Identifying controls on nitrate sources and flowpaths in a forested catchment using a hydropedological framework

L. H. Pardo[1], M. B. Green[2], S. W. Bailey[3], K. J. McGuire[4], and W. H. McDowell[5]

[1]Northern Research Station, USDA Forest Service, Burlington, VT, USA.

[2]Northern Research Station, USDA Forest Service and Center for the Environment, Plymouth State University, Plymouth, NH, USA. current affiliation: Northern Research Station, USDA Forest Service and Department of Earth, Environmental, and Planetary Sciences, Case Western Reserve University, Cleveland, OH, USA.

[3]Northern Research Station, USDA Forest Service, North Woodstock, NH, USA

[4]Department of Forest Resources and Environmental Conservation and Virginia Water Resources Research Center, Virginia Tech, Blacksburg, VA, USA.

[5]Department of Natural Resources and the Environment, University of New Hampshire, Durham, NH USA.

Corresponding author: Linda Pardo (linda.pardo@usda.gov)

Key Point:

- Most catchment nitrate export occurs at high flow when bedrock-controlled areas are most connected hydrologically to the drainage network

Pardo, L. H., Green, M. B., Bailey, S. W., McGuire, K. J., & McDowell, W. H. (2022). Identifying controls on nitrate sources and flowpaths in a forested catchment using a hydropedological framework. *Journal of Geophysical Research: Biogeosciences*, 127, e2020JG006140. https://doi.org/10.1029/2020JG006140

Abstract

Catchment-scale assessments of nitrogen retention and loss rarely account for soil and landscape heterogeneity and are, thus, unable to account for the suite of nitrogen cycling processes that ultimately affect the export of nitrate via stream water. Long-term study at the Hubbard Brook Experimental Forest, NH has generated a unique dataset that facilitates spatially explicit examination of interactions among hydrology, soil development, and nitrogen cycling processes. Using high-frequency streamwater chemistry data with intensive subsurface hydrology and solute monitoring, we tracked areas of the catchment that are hydrologically active under different flow conditions to identify the source area of streamwater nitrate. We hypothesize that as the drainage network expands, increasing hydrologic connection to bedrock outcrop-associated soils, streamwater nitrate concentration and flux at the catchment outlet increase. Most nitrate export (>80%) occurred during high flows when high nitrate, bedrock-controlled areas of the catchment were most connected hydrologically to the drainage network (~15% of the time). End-member mixing analysis demonstrated that the bedrock-controlled upper part of the catchment influences nitrate concentration at the outlet and contributes most to catchment nitrate export compared to the near-stream soil units and seeps. Most of the time, nitrate at the catchment outlet comes from seeps and the near-stream zone; under high flow conditions, bedrock-controlled hotspots for nitrate production contribute more to export of nitrate. This analysis demonstrates how the source area of streamwater nitrate varies under different flow conditions, suggesting that long-term nitrate dynamics may be driven primarily by a relatively small part of the catchment.

Plain Language Summary

Nitrogen export from catchments provides insight into the functioning of forested ecosystems. In this study, we evaluated where in the forest streamwater nitrate comes from, and how it gets to the stream. Because of the intensive instrumentation at our long-term ecological study site, the Hubbard Brook Experimental Forest, we were able to record differences in nitrogen production based on the topography. Compared to the soils near the stream, the soils below bedrock outcrops, higher uphill in the forest, produced more nitrate and were thus considered ‘hotspots’ for nitrate production. Our study showed that the vast majority of nitrate (>80%) flowed out of the forest in stream water at times when stream flow was very high, which occurred only ~15% of the time. At these times, the stream network—which expands and contracts depending on how much rain there is and how much water is moving downstream—connects the nitrate ‘hotspots’ with the stream. Detailed information about nitrate source areas, like we produced in this study, will allow better assessment of long-term nitrogen status in forested catchments.

Keywords

streamwater, nitrification, biogeochemistry, groundwater, soil development, podzolization

1 Introduction

The motivation for this study is to improve understanding of the spatial and temporal heterogeneity in nitrogen (N) cycling dynamics and their influence on catchment N export. Nitrogen can be beneficial or detrimental to forest ecosystems. While it is a key nutrient that supports life, N is typically a limiting nutrient for terrestrial plant growth. Thus, N enhances growth in N-limited systems (Vitousek & Howarth, 1991). However, excess N in forests can lead to detrimental effects including soil and surface water acidification, decreases in tree growth and survival, shifts in community composition of trees, herbaceous plants, and lichens, and increased susceptibility to secondary stresses (Aber et al., 1989, 2003; Bobbink et al., 2010; Pardo et al., 2011). Nitrogen is linked, via organic matter, to the carbon (C) cycle, as N availability affects both photosynthesis and decomposition. In order to model and mitigate the harmful effects of elevated atmospheric CO_2, therefore, it is critical to understand C-N linkages (Luo et al., 2016; Tian et al., 2015). Consequently, scientists have been trying, for decades, to understand what controls N retention and loss from forests. Improving our understanding of the controls of N retention and loss from forests requires linking hydrologic and biogeochemical information (Cirmo & McDonnell, 1997; Creed et al., 1996; Lohse et al., 2009; Pinay et al., 2015; Rose et al., 2015). Although there has been considerable work on this in the past two decades, major questions about the interaction of fundamental processes (e.g., soil nitrification, retention, and hydrologic transport) and about their spatial variation remain, preventing us from predicting the magnitude and timing of nitrate export (Brooks et al., 2015; Burt & Pinay, 2005; Lohse et al., 2013).

