

Water's Way at Sleepers River watershed – revisiting flow generation in a post-glacial landscape, Vermont USA

James B. Shanley,^{1*} Stephen D. Sebestyen,² Jeffrey J. McDonnell,^{3,4} Brian L. McGlynn⁵
and Thomas Dunne⁶

¹ *US Geological Survey, Montpelier, VT, USA*

² *USDA Forest Service, Grand Rapids, MN, USA*

³ *University of Saskatchewan, Saskatoon, Canada*

⁴ *University of Aberdeen, Aberdeen, Scotland, UK*

⁵ *Duke University, Durham, NC, USA*

⁶ *University of California, Santa Barbara, CA, USA*

Abstract:

The Sleepers River Research Watershed (SRRW) in Vermont, USA, has been the site of active hydrologic research since 1959 and was the setting where Dunne and Black demonstrated the importance and controls of saturation-excess overland flow (SOF) on streamflow generation. Here, we review the early studies from the SRRW and show how they guided our conceptual approach to hydrologic research at the SRRW during the most recent 25 years. In so doing, we chronicle a shift in the field from early studies that relied exclusively on hydrometric measurements to today's studies that include chemical and isotopic approaches to further elucidate streamflow generation mechanisms. Highlights of this evolution in hydrologic understanding include the following: (i) confirmation of the importance of SOF to streamflow generation, and at larger scales than first imagined; (ii) stored catchment water dominates stream response, except under unusual conditions such as deep frozen ground; (iii) hydrometric, chemical and isotopic approaches to hydrograph separation yield consistent and complementary results; (iv) nitrate and sulfate isotopic compositions specific to atmospheric inputs constrain new water contributions to streamflow; and (v) convergent areas, or 'hillslope hollows', contribute disproportionately to event hydrographs. We conclude by summarizing some remaining challenges that lead us to a vision for the future of research at the SRRW to address fundamental questions in the catchment sciences. Copyright © 2014 John Wiley & Sons, Ltd.

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INTRODUCTION

The Sleepers River Research Watershed (SRRW) in Vermont, USA, was established by the Agricultural Research Service of the U.S. Department of Agriculture in 1959. Throughout its history, research has focused on the question of how hydrologic runoff is generated in a rugged, post-glacial landscape with forest and pasture cover. The research has been fundamental to understanding how climate, landscape characteristics and gradual land use change in the region affected water yields, stormflow responses and water quality. The earliest work at the SRRW was entirely hydro-metric, and was followed by studies utilizing suites of

isotopic and chemical methods that emerged in later decades. Here, we review the research during the 55-year history of the SRRW with the goal of illustrating how evolving measurement approaches have led to an evolution in understanding of streamflow generation processes. We begin with a review of the widely cited Dunne and Black (1970b) paper that outlined the mechanics of saturation overland flow. We then review the past 20 years of combined hydrometric-isotopic-geochemical analysis that has continued to refine our runoff process understanding at the catchment scale, at the hillslope-riparian interface and across the nested basin scales that comprise the SRRW. In pursuing these objectives, we commemorate the 30th anniversary of the original publication in Sweden of 'Water's Way from Rain to Stream' (Grip and Rodhe, 1985, 1994) in a landscape with strong similarities to the original Swedish research sites.

*Correspondence to: James B. Shanley, US Geological Survey, Montpelier, VT, USA.
E-mail: jshanley@usgs.gov

SRRW RESEARCH: EARLY RESEARCH ON RUNOFF GENERATION PROCESSES

Dunne and Black (1970a, b, 1971), hereafter 'D&B', investigated runoff generation in a small catchment just outside the lower catchment boundary of the SRRW (Figure 1). The work was an attempt to express the variable source area (VSA) of Hewlett and Hibbert (1967) in terms of runoff mechanisms, and thereby to generalize it (Figure 2). Although VSA dynamics had been shown earlier (Hursh and Brater, 1941; Hewlett and Hibbert, 1967; Ragan, 1968) and the main role of the expanding variable near-stream saturated areas as a control on streamflow generation had been conceptualized (Betson, 1964), D&B showed mechanistically how rain or snowmelt on saturated areas combined with return flow of groundwater and subsurface stormflow (SSF) at the base of slope to contribute to the runoff response (Figure 2). The work demonstrated that in a region with infiltration capacities higher than rainfall and snowmelt rates, stormflow from small watersheds is contributed by various amounts of SSF over impeding horizons that were 0.3 to >2 m deep, and overland flow from limited portions of the watershed (Dunne and Black, 1970b, a). In particular, the work

demonstrated the extent of, and controls on, the saturation-excess overland flow (SOF) mechanism of streamflow generation (Figure 2) in certain landscapes.

Saturation-excess overland flow develops because there is a hydrogeological/topographic limit to the conveyance capacity of the subsurface, which depends on soil transmissivity, topographic gradient and the planform curvature of the landscape (Beven, 1978). Where that limit is exceeded, exfiltration (return flow) occurs and is augmented by rainfall or snowmelt onto saturated areas, which can expand seasonally and during individual stormflow events (Figure 2). These processes occur in zones that are identifiable or at least interpretable from geomorphology and hydrogeology (Dunne *et al.*, 1975; Dunne, 1978), and the distribution and amounts of SOF and SSF are together important for stormflow, solute fluxes and pollutant transport. The extensive nature of SOF generation (<5 to ≤50% of catchment area) reflects the post-glacial character of the Vermont landscape, which includes significant areas of shallow, low-permeability soils, impeding horizons, gentle gradients and topographic convergences. The D&B studies, together with contemporaneous and subsequent work at the SRRW (Comer and Zimmermann, 1969; Hendrick and Comer, 1970; Engman, 1981; DeAngelis *et al.*, 1984) collectively linked runoff mechanics to landscape structure, and vice versa, by demonstrating feedbacks of runoff mechanisms on landscape formation (Dunne, 1980).

The principles of D&B were broadly applicable to humid areas, where infiltration capacities typically exceed rainfall or snowmelt intensity (Dunne, 1978). Thereafter, SOF studies proliferated around the world from the 1970s to the 1990s (Dunne *et al.*, 1975; Anderson and Burt, 1978; Beven, 1978; Mosley, 1979; Taylor and Pearce, 1982; O'Loughlin, 1986; Eshleman *et al.*, 1993; Buttle, 1998). These insights also influenced the development of hydrologic models (Freeze, 1974; Beven and Kirkby, 1979) and studies of nutrient flushing (Hornberger *et al.*, 1994; Creed and Band, 1998), geomorphology (Montgomery and Dietrich, 1988), land-atmosphere interactions (Entekhabi and Eagleson, 1989) and tropical hydrology (Bonell and Gilmour, 1978; de Moraes *et al.*, 2006). However, the early studies left many questions open, such as how runoff responses from small areas should be scaled up to predict hydrologic responses of heterogeneous subwatersheds across the broader landscape. Research into these questions at the SRRW and elsewhere advanced understanding by combining hydrometric methods with newer chemical and isotopic techniques (Bishop *et al.*, 1990; Christophersen *et al.*, 1990; McGlynn *et al.*, 2002; McGlynn and McDonnell, 2003; McGuire *et al.*, 2005; Soulsby *et al.*, 2006; Jencso *et al.*, 2010).

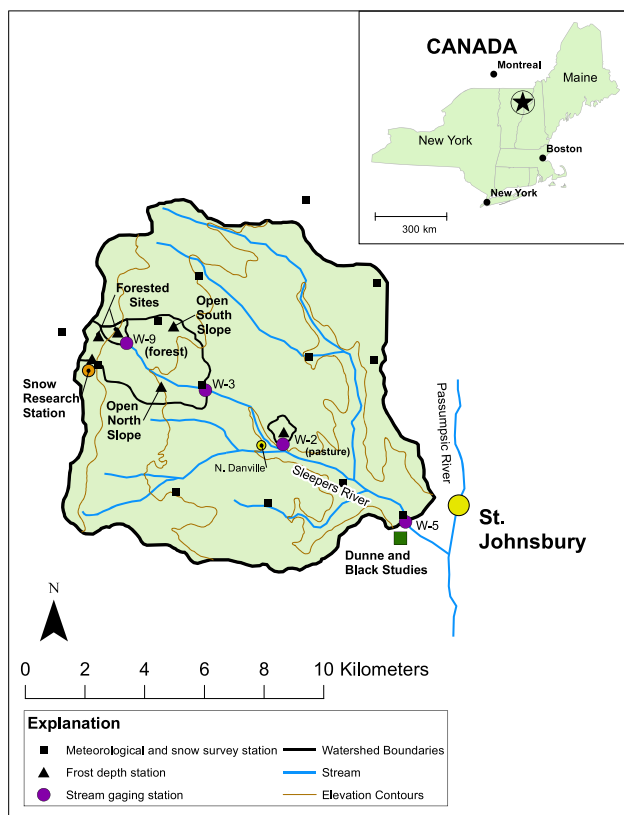


Figure 1. Map of Sleepers River Research Watershed showing study sites and surrounding areas

