or deep till) in the catchment. Thus, we believe REA based on stream chemistry should only be applied to similar sized watersheds and can fluctuate based on stream water sampling density and watershed type.

Previously, groundwater contributions to streams were not considered to be responsible for variation in stream chemistry at HBEF. In the HBEF headwater streams, we see a flashy response to precipitation events, where most of the channel network becomes dry during summer and extended periods with no precipitation, with only a portion near the catchment outlet showing perennial flow (Likens and Bormann, 1995). The shallow, coarse textured soils in these steep upland catchments are thus considered to be well drained (Likens and Bormann, 1995) with no water table development. Likens and Buso (2006) surveyed stream chemistry across the entire HB Valley but did not consider groundwater (saturated subsurface flow) as a major chemical driver in the headwater streams. Johnson *et al.* (1981) suggested chemical variations were driven by varying subsurface water flowpath lengths but did not specify groundwater, defined as saturated zone contributions, as a source. They did not distinguish between unsaturated and saturated flow processes but referred to precipitation with a residence time of less than 16 weeks as the main, if not only source of stream water. Other studies have divided 'old water', water stored in the catchment before an event, and 'new water', precipitation inputs during events, as an explanation for temporal variations in stream chemistry seen at the outlet of a catchment (Swistock *et al.*, 1989; Kirchner, 2003; McGlynn and McDonnell, 2003). Working in the same watershed as the present study, Hooper and Shoemaker (1986) found that Si was the best tracer of old *versus* new water; similarly, we found a strong contrast in Si concentrations in groundwater from seeps *versus* stream segments that showed solute composition suggestive of shallower sources. Johnson *et al.* (2000) compared stream chemistry and vadose zone soil water chemistry through the use of zero-tension lysimeters 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. Further, contributions from groundwater have been shown to vary depending on site. Burns *et al.* (2001) explained 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 at their study site, the Fudoji catchment in Japan. Recently, however, Detty and McGuire (2010a,2010b) showed persistent shallow water table development in the hillslopes in WS3, the hydrologic reference watershed for HBEF and the catchment we used for our study. Our study furthers Detty and McGuire's (2010a,2010b) conclusions by finding that groundwater is an important aspect in determining stream chemistry at HBEF headwater catchments. It is apparent that local topography and water table fluctuations and structure cause the development of distinct soil types. Interactions of groundwater and soils are controlling chemical transformations and thus dictating groundwater 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.

The western tributaries in WS3 show stronger gradients in solute chemistry and higher pH and concentrations in Ca, Si, and Na than the eastern tributaries. The presence of bimodal and Bh podzols in benches and toe slopes along spurs throughout the western tributaries show elevated levels of pH, Si, and Na, compared with transient groundwater developed in other soil types (Figure 3). In contrast, the eastern tributaries are characterized by high concentrations of Al, Fe, DOC, NO_3, Mn and Si, low values in pH, and low concentrations of Ca and Na. The high concentrations of Al and DOC reflect the chemistry seen in the transient water tables of lateral podzols (Figure 3; e.g. Sommer *et al.*, 2000) 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 Bh and bimodal podzols alone may not explain the steeper gradients in solute concentrations or the anomalous perennial flow driven by seepage zones found in select portions of western tributaries. Inceptisols, however, reflect 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 high concentrations of Ca, Si, and Na, which are reflected in the adjacent stream reaches. These high pH and element concentration levels indicate a contribution from weathering of minerals such as plagioclase feldspar 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.

CONCLUSION

Although other studies (e.g. Temnerud and Bishop, 2005; Likens and Buso, 2006) found large variation in stream chemistry of headwater streams in comparing variation of first order streams within a fourth or fifth order basins, we found similar variation within one first order basin by surveying all surface water types, including ephemeral, intermittent channels and groundwater seeps, which otherwise would not have been considered had we surveyed only perennial channels. This demonstrates the importance of high density stream surveying; sampling beyond the perennial network can help us better understand the total range of chemistry variation and lead to a better understanding of controls on surface water chemistry. We found distinct chemical patterns that were persistent over varying flow conditions, contradicting our hypothesis of more spatially uniform stream chemistry at higher flow conditions. We believe groundwater contributions from distinct soil types caused the surface water chemistry patterns we see spatially to be maintained in both low and high flow surveys. We found that surface water chemistry behaves as a fractal with variation independent of scale, which contradicts our initial hypothesis that headwater catchment chemistry from one subwatershed would be less variable than that of its encompassing fifth order basin. That is, we initially believed stream chemistry would be uniform within a subwatershed, but variable between subwatersheds, providing much more variation in chemistry through the aggregation of subwatersheds up to the valley scale. From this, we conclude REA depends on scale and type of surveying (e.g. density of survey sites, or specific discharge *versus* water chemistry surveying), as well as heterogeneity of landscape (e.g. level of variation in topography) within the watershed. We believe REA based on stream chemistry may be dependent on the resolution of sampling within the stream network as well as the size of the catchment. Thus, although thresholds in ranges of solute concentration may be observed, their physical significance may vary with context.

Surface water chemistry showed similar chemical patterns to groundwater in adjacent soil types, as we predicted. The conclusion that groundwater flowing through distinct soil types based on hillslope position and water table dynamics drives stream chemistry contrasts with previous studies at HBEF that assumed groundwater in the saturated zone is non-existent and that soil water in the unsaturated zone controls stream chemistry. Further, the high levels of certain solutes in seeps and their adjacent stream sites indicate a 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 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.

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