Observations at the catchment scale have provided important insights for understanding patterns in solute export and retention. Previous work has demonstrated regional patterns in surface water nitrate concentration and flux as a function of N deposition—even identifying a threshold of deposition above which increased nitrate export is likely (Aber et al., 2003). Many factors may contribute to regulating catchment N loss including N deposition, and its effects on soil C:N ratios and soil N cycling processes (Aber et al., 2003). Other factors contribute to variability in the extent, magnitude, and timing of N losses including land-use history, disturbance, species composition, climate, soil type and heterogeneity and hydrologic pathway (Andersson & Lepistö, 1998; Cirmo & McDonnell, 1997; Compton et al., 1998; Goodale & Aber, 2001; Lohse et al., 2013; Lovett et al., 2002, 2004; Sebestyen et al., 2009). In many systems, denitrification can play a significant role in affecting stream N flux (Hedin et al., 1998).

Despite this progress, previous studies of regional patterns of streamwater nitrate export have been limited in their ability to explain the variation in N loss across the landscape, due to the complexity of catchment structure (Pinay et al., 2015). The structure or the physical organization of catchment topography, geology, and soils controls dynamic transport pathways that connect areas of high nitrate production (i.e., hotspots) to the near-stream environment where N loss (via denitrification or nitrate leaching) can occur and ultimately influence N flux at the catchment outlet (e.g., Welter & Fisher, 2016). Most previous catchment-scale analyses, while acknowledging the confounding effect of soil heterogeneity that is common in forested catchments, have been unable to account for it in their analyses and therefore end up treating the catchment as essentially homogeneous. However, within-catchment variation in stream N concentrations can be high (i.e., coefficient of variations $\gtrsim$ 150%) both spatially and temporally (e.g., Abbott et al., 2018; Asano et al., 2009). The spatial heterogeneity and temporal variation of soil nitrate production and the hydrologic connectivity of different parts of the landscape to the catchment outlet are difficult to characterize (Burt & Pinay, 2005; Covino, 2017; Rose et al., 2015). Generally, near-stream zones have been considered the dominant source of solutes because of persistent groundwater connection to the stream network (e.g., Kiewiet et al. 2020; Nippgen et al. 2015), however distal sources of solutes, particularly dissolved organic carbon, can be a strong influence on the catchment outlet during expansion of the drainage network following precipitation events (Ducharme et al. 2021; Gannon et al. 2015). Soil properties, such as permeability and water retention, as well as mass balance, transport, and cycling at any given location, dictate the hydrologic state and transfer of water and nutrients within the catchment. This transfer (or lack of transfer) along flowpaths in a catchment has major implications on solute transport from spatially disparate parts of the catchment to the outlet where it is exported from the catchment (Ávila et al., 1992; Blaurock et al. 2021; Bracken et al., 2013; Kiewiet et al. 2020; Musolff et al., 2015).

The long-term study at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire has generated a unique dataset that facilitates a spatially explicit approach to examining interactions among hydrology, soils, and N processes that allows us to test some of these ideas more comprehensively than at most sites. These data have produced information on how hydrology drives podzolization and geochemistry across an intensively instrumented catchment and have identified the spatial pattern in these processes and in surface and sub-surface water geochemistry (Bailey et al., 2014; Bourgault et al., 2015; Gannon et al., 2014; Gillin et al., 2015; Zimmer et al., 2013). The backdrop of this understanding, the underlying data, and new high-frequency streamwater chemistry data allow us to track the areas of the catchment that are hydrologically active under different flow conditions in order to identify the source area of streamwater nitrate.

1.1 Background on hydropedology at Hubbard Brook Experimental Forest

1.1.1 Hydrologic influences on soil development

Recent work at the HBEF has shown that the soil heterogeneity observed within this study site is driven by systematic variation in hydrologic flowpaths, shallow groundwater dynamics, and soils. By identifying the underlying controls on soil development—topography, landscape position, and shallow groundwater flow—Bailey et al. (2014) developed a hydropedological soil classification (Figure 1) with distinct spatial structure (Bailey et al., 2014; 2019b). A significant observation at this study site was the importance of transient or ephemeral lateral groundwater flux on the development of soils and how variation in the groundwater regime across the landscape has led to the development of distinct soils along topographic and hydrologic sequences (Bourgault et al., 2017; Gannon et al., 2014; Gannon et al., 2017). The soils formed by vertical leaching processes generally occur in different locations than soils formed under the influence of laterally moving groundwater; the distribution of the different soils is largely predictable by topographic analysis via a terrain model derived from LiDAR and distance to bedrock outcrops. A nonmetric multidimensional scaling ordination was used to determine the relationship between topographic metrics and presence of different soil types. A multinomial logistic regression model used to determine the soil type most likely to be present on a 5m x 5m grid resolution. One quarter of the 172 observations were withheld from model derivation and used for model validation. The model correctly predicted 70% of the validation sites. Recent work has refined and expanded the Gillin et al. (2015) model to map the different soil units across the 3000 ha Hubbard Brook valley (which contains numerous forested catchments) using predicted bedrock outcrops and associated shallow soils in place of field observations (Bailey et al., 2019; Fraser, 2019; Fraser et al., 2020). The predictive modeling of bedrock outcrops and associated shallow soils was 86% accurate in the Hubbard Brook Valley (Fraser et al., 2020). This type of predictive modeling is unprecedented in the region and lays the groundwork for landscape-scale mapping in this region, especially given that most states in the region have or will soon have complete LiDAR DEM coverage.