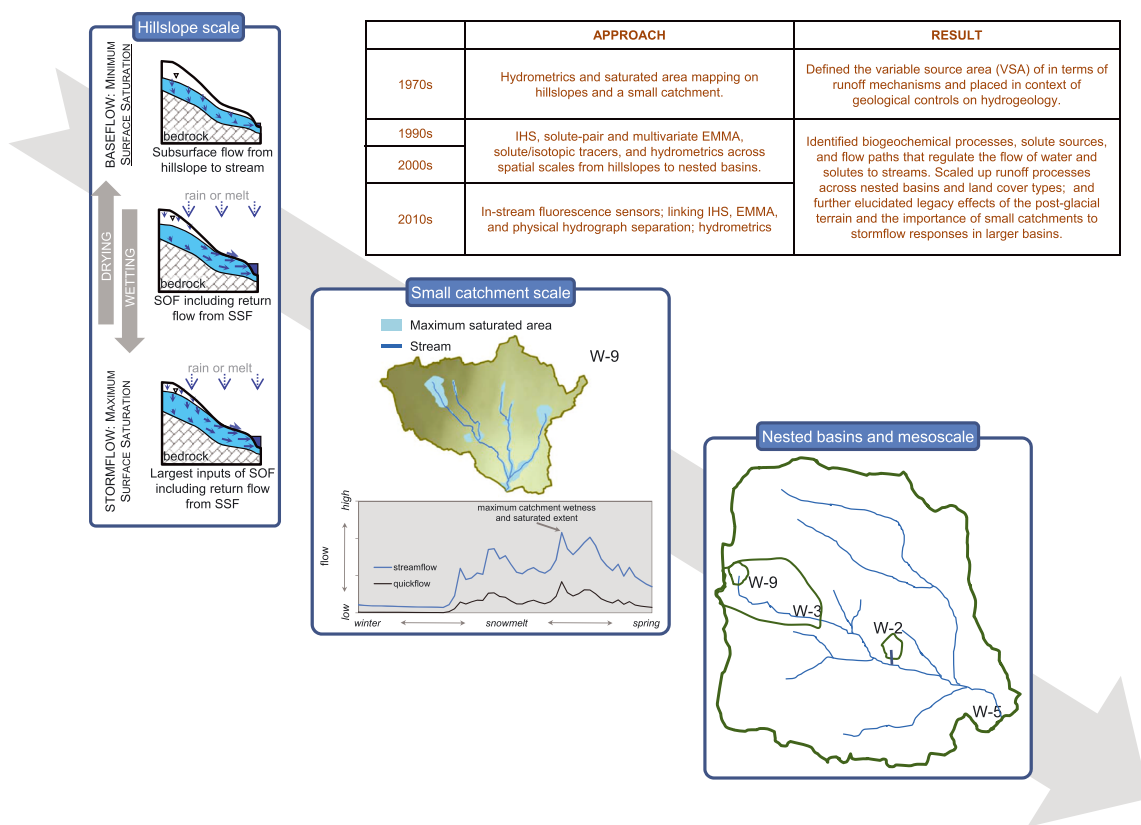


Figure 2. Schematic of flow generation mechanisms and timeline of hydrologic research at Sleepers River Research Watershed

THE SRRW LANDSCAPE

Sleepers River originates in the N-S trending Kittredge Hills west of St. Johnsbury, Vermont, and flows generally SE (Figure 1) to the Passumpsic River, which shortly joins the Connecticut River. Sleepers River drains a landscape of rolling hills (elevation range 201–820 m) that become increasingly rugged, more forested and less populated to the northwest. Lower elevations support a mix of forest and dairy farms, although most land above 500 m is forested. The Wisconsin glacialiation ended ~10 000 years ago and left variably thick deposits of till, outwash and lacustrine clay (Springston and Haselton, 1999). The watershed averages 1000–1500 mm of elevationally controlled precipitation annually.

Newell (1970) illustrated that the topography and geological materials that influence hydrologic responses in the SRRW are controlled by the pre-glacial and glacial history of the landscape. He also demonstrated that the topographic grain of the ridges, hillslopes and stream channels reflects the regional patterns of jointing in the calcareous schist bedrock. He mapped glacial till cover, demonstrating the influence of the underlying bedrock surface. Ridge tops and upper slopes generally have a thin (<2 m) till cover, including sandy ablation till in some places. A dense silty basal till cover generally thickens

downslope and downvalley. The lower elevations also contain sandy outwash and lacustrine clay deposits (Springston and Haselton, 1999). The geological substrate is reflected in regional soil patterns, which thus are indicators of baseflow regimes and water-table responses (Comer and Zimmermann, 1969; Shanley *et al.*, 2003).

The D&B site (Figure 1) was a fluvio-glacial terrace on a structurally controlled bedrock valley sidewall, with both steep and gentle gradients; deep, permeable and shallow, low-permeability soils; and convergent, planar and divergent hillslopes (Figure S2). The site had not been forested for ~30 years, but retained high infiltration capacities and impeding horizons at shallow depth on some parts (but not all) of the monitored catchment, similar to forested soils on various parts of the SRRW. Shortly after the D&B studies, a highway relocation project compromised the site for any subsequent work (Figure S3).

Watershed 9 (W-9, 41 ha), the main research focus since 1991, has 155 m of relief, a mix of steep and gentle hillslopes, mid-slope benches, pocket wetlands and gently sloping riparian zones. The till, up to 4.5 m thick (Shanley *et al.*, 2003), is locally derived from the calcareous Waits River Formation (Springston and Haselton, 1999). It is readily weathered and calcite is absent from the upper 1–2 m (Newell, 1966). W-9, W-3 (837 ha) and W-5

(11 125 ha) form a nested basin sequence with forests in the headwaters to mixed forest and pastures downstream. W-2 (59 ha) is a pasture-dominated low-elevation catchment.

SRRW RESEARCH: THE PAST 20 YEARS

We begin our review of runoff research at the SRRW at the small catchment scale, where we show how hydrologic and biogeochemical processes have been inferred from the timing and amplitude of signals (chemical, isotopic, hydrologic) at the catchment outlet. To support these inferences, we review work that has investigated internal catchment dynamics with detailed studies of water movement from hillslopes to stream and mixing models with potential source waters. Finally, we move back downstream, scaling up the findings through review of work in the nested basins (Figure 1).

Small catchment scale findings

Isotopic hydrograph separation (IHS) at the SRRW has repeatedly underscored the notion that water stored in a catchment prior to an event dominates the event hydrograph (Sklash *et al.*, 1976; Bonell, 1998; Buttle, 1998). Nonetheless, the debate on how old water is delivered to streams has continued (Kirchner, 2003; Bishop *et al.*, 2004). At the SRRW, we have applied IHS to constrain sources, pathways and mechanisms of both water and solute movement to streams, which we interpret with respect to VSA dynamics and the contribution of SOF to streamflow generation.

Much of the IHS work at the SRRW has focused on snowmelt, when VSA extent tends to be the highest. Approximately one third of precipitation at the SRRW falls as snow that typically accumulates starting in December until snowmelt in late March or April. Up to half of the annual runoff occurs during the approximately 2-month snowmelt window. On the basis of a two-component IHS (using meltwater as new water and baseflow as old water), the new water component of the snowmelt period streamflow typically begins as a few percent and gradually increases to a sustained 20–40% with peaks sometimes exceeding 50% (Figure 3) (Shanley *et al.*, 2002). This progressive increase of new water in early melt periods is consistent with increasing direct precipitation inputs and SOF as VSAs expand with increasing cumulative melt inputs (Dunne *et al.*, 1975; Shanley *et al.*, 2002).

Analyses of the chemical signature of streamflow at the SRRW have complemented and supported IHS results. Principal components analysis of conservative chemical tracers (e.g. calcium, magnesium, strontium and silica concentrations) has been used to develop multivariate

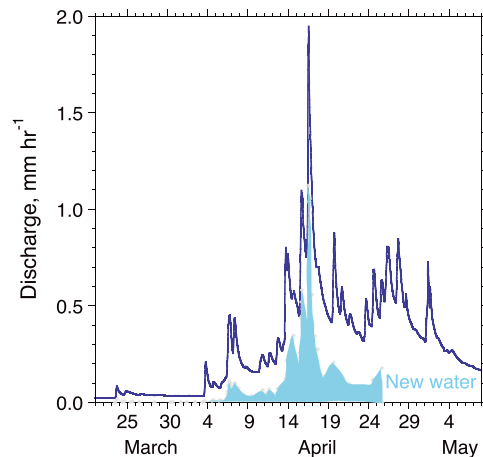


Figure 3. Snowmelt hydrograph at Sleepers River showing new water component (light blue shading) based on isotopic hydrograph separation. The separation stops when isotopic separation between new and old water is lost

end-member mixing analysis (EMMA) (Christophersen and Hooper, 1992). This modelling approach has been used to quantify fractions of source waters (end members) that mixed to form W-9 streamwater (Kendall *et al.*, 1999; Sebestyen *et al.*, 2008). End members typically used were precipitation (rain and meltwater), soil water and groundwater. Groundwater and soil water chemical compositions tend to vary more over space than time in contrast to precipitation composition, which varies strongly over time but is fairly uniform spatially. Smith (1997) used these three end members and found that groundwater dominated the hydrograph and that the groundwater fraction from EMMA closely agreed with the old water fraction from IHS. Kendall *et al.* (1999) sampled many additional potential end members, such as different depths in riparian and hillslope groundwater (nested wells) and saturation overland flow (Figure 4), to

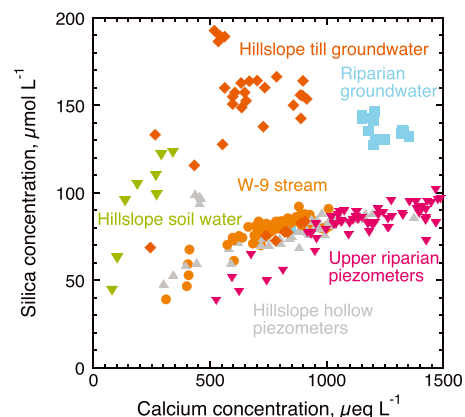


Figure 4. Bivariate Si-Ca plot for W-9 streamwater and potential end members for end-member mixing analysis. Data are from Kendall *et al.* (1999) and Hjerdt (2002)

test for their possible contributions. They concluded that mixing of groundwater and meteoric water could explain 94% of the variance in streamwater composition, suggesting minimal contributions from other source waters, such as soil water or throughfall.