1.1.2 Soil moisture patterns across the landscape

The variations in soil development that led to the different soil or hydropedological units (HPU) result in gradients in moisture, organic matter content, and nutrient availability which, in turn, influence the production, consumption, and transport of nitrate. The strong hillslope-scale gradients in soil development described by Bailey et al. (2014) reflect variation in the frequency and depth of groundwater incursions into the soil zone. The typical podzol soil units, which cover 41.3% of the study catchment, almost never had water table in the solum (median of 3% of the time; only immediately after large storms or snowmelt) and when there was a water table, it seldom rose above the bottom 30% of the solum, i.e., at the B/C interface, approximately the depth of the rooting zone (Gannon et al., 2014; Table 1). At the other extreme, the Bh podzol soil units, in the near-stream zone, which cover about 16% of the catchment (Figure 1), had a persistent water table (which remained about halfway up the solum; Gannon et al., 2014). In contrast, the water tables in the E-podzol and Bhs podzol soil units, areas where shallow bedrock increases groundwater flux in the solum (Figure 1), fluctuated considerably, saturating and draining with nearly every precipitation or snowmelt event (Gannon et al., 2014). These areas are considered to be bedrock controlled because the landscape has soil interspersed with bedrock outcrops and the depth to bedrock in soils is shallow enough to be an important influence on soil properties, rooting depth, and water table fluctuations. The Bhs podzol soil units had a water table in the solum more frequently (median of 57% of the time) than the E podzol soil units (median of 52%) (Gannon et al., 2014). The E podzol soil units were the most responsive to events, with the water table rising to the upper part of the profile during most events; the Bhs podzol soil units were less responsive than the E podzol soil units, but the water table was more persistent when it did rise into the upper parts of the soil profile (Gannon et al., 2014). Soil moisture is important for facilitating microbial transformations, as drier conditions limit microbial activity. The soil moisture conditions in the E and Bhs podzol soil units should be particularly conducive to nitrification, an aerobic microbial transformation which is strongly stimulated by alternating wetting and drying conditions (Fierer & Schimel, 2002). Bedrock Histosol soil units, which consist of organic matter directly on bedrock (Bailey et al., 2019b), and are situated immediately upslope from the E podzol soil units (Figure 1) provide a source of organic N that can be mineralized and nitrified in the E podzol soil units. Conditions in the Bhs podzol soil units should facilitate denitrification as well—given the more persistent water table and deep, C- and N-rich soils (Bailey et al., 2014; Gannon et al., 2015).

1.1.3 Hotspots for nitrate production

Indeed, the net nitrification potential rates in the E and Bhs podzol soil units were more than 6 times greater than those in the typical podzols indicating that these portions of the catchment are hotspots for nitrate production (Pardo et al., 2015). These findings were supported by the soil

$\delta^{15}N$ values in E and Bhs podzol soil units which were also higher than those in the typical podzols (Pardo et al., 2015). Higher $\delta^{15}N$ can indicate that a larger fraction of the soil organic matter pool is microbially transformed to inorganic N and transported from the soil; the product of the microbial transformation is depleted in ^{15}N while the remaining soil organic matter is enriched in ^{15}N (Nadelhoffer & Fry, 1994; Pardo et al., 2002). It is notable that the E podzol soil units, which tend to have N-poor mineral soils compared to the typical podzols, and the Bhs podzol soil units, which tend to be N-rich compared to the typical podzols (Bailey et al., 2014; Table 1), both appear to transform and mobilize a large fraction of their available soil N pool under conditions favorable to nitrification. (The E podzols generally have a thick Oa horizon with a relatively shallow soil profile, so the N mass per unit area shown in Table 1 for the whole profile is greater than the typical podzols, in spite of the mineral soil N concentration being lower (Bailey et al., 2014.)) The greater frequency of alternating wetting and drying conditions in the E podzol soil units should especially enhance nitrification there. These patterns indicate that soil nitrogen cycling pools and process rates vary dramatically with soil unit.

1.2 Objectives

Based on the groundwater and stream chemistry (Bailey et al., 2019b; Zimmer et al., 2013), the favorable soil moisture conditions for nitrification (Gannon et al., 2014), and the elevated potential nitrification rate and soil $\delta^{15}N$ (Pardo et al., 2015), the E and Bhs podzol soil units appear to be hotspots for nitrate production. However, these soil units are often (i.e., during baseflow conditions) distant from an active portion of the stream channel network. Because the spatial extent of the stream network varies as a function of antecedent soil moisture and precipitation (among other things; Jensen et al., 2017; Zimmer et al., 2013), nitrate produced in these areas will not always have an available flowpath to reach the stream (Creed et al., 1996; Sebestyen et al., 2008, 2014, 2019). The connectivity of the stream network has been modeled at Hubbard Brook and is highly variable with discharge, but predictably follows topographic patterns (Jensen et al., 2017). We hypothesize that as the drainage network expands, increasing the hydrologic connection to bedrock outcrops and associated soils, streamwater nitrate concentration and flux at the catchment outlet increase. In order to evaluate this hypothesis, we:

(1) identify the characteristic groundwater chemistry of each soil unit for nitrate, dissolved organic nitrogen (DON), and DOC concentrations and pH ;
(2) compare the pattern of catchment nitrate export during low and high flow periods by identifying different water table responses by soil unit to varying flow conditions;
(3) determine which soil units contribute most to catchment nitrate flux using an end-member mixing model;
(4) determine whether most nitrate export occurs during high discharge (when E-Bhs podzol soil units are more likely to be connected to the drainage network and catchment outlet) using high-frequency sensor data.