Certain solutes or pairs of solutes, isotopic indicators or compositional metrics serve as distinctive tracers that provide an alternative to a multivariate EMMA. At the SRRW, these tracers include dissolved organic carbon (DOC), $\delta^{18}\text{O}$ of nitrate and sulfate, cosmogenic isotopes and optical properties of dissolved organic matter. For example, nitrate and sulfate are nutrients that enter a catchment in precipitation and are cycled by plants and soil microbes (Likens and Bormann, 1995). Microbes break N–O and S–O bonds while assimilating inorganic nutrients into biomass (i.e. organic matter). Upon subsequent mineralization, the nitrate and sulfate compounds include new O atoms from air and water sources (Aleem *et al.*, 1965; Mitchell *et al.*, 1998), which causes a sharp decrease in the $\delta^{18}\text{O}$ of the catchment-derived nitrate and sulfate relative to that of the atmospheric input. These isotopic shifts during terrestrial processing can provide robust tracers of atmospheric versus 'catchment-processed' nitrate and sulfate (Mitchell *et al.*, 1998; Kendall *et al.*, 2007).

The $\delta^{18}\text{O}$ of atmospheric nitrate at the SRRW is +80 to +100 permil, whereas the $\delta^{18}\text{O}$ of soil-nitrified nitrate is –10 to +10 permil (Ohte *et al.*, 2004; Sebestyen *et al.*, 2014). This broad separation allows calculation of unprocessed atmospheric nitrate in streamwater. Unprocessed atmospheric nitrate comprised 30–50% of stream nitrate during several snowmelt and some rainfall-runoff events (Sebestyen *et al.*, 2014). The presence of unaltered atmospheric nitrate in streamwater provides strong evidence of new water input. Sebestyen *et al.* (2008, 2014) invoked both SOF and shallow SSF with unprocessed atmospheric nitrate originating from melt and rainfall on VSAs. This interpretation was further supported by concurrent patterns of streamflow, water-table elevation, chemical indicators and isotopic composition that collectively showed large inputs of unprocessed atmospheric nitrate originating from riparian areas at times when nitrate sources on hillslopes were largely disconnected from the stream. This finding reinforces a basic premise of the D&B studies that some proportion of the water entering streams flows overland and transports particles and solutes.

Like nitrate, sulfate has a sharp contrast in $\delta^{18}\text{O}$ between atmospheric and biologically processed fractions that can be exploited to estimate meteoric inputs to streamwater (Shanley *et al.*, 2008). But unlike nitrate, sulfate adsorbs to soil grains, which may cause underestimates of meteoric water input. Meteoric sulfate

also contains ^{35}S , a cosmogenic isotope with an 87-day half life. ^{35}S is detectable in the SRRW streamwater at low activities relative to precipitation. Stream ^{35}S complements IHS by placing an upper bound on new water contributions, but some ^{35}S is lost by sulfate retention and uptake (Shanley *et al.*, 2005). A strong shift to negative $\delta^{34}\text{S}$ values, which accompanied a tripling of stream sulfate concentrations following a high return-period drought, indicated oxidation of secondary sulfides during soil exposure to air when groundwater levels were unusually low in 2001 (Mayer *et al.*, 2010). This newly oxidized sulfate, unmistakably labelled by its distinct negative $\delta^{34}\text{S}$, was present only at depths below typical summer minimum groundwater levels. That this sulfate was released to streamwater relatively quickly during only moderate fall rainstorms but maintained a prolonged 8-month period of elevated concentrations in the stream (Mayer *et al.*, 2010) suggests both rapid and slow pathways of this deep groundwater. The sulfate isotopes thus reveal information about specific flow path depths (both shallow and deep), complementing information from IHS, EMMA and the nitrate isotopes.

The relations between solute concentrations and streamflow have provided additional insight into changing water sources during high-flow events. Solute derived from the readily weathered calc-silicate rocks at the SRRW (Bailey *et al.*, 2004), including alkalinity, silica, base cations and sulfate, are high in groundwater and low in precipitation, so they dilute during storms and snowmelt (Shanley *et al.*, 2004; Doctor *et al.*, 2008). Nitrate and DOC are primarily derived from topmost organic soil horizons and are flushed to the W-9 stream during high flows (Shanley *et al.*, 2004; Sebestyen *et al.*, 2008). Nitrate concentrations peak early in snowmelt events, and then progressively decrease as snowmelt proceeds (Figure 5; Sebestyen *et al.*, 2009). We have interpreted this pattern as source limitation (Sebestyen *et al.*, 2008; Pellerin *et al.*, 2012) consistent with Creed

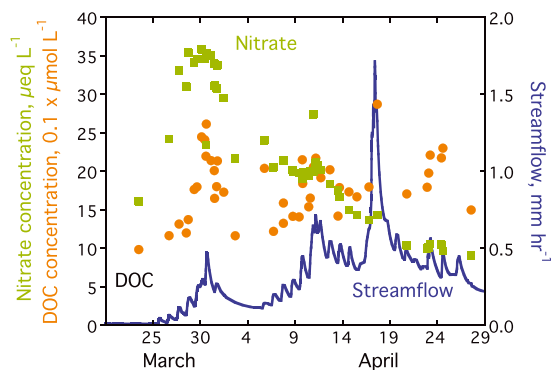


Figure 5. W-9 snowmelt showing differential response of nitrate (supply limited) and dissolved organic carbon (DOC) (transport limited)

et al. (1996). In contrast, DOC increases are fairly proportional to streamflow peaks (Figure 5; Sebestyen *et al.*, 2009), and we have interpreted this as transport limitation. Because DOC continues to increase with successively increasing discharge peaks, corresponding to expanding VSAs, DOC appears to be a strong indicator of VSA extent and the magnitude of SOF inputs, at least during snowmelt.

Insofar as DOC concentration is a useful indicator of shallow flow paths and extent of near-surface saturation, recording in-stream fluorescence sensors can greatly enhance interpretation by providing high temporal resolution signals (Saraceno *et al.*, 2009; Pellerin *et al.*, 2012). Fluorescing DOM (FDOM) is a strong proxy for DOC (Green and Blough, 1994). In particular, hysteresis in the FDOM concentration–discharge relationship and its variation over seasons and among storms may help identify DOC sources in the catchment. For example, hysteresis at the SRRW is consistently counterclockwise (i.e. DOC peaks after the discharge peak) suggesting that the primary DOC sources are distal from the weir, or alternatively that return flow through DOC-rich organic horizons (Sebestyen *et al.*, 2014) is delayed (Pellerin *et al.*, 2012). The size of the hysteresis loop can vary greatly, as illustrated here for snowmelt and a large fall storm (Figure 6). The higher peak and larger loop in the fall storm reflect the large input of fresh organic matter during leaf fall (Sebestyen *et al.*, 2014), and a large areal source yielding a wide distribution of travel times to the weir. Differentiating the effects of carbon source size and distance on hysteresis loops is difficult, but catchment terrain analysis (Figure 7) may help by revealing the landscape positions most likely contributing to streamflow generation. These runoff source areas are also the primary sources of DOC, so knowledge of their distribution is helpful to interpret the continuous fluorescence signal at the catchment outlet. Sources and

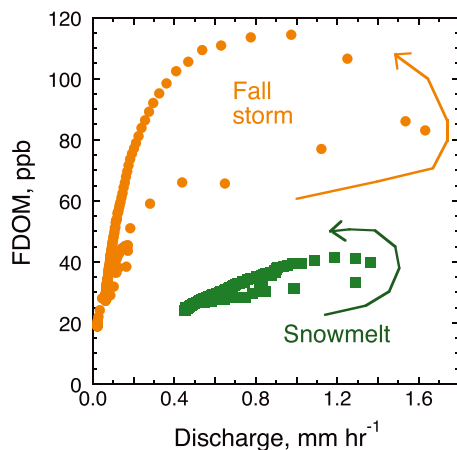


Figure 6. Fluorescing dissolved organic carbon (FDOM)–discharge hysteresis loops (from in-stream fluorometer)

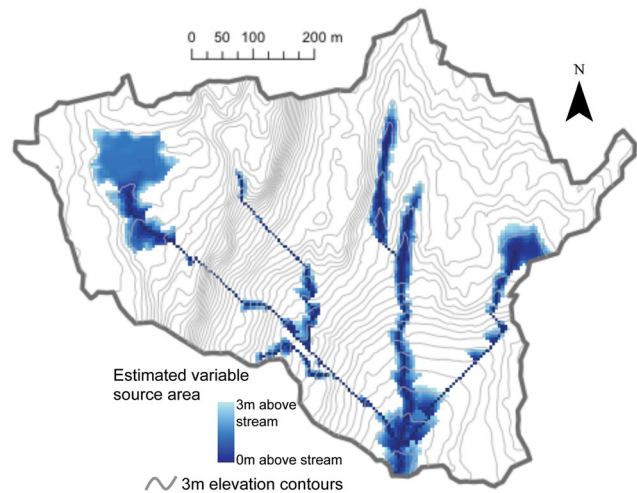


Figure 7. Approximation of variable source area expansion areas in W-9 based on terrain analysis. The shaded sections indicate watershed areas less than 3 m above the stream entry point along the flow path. (For methods, see Jencso *et al.*, 2010)

flow paths may be further constrained by stable water isotopes. Our next research step at Sleepers River is to tease out the ‘distance versus source’ question with internal catchment measurements (e.g. longitudinal surveys along streams, groundwater table monitoring) under different hydrologic conditions.

The EMMA at the SRRW has typically indicated contributions of surficial soil water and precipitation to streamwater during events. These sources necessarily followed fast flow paths – SOF or SSF in association with surficial soils in VSAs. As such, we argue that the sum of these two components is a measure of quickflow, or water that directly ran off in response to an event (Sebestyen *et al.*, 2008). Quickflow may also be quantified from hydrograph recession analysis (Hewlett and Hibbert, 1967; Jakeman *et al.*, 1990). Among the various approaches to separate hydrographs, recession analysis is nearly a century older than IHS and EMMA and includes numerous formulations (Hall, 1968). Hewlett and Hibbert (1967) referred to hydrograph recession as ‘one of the most desperate analysis techniques in use in hydrology’, because the mathematically derived flow components offer little potential to identify flow paths through catchment soils. The advantage, however, is that these methods are objective and reproducible and require only streamflow data, which are often readily available. Chemical and isotopic approaches to hydrograph separation are typically applied to a limited number of events, which make them difficult to generalize. In contrast, quickflow determination by recession analysis ($\text{quick}_{\text{recession}}$) can be readily applied to all events over a long time series and extend the interpretability of flow paths during periods lacking chemical and isotopic data.

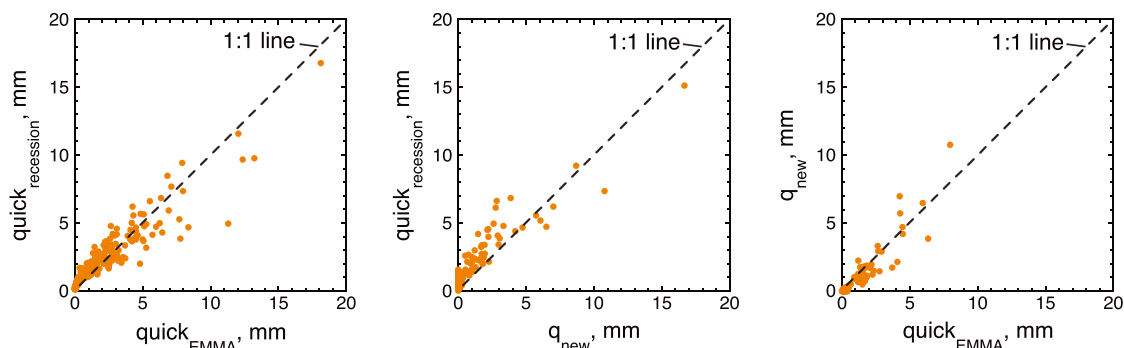


Figure 8. Relationships among quickflow from recession analysis ($quick_{recession}$), quickflow from end-member mixing analysis (EMMA) ($quick_{EMMA}$) and new water (q_{new}) from isotopic hydrograph separation (IHS) for W-9. Several snowmelt events are shown with each data point representing a daily value. Fewer data points for the q_{new} versus $quick_{EMMA}$ plot reflect periods when IHS and EMMA could not be calculated because of isotopic overlap among end members or incomplete stream chemistry data

At the SRRW, we have rich data sets to assess relationships between flow separations using IHS, EMMA and recession analysis. Three independent determinations of quickflow, (1) from recession analysis ($quick_{recession}$) using the Eckhardt method (Eckhardt, 2005), (2) calculated as precipitation+soil water from multi-solute EMMA ($quick_{EMMA}$) and (3) computed as new water (q_{new}) from IHS, were all strongly intercorrelated (Figure 8). We used the Eckhardt method to illustrate basic principles that may also be derivable through other published methods (Horton, 1933; Hall, 1968; Brutsaert and Nieber, 1977; Eckhardt, 2008). Correlations among the three hydrograph separation approaches, along with concurrent hydrometrics (Sebestyen *et al.*, 2008; Sebestyen *et al.*, 2014), show links among metrics of quick flow, water sources and flow path routing. The similarity of hydrograph separation results provides validation for a physical interpretation of Eckhardt method results for quantifying the magnitude of SOF inputs to streams at several SRRW catchments during snowmelt (Figures 8 and 9). By extension, we have a new tool that allows us to estimate new water inputs and flow path routing for other melt periods when chemical or isotopic tracers were not measured. Our next step is to calibrate the method for rainfall-runoff events. If successful, we can apply the approach to assess water sources throughout periods when streamflow measurements are available.

Findings at the hillslope/riparian/stream interface

Thus far, we have interpreted water flow paths and solute sources from observations at the catchment outlet. Some a priori knowledge of ‘how the watershed works’ was implicit in this discussion. Now, we venture into the catchment to see how smaller scale studies have informed these inferences. We present an example of the multi-pronged approach that led to an interpretation of streamflow generation different from

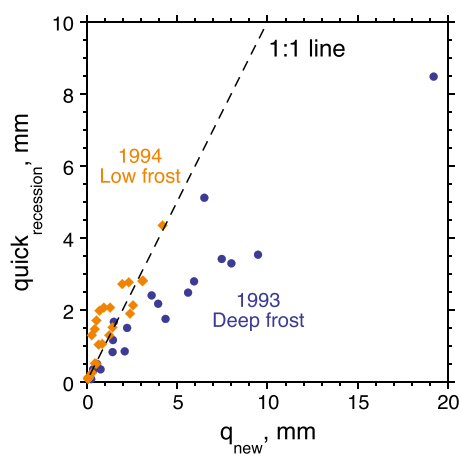


Figure 9. Relation between quickflow from recession analysis ($quick_{recession}$) and new water (q_{new}) from isotopic hydrograph separation at W-2, the agricultural catchment, during a deep-frost and low-frost year

that we would have made from hydrometric measurements alone.

To better understand the sources and timing of water and solute delivery to the stream, as well as chemical evolution along hydrologic flow paths, Kendall *et al.* (1999) instrumented W-9 with nested piezometers along a hillslope–riparian transect. They measured hydraulic head and sampled frequently for major ion chemistry before, during and after the main spring snowmelt event. Water tables in the riparian zone were already within 50 cm of land surface when snowmelt began, and saturation rose to the land surface and expanded outward as the melt progressed (McGlynn *et al.*, 1999). Water table elevations in the upper hillslope position were at 3-m depth before melt and rose to near-land surface during melt (Kendall *et al.*, 1999). The resulting increased hydraulic gradients, coupled with measured increases in transmissivity upward toward the land surface (Kendall *et al.*, 1999), suggest that hillslope water should have been a major contributor to streamflow. However, the chemistry of the hillslope water was markedly different from the stream, and there

was no discernible shift in streamwater composition toward the hillslope water composition during the melt (Figure 4). In particular, hillslope waters had a large silica (Si) excess relative to the stream. The contradictory hydrometric and chemical data posed an enigma.

During this same snowmelt period, McGlynn *et al.* (1999) studied a smaller scale hillslope/riparian transect upstream of the Kendall *et al.* (1999) study. They used five sets of nested piezometers for a detailed investigation of the evolution of flow paths and chemistry during the melt. Despite upward hydraulic gradients, riparian water stratified because of the presence of a fragipan. Solute chemistry became more concentrated toward the stream and with depth, but diluted by a factor of two at peak snowmelt, accompanied by a shift in $\delta^{18}\text{O}$ toward that of meltwater. This pattern suggests an initial displacement of old water by infiltrating snowmelt and from transient groundwater delivered from upslope (Rodhe, 1987). At this smaller hillslope scale, excess Si again was present in the hillslope groundwater, but less so than on the Kendall *et al.* (1999) hillslope.

Attempting to resolve the paradox, Hjerdt (2002) searched for the water that truly contributed to the stream during snowmelt. Most sampling sites of Kendall *et al.* (1999) were on planar or convex hillslopes, but one site in a hillslope hollow (concave landform) had a groundwater composition most like stream chemistry. Hjerdt (2002) sampled several other hillslope hollows and found that their groundwater composition was generally a viable end member of stream chemistry. Some hillslope hollow sites had slightly lower Si/calcium than streamwater, a composition that would allow mixing with a small percentage of hillslope waters to match the streamwater composition (Figure 4). Bullen and Kendall (1998) had also inferred a hillslope groundwater contribution to streamflow at W-9 based on strontium isotope compositions that reflected silicate weathering. But the high Si concentration of the planar hillslope water ruled it out as a major contributor to streamflow.

It was chemistry, rather than any hydrometric measurements, that revealed the function of the hillslope hollows. Groundwater chemistry from the planar hillslope wells screened in the till reflects weathering of silicate minerals rather than calcite (Bullen and Kendall, 1998; Hjerdt, 2002). Groundwater chemistry from the planar hillslope hollows, in contrast, reflects calcite weathering, suggesting that water has travelled along a deeper flow path (and/or has had a longer residence time) within the lower unweathered till or the bedrock. A plausible scenario is that the landscape setting of the hollows is controlled by jointing in the bedrock (Newell, 1970) and that most infiltrating water eventually enters fractures and ultimately discharges in hillslope hollows or directly to the stream/riparian zone. Storage and travel time within

the fracture system must be sufficient for the chemistry to evolve to a concentrated state.