2 Methods

2.1 Site description

The study was conducted at the HBEF, in the White Mountains of central New Hampshire (43°56'N, 71°45'W). The HBEF extends over 3160 ha; the south-facing catchments, where most prior research has been conducted, range in elevation from 500-800 m (Likens et al., 1977). The climate is predominantly humid continental; mean annual precipitation is approximately 140 cm with stream runoff of 90 cm (A. S. Bailey et al., 2003). The dominant tree species in the south-facing catchments are *Acer saccharum* Marsh. (sugar maple), *Betula alleghaniensis* Britt. (yellow birch), and *Fagus grandifolia* Ehrh. (American beech) on deeper and better drained soils; mixed conifers dominated by *Picea rubens* Sarg. (red spruce), *Abies balsamea* (L.) Mill. (balsam fir), and *Betula papyrifera* var. *cordifolia* (Regel) Fern. (mountain paper birch) occupy wetter sites and areas where soils are shallow to bedrock (Siccama et al., 2007). The region was colonized by Europeans in the 1800s and selectively logged from about 1900 to 1917 (Whittaker et al., 1974). The HBEF experienced partial blowdown during a hurricane in 1938, followed by some salvage logging. Since establishment of the Experimental Forest in 1955 there has been no direct human disturbance or management except in several experimental areas. The present study was conducted in Watershed 3 (W3), the hydrologic reference catchment at the HBEF, which is 42 ha with an average slope of 25% and has not had any experimental manipulations.

Bedrock in W3 is the Silurian Rangeley Formation, a sillimanite-grade metapelite consisting of mica schist with minor amounts of calc-silicate granulite (Burton et al., 2000). Bedrock is poorly exposed, outcropping mostly along the upper catchment divide and is covered by unsorted late Wisconsinan glacial drift varying up to about 10 m thick. Glacial drift is dominated by granitic lithologies, transported from the north and west of the study catchments, with lesser contributions from local bedrock (S. W. Bailey et al., 2003), and is the parent material for soil development. Where not confined by shallow bedrock, soils average 0.7 m to the top of the C-horizon, corresponding to the depth of major alteration of glacial drift by soil forming processes, approximately the limit of the rooting zone (Bailey et al., 2014).

Soils at Hubbard Brook are generally Spodosols in the great groups of Endoaquods, Durihumods, Haplohumods, Durorthods, and Haplorthods (Soil Survey Staff, 2014). However, strict application of the keys to soil taxonomy in mountainous portions of northern New England leads to the classification of some soil profiles as Histosols, Inceptisols and Entisols (Villars et al., 2015). These profiles have been considered to be soils where podzolization is a dominant soil forming process, but at the hillslope rather than the soil profile scale (Bailey et al., 2014; Bourgault et al., 2015). Functional soil groups have been classified based on relationships with landscape position and influence of shallow and exposed bedrock (Gillin et al., 2015), shallow groundwater regime (Gannon et al., 2014), and soil chemistry (Bourgault et al., 2015). These functional soil units, termed as types of podzols to emphasize that they are not units within US soil taxonomy, are being investigated for their utility in understanding spatial variation in biogeochemical processes and surface and groundwater chemistry (Bailey et al., 2019b; Gannon et al., 2015).

2.2 Field measurements

Watershed 3 is a site of extensive hydrologic monitoring since the mid-1950s (e.g., A.S. Bailey et al., 2003). During our study, one NOAH IV automated precipitation gauge (ETI Instrument Systems, Inc.) was located in W3 which measured accumulated precipitation on a 15-minute interval (USDA Forest Service, 2019b). Stream discharge at the outlet of W3 was monitored using a 120-degree v-notch weir (A.S. Bailey et al., 2003; USDA Forest Service, 2019a). Groundwater wells were constructed of standard dimension ratio 21 PVC pipe (3.76 cm inner diameter) that extended approximately 10 cm into the C-horizon of the soil. The wells were screened for 31 cm just above their base. Water table height was recorded on a 10-minute interval with an Odyssey Water Level Logger (Gannon et al., 2014; McGuire et al., 2016). Groundwater sampling site locations are mapped in Supplemental Information Figure S1.