Further support for the important role of hillslope hollows comes from the western USA at the snowmelt-dominated Tenderfoot Creek Experimental Forest, where Jencso *et al.* (2009) found that the duration of hydrologic connectivity of a hillslope is related to its upslope contributing area, and hillslope hollows generally have greater upslope areas. Streamflow contributions from hillslopes are a function of variable riparian water displacement/turnover (Jencso *et al.*, 2010) due to hillslope water mobilization following a predictable sequence from larger to smaller hillslopes (hollows, to planar, to divergent) during snowmelt. This hypothesis provides an explanation for the seemingly paradoxical co-occurrence of large fractions of old water from the hillslope and reactive solutes from precipitation and snowmelt (Kirchner, 2003). The hypothesis is also consistent with the interpretation of Sebestyen *et al.* (2008, 2014) that return flow of hillslope hollow water across VSAs results in mixing of weathering-product solutes in SSF with unprocessed atmospheric nitrate and DOM in SOF. In sum, our smaller scale 'within the watershed' investigations have supported the fundamental role of the landscape setting as a first-order control on hydrology, and validated the multiple-tracer approach by revealing water sources and flow paths that were not evident through a purely hydrometric lens.

Findings across nested basin scales

A central research theme at the SRRW in the 1990s was how hydrologic processes and new water inputs would change with catchment scale. The SRRW includes several catchments, three of which formed a nested basin sequence, which we used to address the scale question. We hypothesized that the old water fraction would increase with increasing catchment scale, as a consequence of increasing groundwater contributions with increasingly larger aquifers downgradient, as predicted by the idealized Tóth (1963) regional groundwater model.

The hypothesis was not supported; percent new water contributions during snowmelt and a summer storm were either constant or generally increased with basin scale (Smith, 1997; Shanley *et al.*, 2002). Stream chemistry, e.g. the extent of dilution of baseflow alkalinity, followed the identical pattern. In contrast, there is support for the hypothesis in other settings, e.g. the Catskill Mountain of New York (Brown *et al.*, 1999) and Scotland (Tetzlaff *et al.*, 2011). The latter study found that overland flow inputs are important in headwaters, but are less important downstream where groundwater inputs and other sources mix to damp isotopic signatures, suggesting diminished new water inputs with increasing catchment size. A possible explanation for the lack of the expected scale

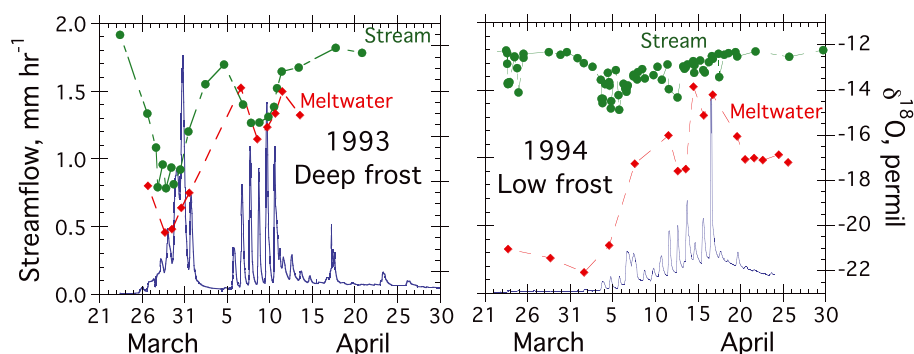


Figure 10. Differential isotopic response at W-2 in (a) 1993 (deep ground frost) and (b) 1994 (low ground frost)

effect at Sleepers River is that the relatively narrow valleys in rugged topography do not support extensive aquifers, yet these valleys have well-developed flood plains that allow SOF over extensive VSAs. A topographic analysis of the Sleepers River landscape by Wolock (1995) further helped to explain a lack of scale effect. He showed that topographic variability, and by inference hydrologic flow paths and stream chemistry, stabilized at catchment areas greater than 5 km².

Soil compaction and patterns of snow accumulation/ground frost development in pastures, which are a greater fraction of the SRRW landscape area at larger spatial scales, may have contributed to increases in new water runoff (Shanley and Chalmers, 1999). A notable result from that study was the finding of much greater new water runoff in one of the two snowmelt years studied, which they attributed to deep ground frost that prevented the infiltration of meltwater in spring. Overall, new water inputs ranged from 41 to 74% in the deep-frost year compared with 30 to 36% in the low-frost year (Shanley *et al.*, 2002). Overland flow on frozen ground was directly observed at the small agricultural W-2 catchment, which had the highest fraction of open land (73%) and the highest fraction of new water (74%). The isotopic response at W-2 was quite muted in the low-frost year in comparison with the deep-frost year, when the streamwater isotopic signal approached that of meltwater (Figure 10). Direct runoff over frozen ground also explained the larger q_{new} amount relative to quickflow estimated from recession analysis in the deep-frost year (Figure 9). Ground frost is minimal in the SRRW forest but develops in many winters in open land because of less insulating organic duff, lower insulating snow cover and greater radiational cooling at night (Shanley and Chalmers, 1999). Dunne and Black (1971) likewise documented infiltration-excess overland flow of meltwater, even on the steep, permeable grassy hillslopes of their plots, due to concrete frost. A summer storm had lower new water inputs of 28–46% (Shanley *et al.*, 2002), but in the same catchment order as the deep-frost year snowmelt, i.e. more new water runoff in agricultural lands. This summer pattern may have

resulted from a greater tendency for overland runoff on compacted soils in the agricultural fields.

Multi-year time series (2003–2011) of water isotopes across sites provided an additional assessment of scale and land use effects on water residence times in the SRRW. The isotopic pattern of monthly streamwater at the three nested basins and at W-2 compared with the pattern of weekly precipitation show that the stream signal is strongly damped relative to the precipitation signal (Figure 11). The standard deviation of $\delta^{18}\text{O}$ in precipitation was nearly an order of magnitude greater than that for any of the streams, which all had quite similar standard deviations. Applying the approach of Soulsby *et al.* (2000), an ~8 : 1 ratio in standard deviations suggests a mean residence time (MRT) for water in the catchments of about 1.3 years. The similarity in MRT and variability of $\delta^{18}\text{O}$ in the three nested basins and the small agricultural catchment is consistent with the lack of a strong scale or land use effect (at least in the typical low-frost year) in new water contributions (Shanley *et al.*, 2002). Thus, surprisingly, the chemical and isotopic approaches confirm that the runoff processes (SOF, SSF)

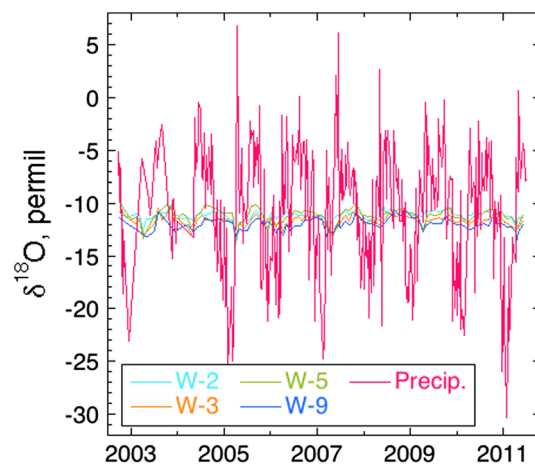


Figure 11. Nine-year time series of $\delta^{18}\text{O}$ in precipitation as well as streamwater at W-9, W-3, W-5 and W-2

demonstrated by D&B on the hillslope scale proved also to be important at the 100-km² scale of the greater Sleepers River watershed.

SUMMING UP

More than 50 years have passed since the SRRW was established for hydrologic research. The early investigations of D&B linked runoff generation processes to the topographic and hydrogeological characteristics of the landscape. D&B illustrated the functioning of the VSA concept as it relates to landscapes that have extensive areas with a hydrogeological/topographic limit to the conveyance capacity of the shallow subsurface. When and where that limit was exceeded, return flow/exfiltration occurred and was augmented by rainfall and/or snowmelt as SOF. This work has resonated with hydrologic researchers in other glaciated as well as non-glaciated landscapes (Bonell, 1998; Grip and Rodhe, 1985, 1994; Walter *et al.*, 2000; Grayson *et al.*, 2002; Verry and Kolka, 2003). In turn, subsequent studies in glaciated landscapes employing isotopic techniques, such as Water's Way (Grip and Rodhe, 1985, 1994), inspired later research at the SRRW, bringing the research path full circle. The more recent isotopic and chemical approaches applied at the SRRW have complemented the hydrometric approaches of D&B, constraining the flow path possibilities and thereby improving understanding of streamflow generation mechanisms.