Water samples at the catchment outlet were collected weekly by filling high density polyethylene (HDPE) bottles for laboratory analysis. Some additional sampling occurred during snowmelt and storm events, in some cases using an ISCO automated sampling device (Teledyne ISCO). Groundwater samples were collected by pumping water from wells with a portable peristaltic pump. At least one well volume was evacuated and discarded before filling sample bottles. Natural groundwater seeps were collected as grab samples. Water samples were transferred back to the field laboratory in coolers and held in cool conditions (as described below) until chemical analysis. Fresh untreated samples were analyzed for pH potentiometrically with a Thermo Scientific Orion 3-Star pH meter at HBEF. Samples were then filtered with 0.45 micron pre-ashed glass fiber filters via a vacuum filter apparatus within hours of collection. Lab-filtered samples were transported refrigerated or frozen to the USDA Forest Service lab in Durham NH for all other analyses. Dissolved Organic Carbon and Total Dissolved Nitrogen were analyzed using a Shimadzu TOCV with TNM-1 nitrogen detector (high-temperature catalytic oxidation with chemiluminescent detection for TDN). Anions were analyzed on a Metrohm 761 Compact IC (ion chromatography with chemical suppression). Ammonium and o-phosphate were analyzed colorimetrically with a SEAL Analytical AQ2 discrete analyzer (alkaline salicylate and acidic molybdate blue, respectively). Total and organic monomeric aluminum were measured on a Lachat QuikChem (flow injection analyzer, pyrocatechol violet). Cations were measured on an Agilent 730 ICP-OES. Further analytical details (and water chemistry sample data) are available at https://doi.org/10.6073/pasta/4022d829f3a1fa4057b63b5db8b1a172 (Bernhardt et al., 2019). Precision and analytical limits are documented in https://doi.org/10.6073/pasta/890b1fadb61d3e86dc6f3d9afea79705 (USDA Forest Service, 2019)

Streamwater at the catchment outlet was monitored at a 15-minute frequency with water quality sensors from 2013-present (Potter et al., 2018). A Satlantic Submersible Ultraviolet Nitrate Analyzer estimated streamwater nitrate concentrations. A Yellow Springs Instruments, Inc. multi-parameter EXO sonde measured pH and fluorescent dissolved organic matter (FDOM). Comparison of grab samples (Bernhardt et al., 2019) with *in-situ* measurements allowed assessment of the accuracy of the sensor. DOC was predicted reasonably well across 10 NH streams by corrected FDOM with $r^2 = 0.41$ found at Hubbard Brook W3 (Snyder et al., 2018). The relationship between measured and sensor nitrate was very strong, $r^2 = 0.98$ for Hubbard Brook W3 (Snyder et al., 2018). All sensors were calibrated on a monthly basis (Snyder et al., 2018).

2.3 Data analysis

The flux of nitrate was estimated using the sensed streamwater nitrate concentration and the discharge values. The 15-minute nitrate data were linearly interpolated to estimate the concentration at each 5-minute discharge measurement. The concentration was then multiplied by the discharge, and the units were converted to kg N per hectare per 15 minutes.

An end-member mixing analysis (EMMA) was conducted with the Christophersen and Hooper (1993) approach which uses principal component analysis (PCA) to decompose the variance into two primary orthogonal axes that contain multidimensional information about the solute chemistry of each water sample. Sodium (Na), calcium (Ca), total aluminum (Al), pH, and DOC were the solutes used for the EMMA analysis. The PCA was performed on all groundwater and streamwater samples, producing a first and second component score for each sample. The first and second components were used in a three end-member mixing model to estimate the fractional contribution of each end member to streamwater samples (equations below). The end members were identified using existing information about differences in groundwater solute concentrations across the soil units in W3 (Bailey et al., 2019b; Gannon et al., 2015; Zimmer et al., 2013). We used the E/Bhs podzol soil units (combined), Bh podzol soil units, and seeps as our three end members. Seeps represent where deeper groundwater with high concentrations of weathering-derived solutes returns to the surface and have been shown to influence stream water solute concentrations particularly at baseflows (Zimmer et al., 2013; Benettin et al., 2015). The E/Bhs podzol soil units contribute high organic matter waters to streams during high discharge rates (Gannon et al., 2015) and have high Al concentrations which is apparent in synoptic sampling (Bailey et al., 2019b). The Bh podzols are near-stream, and synoptic surveys have shown that streamwater lower in the catchments resembles their chemistry (Bailey et al., 2019b). Typical podzol groundwaters were not used as end members because their water chemistry is very similar to the Bh podzols (Bailey et al., 2019b) and the Bh podzols are more proximate to the stream. The contribution of each end member to each water sample was calculated by solving the following set of equations:

(1) $1 = f_1+f_2+f_3$

(2) $S_A = f_1EM_{1A} + f_2EM_{2A} + f_3EM_{3A}$

(3) $S_B = f_1EM_{1B} + f_2EM_{2B} + f_3EM_{3B}$

where f is the fractional contribution of end members 1, 2, and 3, S is the PC score, A and B, for a streamwater sample, and the EM is the PC score, A and B, for end members 1, 2, and 3. Correlations between catchment fluxes (water and nitrate) and the fractional contribution of different water sources, from the EMMA, were quantified with Spearman's rank correlation coefficient (ρ) to gain insight into how different water sources contribute water and nitrate to the catchment outlet.

The timing of maxima or minima in biogeochemical or hydrological variables were automatically extracted from the multivariate time series and then differences in the timing were compared. Events were identified by selecting 95th percentile discharge values within a 12-hour moving window that were greater than twice the median discharge and greater than 2 mm/hour. If an event occurred, the timing of the maxima in water table height in wells, discharge nitrate concentration, and FDOM, and minimum pH at the catchment outlet were identified. Time lags between these values were calculated for each event.