Like the Scandinavian catchments of Water's Way (Grip and Rodhe, 1985, 1994), hydrology at the SRRW is profoundly influenced by the glacial deposits that mantle the landscape. In particular, the dense silty basal till provides high storage capacity in a low-permeability material, which sustains baseflow. However, spatial heterogeneity in slope, soil drainage class and presence of a fragipan gives rise to contrasting hydrograph recession characteristics even in adjacent catchments at the SRRW (Comer and Zimmermann, 1969; Engman, 1981). Relative to the Scandinavian catchments of Water's Way, the SRRW has more rugged topography; thus, steeper hydraulic gradients are a greater consideration in water delivery from hillslope to stream. Another important factor in the hydrology is the jointing and fracturing, which form primary controls on drainage patterns (Newell, 1970) and spring locations (Dunne, 1980). The glacial advances scoured and re-deposited material in patterns determined by the direction of ice flow over the pre-existing topography (Newell, 1970). The post-glacial hydrology likely reflects only minor adjustments from pre-glacial drainage patterns, but major shifts in storage capacity, permeability and hydrologic flow paths.

Our review demonstrates how the latest generation of studies has used solute transport to directly link when and where SOF develops in portions of the landscape. These findings provide mechanistic explanation to the double paradox in catchment hydrology and geochemistry (Kirchner, 2003) that is consistent with routing of water along shallow flow paths and flushing of solutes during storm events (Burns *et al.*, 1998; Bishop *et al.*, 2004). In the Swedish catchment studied by Bishop *et al.* (2004), SSF along shallow, highly transmissive flow paths to incised stream channels explained the double paradox. At the SRRW, mixing of return flow and direct precipitation to generate SOF provides an explanation for variation in stream chemistry and new water and solute inputs while old water dominates stormflow. Such processes were theorized through streamflow generation mechanisms explored by Dunne and Black (1970a, 1970b, 1971) and hydrogeologic controls of the landscape by Newell (1970).

Of course, the portion of the double paradox related to differences in hydrograph and conservative tracer response (Kirchner, 2003; Bishop *et al.*, 2004) is really not a paradox at all. As McDonnell and Beven (2014) note, these responses are differences between celerity (i.e. the propagation of hydraulic potentials) and velocity (i.e. the movement of particles). It is interesting to note that perhaps the clearest exposition of these celerity-velocity distinctions exists within the Water's Way textbook. Grip and Rodhe (1985, 1994) were ahead of their time in making this distinction and applying conservative tracer approaches to the understanding of Nordic catchments.

LOOKING AHEAD

At the SRRW, we have expanded on the early VSA work of Dunne and Black with targeted studies aimed at identifying or at least constraining specific pathways of water and solute movement to the stream. Our advancements have been incremental, shaped largely by inference from the stream hydrograph and chemograph, guided by limited, at best, understanding of internal catchment plumbing.

One way forward is to exploit emerging sensor technologies to increase the frequency of information acquisition. Despite our high-frequency discrete sampling (limited by labour, event stochasticity, budgets and laboratory capacity), we have lingering questions about flow pathways, solute sources and mixing dynamics. By measuring tracers at high-frequency using new tools such as in-stream fluorometers for DOC (as we have started to do) and embracing possibilities for field deployment of laser spectrometry for continuous water isotopes (McDonnell and Beven, 2014), we hope to better

constrain discrete water sources and discover how 'packets of water' move and mix. We may need to deploy these instruments on the scale that these processes operate such as hillslope transects. Even still, solving the age-old question of just how water moves to the stream, and being able to transfer this knowledge to other settings, will require further innovations in analytical approaches.

We imagine future work at the SRRW exploring three related fronts. (i) Examination of the time-varying transit time of water through the SRRW catchments. This is the grand challenge for determining how different catchment states store and release water. The community challenge in this regard is to unpack the transit time distribution to understand in time and space how velocity and celerity are manifested at the catchment outlet (McDonnell *et al.*, 2010). For snowmelt-driven systems like the SRRW, this is an especially vexing challenge because the inputs are highly variable and have evolving isotopic signatures during the melt period. (ii) Examination of the hierarchy of influences on streamflow generation across flow states that may shift from topographically driven redistribution of water at wet states, to vegetation and geologic structure influences at lower flow states (Jencso and McGlynn, 2011). The relative strength of these influences and their reordering through time highlight direct and quantifiable linkages between catchment structure (topography, vegetation, geology, their topology) and streamflow dynamics (Jencso and McGlynn, 2011; Nippgen *et al.*, 2011). (iii) Perhaps in the end, the perceived differences between runoff dynamics across different sites are really expressions of the same fundamental processes related to fill and spill, transmission losses, connectivity and thresholds (McDonnell, 2013). New work at the SRRW will seek to better quantify controls on these characteristic forms of non-linearity at the catchment scale and in so doing, improve our understanding of the temporal and spatial sources of water and solutes at the catchment outlet.

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REFERENCES

- Alem MI, Hoch GE, Varner JE. 1965. Water as the source of oxidant and reductant in bacterial chemosynthesis. *PNAS* **54**: 869–873.
- Anderson MG, Burt TP. 1978. The role of topography in controlling throughflow generation. *Earth Surface Processes* **3**: 331–344. DOI: 10.1002/esp.3290030402
- Bailey SW, Mayer B, Mitchell MJ. 2004. Evidence for influence of mineral weathering on stream water sulphate in Vermont and New Hampshire (USA). *Hydrological Processes* **18**: 1639–1653. DOI: 10.1002/hyp.1410
- Betson RP. 1964. What is watershed runoff? *Journal of Geophysical Research* **69**: 1541–1552.
- Beven KJ. 1978. The hydrological response of headwater and sideslope areas. *Hydrological Sciences Bulletin* **23**: 419–437.
- Beven KJ, Kirkby MJ. 1979. A physically based, variable contributing area model of basin hydrology. *Hydrological Sciences Bulletin* **24**: 43–69.
- Bishop KH, Grip H, O'Neill A. 1990. The origins of acid runoff in a hillslope during storm events. *Journal of Hydrology* **116**: 35–61. DOI: 10.1016/0022-1694(90)90114-D
- Bishop KH, Seibert J, Köhler S, Laudon H. 2004. Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry. *Hydrological Processes* **18**: 185–189. DOI: 10.1002/hyp.5209
- Bonell M. 1998. Selected challenges in runoff generation research in forests from the hillslope to headwater drainage basin scale. *Journal of the American Water Resources Association* **34**: 765–785.
- Bonell M, Gilmour DA. 1978. The development of overland flow in a tropical rainforest catchment. *Journal of Hydrology* **39**: 365–382. DOI: 10.1016/0022-1694(78)90012-4
- Brown VA, McDonnell JJ, Burns DA, Kendall C. 1999. The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. *Journal of Hydrology* **217**: 171–196. DOI: 10.1016/S0022-1694(98)00247-9
- Brutsaert W, Nieber JL. 1977. Regionalized drought flow hydrographs from a mature glaciated plateau. *Water Resources Research* **13**: 637–643.
- Bullen TD, Kendall C. 1998. Tracing of weathering reactions and flowpaths: a multi-isotope approach. In *Isotopes Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 611–646.
- Burns DA, Hooper RP, McDonnell JJ, Freer JE, Kendall C, Beven KJ. 1998. Base cation concentrations in subsurface flow from a forested hillslope: the role of flushing frequency. *Water Resources Research* **34**: 3535–3544.
- Buttle JM. 1998. Fundamentals of small catchment hydrology. In *Isotope Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier: Amsterdam; 1–49.
- Christophersen N, Hooper RP. 1992. Multivariate analysis of stream water chemical data: the use of principal components analysis for the end-member mixing problem. *Water Resources Research* **28**: 99–107.
- Christophersen N, Andersen S, Neal C, Hooper RP, Vogt RD. 1990. Modelling streamwater chemistry as a mixture of soilwater end-members – a step towards second-generation acidification models. *Journal of Hydrology* **116**: 307–320. DOI: 10.1016/0022-1694(90)90130-P
- Comer GH, Zimmermann RH. 1969. Low-flow and basin characteristics of two streams in northern Vermont. *Journal of Hydrology* **7**: 98–108. DOI: 10.1016/0022-1694(68)90197-2

- Creed IF, Band LE. 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resources Research* **34**: 3105–3120.
- Creed IF, Band LE, Foster NW, Morrison IK, Nicolson JA, Semkin RG, Jeffries DS. 1996. Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. *Water Resources Research* **32**: 3337–3354.
- DeAngelis RJ, Urban JB, Gburek WJ, Contino MA. 1984. Precipitation and runoff on eight New England basins during extreme wet and dry periods. *Hydrological Sciences Journal* **29**: 13–28.
- Doctor DH, Kendall C, Sebestyen SD, Shanley JB, Ohte N, Boyer EW. 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. *Hydrological Processes* **22**: 2410–2423. DOI: 10.1002/hyp.6833
- Dunne T. 1978. Field studies of hillslope flow processes. In *Hillslope Hydrology*, Kirkby MJ (ed). John Wiley and Sons: Chichester; 227–293.
- Dunne T. 1980. Formation and controls of channel networks. *Progress in Physical Geography* **4**: 211–239. DOI: 10.1177/030913338000400204
- Dunne T, Black RD. 1970a. An experimental investigation of runoff production in permeable soils. *Water Resources Research* **6**: 478–490. DOI: 10.1029/WR006i002p00478
- Dunne T, Black RD. 1970b. Partial area contributions to storm runoff in a small New England watershed. *Water Resources Research* **6**: 1296–1311. DOI: 10.1029/WR006i005p1296
- Dunne T, Black RD. 1971. Runoff processes during snowmelt. *Water Resources Research* **7**: 1160–1172. DOI: 10.1029/WR007i005p1160
- Dunne T, Moore TR, Taylor CH. 1975. Recognition and prediction of runoff-producing zones in humid regions. *Hydrological Sciences Bulletin* **20**: 305–327.
- Eckhardt K. 2005. How to construct recursive digital filters for baseflow separation. *Hydrological Processes* **19**: 507–515. DOI: 10.1002/hyp.5675
- Eckhardt K. 2008. A comparison of baseflow indices, which were calculated with seven different baseflow separation methods. *Journal of Hydrology* **352**: 168–173. DOI: 10.1016/j.jhydrol.2008.01.005
- Engman ET. 1981. Rainfall-runoff characteristics for a mountainous watershed in the Northeast United States. *Nordic Hydrology* **12**: 247–264.
- Entekhabi D, Eagleson PS. 1989. Land surface hydrology parameterization for atmospheric general circulation models including subgrid scale spatial variability. *Journal of Climate* **2**: 816–831. DOI: 10.1175/1520-0442(1989)002<0816:LSHPFA>2.0.CO;2
- Eshleman KN, Pollard JS, O'Brien AK. 1993. Determination of contributing areas for saturation overland flow from chemical hydrograph separations. *Water Resources Research* **29**: 3577–3587.
- Freeze RA. 1974. Streamflow generation. *Reviews of Geophysics* **12**: 627–647. DOI: 10.1029/RG012i004p00627
- Grayson RB, Blöschl G, Western AW, McMahon TA. 2002. Advances in the use of observed spatial patterns of catchment hydrological response. *Adv Water Resources* **25**: 1313–1334. DOI: 10.1016/S0309-1708(02)00060-X
- Green SA, Blough NV. 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnology and Oceanography* **39**: 1903–1916.
- Grip H, Rodhe A. 1985. *Vattnets väg från regn till bäck* (Swedish title, in English: *Water's way from rain to stream*). Forskningsrådets förlagstjänst: Stockholm; 156 p.
- Grip H, Rodhe A. 1994. *Vattnets väg från regn till bäck* (Swedish title, in English: *Water's way from rain to stream*). Hallgren och Fallgren: Uppsala (3rd ed.), ISBN: 9789173827621, 155 p.
- Hall FR. 1968. Base-flow recessions – a review. *Water Resources Research* **4**: 973–983.
- Hendrick RL, Comer GH. 1970. Space variations of precipitation and implications for raingage network design. *Journal of Hydrology* **10**: 151–163. DOI: 10.1016/0022-1694(70)90185-X
- Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. In *Forest Hydrology*, Sopper WE, Lull HW (eds). Pergamon Press; 275–291.
- Hjerdt KN. 2002. Deconvoluting the hydrologic response of a small till catchment: spatial variability of groundwater level and quality in relation to streamflow. In *Forestry*, State University of New York College of Environmental Science and Forestry: Syracuse, NY, USA; 204.
- Hornberger GM, Bencala KE, McKnight DM. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry* **25**: 147–165. DOI: 10.1007/BF00024390
- Horton RE. 1933. The role of infiltration in the hydrologic cycle. In *Trans., American Geophysical Union Fourteenth Annual Meeting*, National Research Council of the National Academy of Sciences; 446–460.
- Hursh CR, Brater EF. 1941. Separating storm-hydrographs from small drainage-areas into surface- and subsurface-flow. *Transactions, American Geophysical Union* **22**: 863–871.
- Jakeman AJ, Littlewood IG, Whitehead PG. 1990. Computation of the instantaneous unit hydrograph and identifiable component flows with application to two small upland catchments. *Journal of Hydrology* **117**: 275–300. DOI: 10.1016/0022-1694(90)90097-H
- Jencso KG, McGlynn BL. 2011. Hierarchical controls on runoff generation: topographically driven hydrologic connectivity, geology, and vegetation. *Water Resources Research* **47**: W11527. DOI: 10.1029/2011wr010666
- Jencso KG, McGlynn BL, Gooseff MN, Wondzell SM, Bencala KE, Marshall LA. 2009. Hydrologic connectivity between landscapes and streams: transferring reach- and plot-scale understanding to the catchment scale. *Water Resources Research* **45**. DOI: 10.1029/2008WR007225
- Jencso KG, McGlynn BL, Gooseff MN, Bencala KE, Wondzell SM. 2010. Hillslope hydrologic connectivity controls riparian groundwater turnover: implications of catchment structure for riparian buffering and stream water sources. *Water Resources Research* **46**: W10524. DOI: 10.1029/2009WR008818
- Kendall KA, Shanley JB, McDonnell JJ. 1999. A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. *Journal of Hydrology* **219**: 188–205. DOI: 10.1016/S0022-1694(99)00059-1
- Kendall C, Wankel SD, Elliott EM. 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. In *Stable Isotopes in Ecology and Environmental Science*, Michener RH, Lajtha K (eds). Blackwell Scientific: Malden, MA, USA; 375–449.
- Kirchner JW. 2003. A double paradox in catchment hydrology and geochemistry. *Hydrological Processes* **17**: 871–874. DOI: 10.1002/hyp.5108
- Likens GE, Bormann FH. 1995. *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag: New York.
- Mayer B, Shanley JB, Bailey SW, Mitchell MJ. 2010. Identifying sources of stream water sulfate after a summer drought in the Sleepers River watershed (Vermont, USA) using hydrological, chemical, and isotopic techniques. *Applied Geochemistry* **25**: 747–754. DOI: 10.1016/j.apgeochem.2010.02.007
- McDonnell JJ. 2013. Are all runoff processes the same? *Hydrological Processes* **27**: 4103–4111. DOI: 10.1002/hyp.10076
- McDonnell JJ, Beven K. 2014. Debates – the future of hydrological sciences: a (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph. *Water Resources Research* **50**: 5342–5350. DOI: 10.1002/2013WR015141
- McDonnell JJ, McGuire K, Aggarwal P, Beven KJ, Biondi D, Destouni G, Dunn S, James A, Kirchner J, Kraft P, Lyon S, Maloszewski P, Newman B, Pfister L, Rinaldo A, Rodhe A, Sayama T, Seibert J, Solomon K, Soulsby C, Stewart M, Tetzlaff D, Tobin C, Troch P, Weiler M, Western A, Wörman A, Wrede S. 2010. How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. *Hydrological Processes* **24**: 1745–1754. DOI: 10.1002/hyp.7796
- McGlynn BL, McDonnell JJ. 2003. Quantifying the relative contributions of riparian and hillslope zones to catchment runoff. *Water Resources Research* **39**: 1310. DOI: 10.1029/2003WR002091
- McGlynn BL, McDonnell JJ, Shanley JB, Kendall C. 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. *Journal of Hydrology* **222**: 75–92. DOI: 10.1016/S0022-1694(99)00102-X
- McGlynn BL, McDonnell JJ, Brammer DD. 2002. A review of the evolving perceptual model of hillslope flowpaths at the Maimai catchments, New Zealand. *Journal of Hydrology* **257**: 1–26. DOI: 10.1016/S0022-1694(01)00559-5
- McGuire KJ, McDonnell JJ, Weiler M, Kendall C, McGlynn BL, Welker JM, Seibert J. 2005. The role of topography on catchment-scale water