3 Results

3.1 Variation in groundwater chemistry by soil unit

Groundwater composition was distinct among soil units in W3 (Figure 2), as was reported for pH and DOC in 3 catchments across the Hubbard Brook Valley (Bailey et al., 2019b). DOC and DON concentrations were highest in the bedrock Histosol areas (median of 35 μM for DON and 2570 μM for DOC) and showed a regular gradient decreasing across the general hillslope sequence (Figure 1.c). pH was highest in the seep (median of 6.2) and showed a regular gradient increasing across the general hillslope sequence; Bh podzol soil units had similar pH, DOC and DON to typical podzols. Since acidic inputs in atmospheric deposition have declined as a result of the Clean Air Act and Amendment of 1990 (Warby et al., 2005), the main driver of low stream pH has switched from sulfuric and nitric acid inputs to the organic acids in DOC (Bailey et al., 2019b; Monteith et al., 2007), which has led to an inverse relationship between DOC and pH. Nitrate concentrations were highest in the Bhs and E podzol soil units (medians of 26 and 18 μM, respectively). It is notable that the concentration of nitrate was more variable than that of other ions (Figure 2), especially in the E, Bhs, and typical podzol soil units.

When we compare groundwater pH and nitrate concentration, we observe a separation among soil units (Figure 3). The range defined by the 10^{th} to 90^{th} percentiles for groundwater pH and nitrate concentration of all the soil units and the seeps encompasses all of the sensor data (Figure 3). The high-frequency stream sensor measurements provide new information both about the frequency of various chemical conditions and about how the chemistry at the catchment outlet compares to that in groundwater. Most of the sensor data for pH and nitrate in streamwater fall between the median values for groundwater in the Bh soil unit and the seeps, with pH ranging from 5.1-6.5 and nitrate concentration <0.2 μM. The E and Bhs podzol soil units have lower median pH and higher median groundwater nitrate concentration than the other soil units (Figure 3).

3.2 Differing water table responses by soil unit to varying flow conditions

Using groundwater water table measurements in concert with stream outlet sensor data allows us to discern two different types of events: Type 1—when there is water table only in the E podzol solum and Type 2 when there is water table in both the E and Bhs podzol solum (Figure 4).

The responsiveness of the E podzol to precipitation events is evident: even during moderate and smaller precipitation events (e.g., 23 July- 3 August, 25 August and 10 September 2015*)* which do not increase stream discharge substantially, the water table often rises to within 20 cm of the surface for moderate events and increases often more than 20 cm above baseflow conditions during small events (Figure 4.b). In each of these cases (small and moderate events), there is a coincident spike in nitrate concentration at the stream outlet (Figure 4.d). (Annual hydrographs for 2013-2017 are shown in Supplemental Information Figure S2. Time series of sensor data for 68 storm events are shown in Supplemental Information Figure S4.)

3.3 Influence of soil units on streamwater chemistry and flux

The E/Bhs podzol soil units, Bh podzol soil unit, and Seep were used as source water end members in an end-member mixing model to evaluate the influence of the different soil units on streamwater chemistry and flux at the catchment outlet. The two principal components used for the mixing analysis explained 70% and 17% of the total variance. The first principal component had the largest loading from pH, Na, Ca, and Al, with Al having an opposite impact on the principal component compared to the other three solutes. All solutes had the same directional loading for the second principal component, with DOC and Ca contributing the most. Although ~40% of the stream sensor values fell outside of the triangular mixing space defined by the end member medians, most of those were within the interquartile range for the near-stream Bh podzol soil unit end member. The majority of the samples (200 of 342) fell fully within the end member median values, allowing estimation of the source water contribution with the mixing model (Figure 5). Of these, the Spearman correlations between nitrate concentration and the fraction of E/Bhs, Bh, and Seep water contributing to streamwater were 0.24, -0.02, and -0.20, respectively; only the E/Bhs soil unit correlation was significant ($p=0.01$). The correlation between discharge and the fraction of each end member (Figure 6) was significant and strongest for E/Bhs soil units ($\rho = 0.66$; $p<0.001$), followed by the seep fraction ($\rho = -0.44$; $p<0.001$); there was no significant correlation with the Bh soil unit fraction ($\rho = 0.08$; $p=0.36$). The Spearman correlation between instantaneous nitrate flux and the fraction of each end member (Figure 6) was significant and strongly positive for the E/Bhs podzols soil unit ($\rho=0.57$; $p<0.001$), significant and negative for the Seep ($\rho= -0.4$; $p<0.001$), and was not significant for Bh podzol soil units ($\rho= -0.07$).

3.4 Timing of nitrate export relative to stream discharge

In order to examine the extent to which the source areas of streamwater nitrate shift from near-stream source areas at low flow to source areas further from the stream (E-Bhs podzol soil units) as flow increases, we evaluated the discharge and nitrate concentration data from the sensors at the catchment outlet. Streamwater nitrate export from W3 occurs predominantly during high flows (Figure 7). Although event flow occurs only 15% of the time, it accounts for nearly 70% of the discharge and over 80% of the nitrate export (Figure 7).

4 Discussion

The objective of this study was to track areas of the catchment that are hydrologically active under different flow conditions in order to identify the source area of streamwater nitrate. Our data evaluating the systematic spatial variation of solution chemistry with soil unit within the catchment demonstrate that as the drainage network expands, the hydrologic connection to shallow soils near bedrock outcrops increases, and streamwater nitrate concentration and flux at the catchment outlet increase. The spatially explicit, intensive dataset at the HBEF allows us to address the issue of source area nitrate varying as the drainage network expands at a finer resolution than has been possible heretofore. In this catchment, the nitrogen cycling hotspots, E and Bhs podzol soil units, make a disproportionate contribution to streamwater nitrate export. This understanding represents a significant step towards being able to better predict the magnitude and timing of nitrate export from this forested catchment.