- residence time. *Water Resources Research* **41**: W05002. DOI: 10.1029/2004WR003657
- Mitchell MJ, Krouse HR, Mayer B, Stam AC, Zhang Y. 1998. Use of stable isotopes in evaluating sulfur biogeochemistry of forest ecosystems. In *Isotopes Tracers in Catchment Hydrology*, Kendall C, McDonnell JJ (eds). Elsevier; 489–518.
- Montgomery DR, Dietrich WE. 1988. Where do channels begin? *Nature* **336**: 232–234. DOI: 10.1038/336232a0
- de Moraes JM, Schuler AE, Dunne T, Figueiredo RO, Victoria RL. 2006. Water storage and runoff processes in plinthic soils under forest and pasture in eastern Amazonia. *Hydrological Processes* **20**: 2509–2526. DOI: 10.1002/hyp.6213
- Mosley MP. 1979. Streamflow generation in a forested watershed, New Zealand. *Water Resources Research* **15**: 795–806. DOI: 10.1029/WR015i004p00795
- Newell WL. 1966. *Saprolite Development in the Sleepers River Watershed, Danville, Vermont*. Dartmouth College: Hanover, NH, USA; 71.
- Newell WL. 1970. Factors influencing the grain of the topography along the Willoughby Arch in northeastern Vermont. *Geografiska Annaler. Series A. Physical Geography* **52**: 103–112. DOI: 10.2307/520603
- Nippen F, McGlynn BL, Marshall LA, Emanuel RE. 2011. Landscape structure and climate influences on hydrologic response. *Water Resources Research* **47**: W12528. DOI: 10.1029/2011WR011161
- Ohte N, Sebestyen SD, Kendall C, Shanley JB, Wankel SD, Doctor DH, Boyer EW. 2004. Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique. *Geophysical Research Letters* **31**: L21506. DOI: 10.1029/2004GL020908
- O'Loughlin EM. 1986. Prediction of surface saturation zones in natural catchments by topographic analysis. *Water Resources Research* **22**: 794–804.
- Pellerin BA, Saraceno J, Shanley JB, Sebestyen SD, Aiken GR, Wollheim WM, Bergamaschi BA. 2012. Taking the pulse of snowmelt: *in situ* sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry* **108**: 183–198. DOI: 10.1007/s10533-011-9589-8
- Ragan RM. 1968. An experimental investigation of partial area contributions. In *Hydrological Aspects of the Utilization of Water*. General Assembly of Bern, 25 September–7 October 1967, IAHS (ed). International Association of Scientific Hydrology; Exeter, UK; 241–251.
- Rodhe A. 1987. The origin of streamwater traced by oxygen-18. In *Dept. Phys. Geogr., Div. Hydrol., Uppsala University*; 260.
- Saraceno JF, Pellerin BA, Downing BD, Boss E, Bachand PAM, Bergamaschi BA. 2009. High-frequency *in situ* optical measurements during a storm event: assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes. *Journal of Geophysical Research* **114**. DOI: 10.1029/2009jg000989
- Sebestyen SD, Boyer EW, Shanley JB, Kendall C, Doctor DH, Aiken GR, Ohte N. 2008. Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. *Water Resources Research* **44**: W12410. DOI: 10.1029/2008WR006983
- Sebestyen SD, Boyer EW, Shanley JB. 2009. Responses of stream nitrate and dissolved organic carbon loadings to hydrological forcing and climate change in an upland forest of the northeast USA. *Journal of Geophysical Research, Biogeosciences* **114**: G02002. DOI: 10.1029/2008JG000778
- Sebestyen SD, Shanley JB, Boyer EW, Kendall C, Doctor DH. 2014. Coupled hydrological and biogeochemical processes controlling variability of nitrogen species in streamflow during autumn in an upland forest. *Water Resources Research* **50**: 1569–1591. DOI: 10.1002/2013WR013670
- Shanley JB, Chalmers A. 1999. The effect of frozen soil on snowmelt runoff at Sleepers River, Vermont. *Hydrological Processes* **13**: 1843–1857.
- Shanley JB, Kendall C, Smith TE, Wolock DM, McDonnell JJ. 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes* **16**: 589–609. DOI: 10.1002/hyp.312
- Shanley JB, Hjerdt KN, McDonnell JJ, Kendall C. 2003. Shallow water table fluctuations in relation to soil penetration resistance. *Ground Water* **41**: 964–972.
- Shanley JB, Krám P, Hruška J, Bullen TD. 2004. A biogeochemical comparison of two well-buffered catchments with contrasting histories of acid deposition. *Water, Air, & Soil Pollution* **4**: 325–342. DOI: 10.1023/B:WAFO.0000028363.48348.a4
- Shanley JB, Mayer B, Mitchell MJ, Michel RL, Bailey SW, Kendall C. 2005. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ³⁵S activity. *Biogeochemistry* **76**: 161–185. DOI: 10.1007/s10533-005-2856-9
- Shanley JB, Mayer B, Mitchell MJ, Bailey SW. 2008. Seasonal and event variations in $\delta^{34}\text{S}$ values of stream sulfate in a Vermont forested catchment: Implications for sulfur sources and cycling. *Science of the Total Environment* **404**: 262–268. DOI: 10.1016/j.scitotenv.2008.03.020
- Sklash MG, Farvolden RN, Fritz P. 1976. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. *Can. J. Earth Science* **13**: 271–283.
- Smith TE. 1997. Comparison of runoff flow paths in four basins at Sleepers River Research Watershed, Vermont. In *Hydrology and Water Resources*. University of New Hampshire: Durham, NH, USA; 197.
- Soulsby C, Malcolm IA, Helliwell RC, Ferrier RC, Jenkins A. 2000. Isotope hydrology of the Allt a' Mharcaidh catchment, Cairngorms, Scotland: implications for hydrological pathways and residence times. *Hydrological Processes* **14**: 747–762. DOI: 10.1002/(SICI)1099-1085(200003)14:4<747::AID-HYP970>3.0.CO;2-0
- Soulsby C, Tetzlaff D, Dunn SM, Waldron S. 2006. Scaling up and out in runoff process understanding: insights from nested experimental catchment studies. *Hydrological Processes* **20**: 2461–2465. DOI: 10.1002/hyp.6338
- Springston GE, Haselton GM. 1999. *Surficial Geologic Map of the Eastern Portion of the St. Johnsbury Quadrangle, Vermont*. Vermont Geological Survey; 1.
- Taylor CH, Pearce AJ. 1982. Storm runoff processes and subcatchment characteristics in a new Zealand hill country catchment. *Earth Surface Processes and Landforms* **7**: 439–447. DOI: 10.1002/esp.3290070505
- Tetzlaff D, Soulsby C, Hrachowitz M, Speed M. 2011. Relative influence of upland and lowland headwaters on the isotope hydrology and transit times of larger catchments. *Journal of Hydrology* **400**: 438–447. DOI: 10.1016/j.jhydrol.2011.01.053
- Tóth J. 1963. A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research* **68**: 4795–4812.
- Verry ES, Kolka RK. 2003. Importance of wetlands to streamflow generation. In *Proceedings of the First Interagency Conference on Research in the Watersheds*, 27–30 October 2003; Renard KG, McElroy SA, Gburek WJ, Canfield HE, Scott RL (eds). U.S. Department of Agriculture, Agricultural Research Service; 126–132.
- Walter MT, Walter MF, Brooks ES, Steenhuis TS, Boll J, Weiler K. 2000. Hydrologically sensitive areas: variable source area hydrology implications for water quality risk assessment. *J. Soil & Water Conservation* **55**: 277–284.
- Wolock DM. 1995. Effects of subbasin size on topographic characteristics and simulated flow paths in Sleepers River watershed, Vermont. *Water Resources Research* **31**: 1989–1997.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article at publisher's web-site.

Supporting Information

The SI contains one file with 14 photos depicting some of the sites, instrumentation, and hydrologic processes at Sleepers River Research Watershed. Following are the Figure captions.

1. The Sleepers River sign at the Snow Research Station (Figure 1), with meteorological instrumentation in the background.
2. Dunne and Black study area (Figure 1) in the late 1960s with trench installation visible at the base of the hillslope. Note convex, concave, and planar hillslope sections.
3. "Where is it?" Tom Dunne in 2001 standing at the site of his hillslope, which was removed for a highway relocation project in the 1970s.
4. View to the west depicts the mixed agricultural and forested land use within the Sleepers River watershed. The pasture slopes down to Pope Brook near the W-3 gage (837 ha) (Figure 1, Figure S5). The W-9 watershed (41 ha) (Figure 1), nested within W-3, is in the forested Kittridge Hills in the background.
5. From near the same site as Figure S4, but looking to the east, down the axis of the Sleepers River watershed and across the Connecticut River to the White Mountains of New Hampshire.
6. The W-3 gage (837 ha) (Figure 1), built in 1959.
7. The W-9 gage (41 ha) (Figure 1), built in 1963.
8. The W-9 gage near the peak flow response from an intense storm, 24 July 2008. Flow peaked at 476 L sec^{-1} (4.23 mm hr^{-1}), the second highest flow recorded over about 30 years of total record at this site.
9. Nighttime snowmelt sampling at the W-9 weir by the second author in 2003.
10. Ablating snowpack within W-9, just upstream of the weir at the confluence of the A and B tributaries.
11. Saturation-excess overland flow at W-9 during snowmelt.
12. Hillslope within W-9 studied by Kendall et al. (1999) and referenced in the text (Figure 4). Groundwater from the white wells and piezometers that are visible plots as the hillslope till groundwater in Figure 4, and had Si concentrations much higher than streamwater. The hillslope hollow, where groundwater chemistry was closer to streamwater composition (hillslope hollow piezometers in Figure 4), can be seen to the right (no hillslope hollow piezometers are visible). The B tributary stream is visible in the lower right.
13. Nested piezometers in tributary BY of tributary B, W-9. Groundwater here has composition similar to hillslope hollows, and is designated as upper riparian piezometers in Figure 4.
14. The lead author in the W-9 weir pool, drained to service the two fluorometers and turbidity sensor. Here the submersible cables that lead to a datalogger (not visible) to the right are disconnected.

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Figure S1. The Sleepers River sign at the Snow Research Station (Figure 1), with meteorological instrumentation in the background.



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Figure S3. “Where is it?” Tom Dunne in 2001 standing at the site of his hillslope, which was removed for a highway relocation project in the 1970s.



Figure S4. View to the west depicts the mixed agricultural and forested land use within the Sleepers River watershed. The pasture slopes down to Pope Brook near the W-3 gage (837 ha) (Figure 1, Figure S5). The W-9 watershed (41 ha) (Figure 1), nested within W-3, is in the forested Kittridge Hills in the background.



Figure S5. From near the same site as Figure S4, but looking to the east, down the axis of the Sleepers River watershed and across the Connecticut River to the White Mountains of New Hampshire.



Figure S6. The W-3 gage (837 ha) (Figure 1), built in 1959.



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Figure S8. The W-9 gage near the peak flow response from an intense storm, 24 July 2008. Flow peaked at 476 L sec^{-1} (4.23 mm hr^{-1}), the second highest flow recorded over about 30 years of total record at this site.



Figure S9. Nighttime snowmelt sampling at the W-9 weir by the second author in 2003.



Figure S10. Ablating snowpack within W-9, just upstream of the weir at the confluence of the A and B tributaries.



Figure S11. Saturation-excess overland flow at W-9 during snowmelt.



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Figure S13. Nested piezometers in tributary BY of tributary B, W-9. Groundwater here has composition similar to hillslope hollows, and is designated as upper riparian piezometers in Figure 4.



Figure S14. The lead author in the W-9 weir pool, drained to service the two fluorimeters and turbidity sensor. Here the submersible cables that lead to a datalogger (not visible) to the right are disconnected.