4.1 Factors that affect the timing and magnitude of nitrate export

The factors that can affect the occurrence and magnitude of nitrate export include those that affect the production and consumption of nitrate within the catchment and those that affect the transport of nitrate to the stream network and thence to the catchment outlet. The main environmental factors that influence the production of nitrate are temperature, soil moisture, and wetting and drying conditions (Booth et al., 2005; Stark & Firestone, 1995). In addition, low soil pH may inhibit nitrification rates, and N mineralization depends upon an adequate source of available organic matter (Bäckman & Klemedtsson, 2003; De Boer & Kowalchuk, 2001). The main environmental factors that affect the microbial consumption of nitrate (via denitrification and immobilization) are also temperature, oxygen supply, and moisture as well as DOC, OM, and nitrate availability, although the optimal conditions for the processes vary (Hedin et al., 1998; Johnson et al., 2000). Hydrologic flow paths are difficult to predict precisely, but generally the factors that affect whether there will be water moving from the upper portions of the catchment to the stream channel (via saturated subsurface flow) include antecedent storage (groundwater and soil moisture), precipitation volume and duration, and precipitation intensity (Jencso et al., 2009; Stieglitz et al., 2003). For example, Benettin et al. (2015) demonstrated that lower antecedent storage and lower precipitation amounts result in greater catchment transit time distributions in our study catchment. In addition to water transport, the frequency and intensity of precipitation can be important in determining the source area and flowpath of nitrate to the stream (Creed et al., 1996), and the catchment transit time (e.g., Benettin et al. 2015). For example, the length of the period without precipitation prior to a precipitation event can affect how much nitrate accumulates in the soil and stream channel and thus the magnitude of the flux due to flushing. The antecedent soil moisture and the drying pressure will also play a role in regulating the timing and magnitude of discharge following a precipitation event (Ávila et al., 1992). The intensity of the rainfall, the degree of intermittency of the rainfall, and storage thresholds (see Gannon et al., 2014) can also affect which portions of the catchment are connected to the stream (Gannon et al., 2015; Rusjan et al., 2008). As the extent of the drainage network shifts with stream flow, soil solution and groundwater from different portions of the catchment will make up varying proportions of the water and ions exported (Creed & Band, 1998; Welter & Fisher, 2016; Zimmer & McGlynn, 2018).

4.2 Variation in groundwater chemistry by soil unit

In general, we observed that the variation in groundwater chemistry across the broader landscape of the Hubbard Brook Valley is lower than the variation among soil units (Figures 2 and 3; Bailey et al., 2019b). We also observed that soil units composed of bedrock-associated shallow soils have higher concentrations of groundwater nitrate than other soil units. This means that a map of soil units will show the fraction of the catchment that is made up of bedrock-associated shallow soils, which produce nitrate at higher rates than other areas of the catchment (e.g., Fraser et al., 2020). Such soil maps would facilitate comparison of catchments, for example, for predicting relative nitrate export, based on the fraction of each catchment made up of nitrate-producing hotpots. The systematic and predictable pattern of groundwater chemistry has important implications; it can greatly improve the accuracy of scaling up to the landscape scale and thereby improve spatially explicit modelling.

4.3 Timing of nitrate export relative to stream discharge

The timing of stream nitrate export relative to discharge indicates that the vast majority of nitrate export occurs during periods of high flow, which occur infrequently (Figure 7). Such patterns have been reported at other forested sites (Bernal, et al. 2002; Inamdar, et al. 2006; Sebestyen et al., 2014; Winter et al. 2020). Early observations at the HBEF (Johnson et al., 1969) also found that the highest nitrate concentrations occurred during periods of high discharge, while nitrate concentrations were low during baseflow. Other recent work at the HBEF (Detty & McGuire, 2010; Gannon et al., 2014) determined flow generation thresholds—below the threshold, runoff was generated primarily in the near-stream zone, above the threshold, the contributing area expanded across the hillslope. The expansion of the intermittent stream network at high flows occurs about 15% of the time (Figure 7; Zimmer et al., 2013), connecting the E and Bhs podzol soil units to the catchment outlet under these flow conditions. The water table in the E and Bhs podzol soil units is more responsive to precipitation events than that in the widespread typical podzol soil units: the water table rises more consistently even for small storms, rises earlier in precipitation events and a greater fraction of the solum is saturated (Figure 4; Gannon et al., 2014). The travel distance for interflow or transient shallow groundwater during events at Hubbard Brook can extend one to several meters according to Klaus & Jackson (2018), based on data from Detty & McGuire (2010). But the E podzol soils are shallow, implying a strong permeability contrast, which, following the theory in Jackson et al. (2014) and Klaus & Jackson (2018), suggests a greater travel distance. Revised calculations using the method of Jackson et al. (2014) and additional measurements at the HBEF (Benton, 2020; Cedarholm, 1994), suggest a travel distance of 10-80 m during events (see Supplemental Information T1 for calculations) which would be adequate to connect the E and Bhs podzols to the intermittent stream network during events and potentially transport nitrate over that distance. Benettin et al. (2015) also showed that water transit time distributions during wet conditions (e.g., large storm events) had median ages of 40-60 days, but were highly skewed with about 25% of the water having ages < 1 day. This further supports potential connectivity with the E and Bhs podzol region of the catchment. This indicates that the upper catchment soils are periodically hydrologically connected to the outlet stream when most of the nitrate export occurs, suggesting that the E and Bhs podzols, hotspots for nitrate production in the catchment (Pardo et al., 2015), could contribute significantly to catchment nitrate flux.

4.4 Differing water table responses by soil unit to varying flow conditions

The responsiveness of the water table in the E podzol soil unit to precipitation, even during small events reported by Gannon et al. (2014) and shown in (Figure 4), provides a potential opportunity for nitrate movement to the stream channel. The water table rise often coincides with a spike in nitrate concentration at the stream outlet. This spike in nitrate concentration could be caused by: (1) the wetting up of the stream channel mobilizing nitrate that had accumulated during the period since the last precipitation event (Austin & Strauss, 2011; Bernal et al., 2005; von Schiller et al., 2011); or (2) a near-stream source of high nitrate concentration (possibly deep groundwater; Burns et al., 1998); or (3) a shallow flow path that permits nitrate from the E podzols to enter the stream channel and be transported to the stream outlet (Gannon et al., 2015). When precipitation volume is higher, the water tables in the E and Bhs podzol soil units rise near the same time ('Type 2' events), discharge is generally greater and the spikes in nitrate concentration larger. (Time series of sensor data for 68 storm events are shown in Supplemental Information Figure S4.) These "Type 2' events often coincide with a spike in DOC concentration (shown in an example event in Supplemental Information Figure S3). Since the only sources for high DOC are E and Bhs podzol soil units (Figure 3), the coincident nitrate and DOC spikes point to the E and Bhs podzols soil units as source areas for these nitrate spikes. The hydrologic flowpaths for nitrate could be rapid, shallow flowpaths (including macropores) to reach the stream channel (Gannon et al., 2015) or deeper, slower flow paths via groundwater displacement (Germann et al., 1986; Sklash & Farvolden, 1979).

4.5 Influence of soil units on streamwater chemistry and flux

The end-member mixing model results (Figures 5 and 6) demonstrate that the bedrock-controlled upper part of the catchment containing E and Bhs podzol soil units influences the concentration of nitrate at the outlet, but more importantly, it appears to be connected to the outlet at high discharge rates when the intermittent upper portions of the stream network are activated, contributing the most to catchment nitrate flux. While the catchment streamwater is a mixture of all of the end members, the higher correlations between streamwater (discharge and nitrate flux) and the E/Bh end member suggests that this zone is the most important control on export of water and nitrate from the catchment. Note that during these higher flows, biotic processing of N in the stream is expected to be low (e.g., Wollheim et al., 2017). The chosen source water end members represented the range of stream chemistry well, with almost all samples falling within the triangular mixing space, when accounting for the temporal variation of the end members. This suggests that waters from other source units - typical, bimodal, and histosols - are represented by our chosen end members, likely due to the water from the soil units that were not included being transported through the end members. For example, the bedrock Histosols lie upslope of the E/Bhs units and rarely intersect the flowing section of the stream network, preventing their waters from reaching the stream without passing through the E/Bhs units. A similar process likely happens with typical and bimodal soil waters, which, because of their position, must be transported through Bh units before reaching a flowing stream channel.

4.6 Importance of distal sources of nitrate as flow increases

Our evidence of high nitrate transport from distal sources generally agrees with observations from two other sites in eastern North America. In the Archer Creek catchments in the Adirondack mountains (NY), two studies suggest that high nitrate groundwater that fed streams resulted from high nitrification and hydrologic transport from steep terrain (McHale et al. 2002; Inamdar and Mitchell 2006). Similarly, steep slopes were suggested as a factor causing large variation in nitrate export between watersheds at the Harp Lake site in eastern Ontario, Canada (Schiff et al. 2002). The catchment with a ten-fold greater nitrate export had steeper slopes and higher groundwater nitrate concentration, which was hypothesized to be caused by rapid percolation of high nitrate soil water to depths where roots could no longer access the nitrate. These studies underscore the importance of considering the contribution of distal sources of N to catchment N export and the influence that catchment structure can have on hydrologic flow.

The increasing influence of the E and Bhs podzol soil units as flow rate increases is evident in Figure 8 which shows how both the drainage network and associated chemistry shift with increasing precipitation and discharge. In the contracted portion of the stream network that is active at low flow (q=0.1 mm/d), high pH and Si concentration characteristic of deeper flow paths predominate in streamwater (Figure 8.a, b). As the drainage network expands into the bedrock-controlled upper part of the catchment with increasing flow rate (q=0.3 mm/d), low pH inputs are observed (Figure 8a, b) in both east and west upper parts of the catchment. As flow increases further ($q \geq 0.6$ mm/d), the pH of streamwater closest to the bedrock-controlled units drops further still and the whole network exhibits depressed pH, except the seep sites, which remain above a pH of 5.4 (Zimmer et al., 2013). The pattern of pH decreasing in streamwater does not track exactly with the pattern of Si concentration in streamwater during the snowmelt period (April 2010; q= 6.7 mm/d); although Si concentration in streamwater is low except in the seep influenced areas (Zimmer et al., 2013), the pH is consistently low only on the eastern side of the catchment. On the western side of the catchment, DOC is lower than on the east side and the pH is low where nitrate is high and pH is high where nitrate is low, suggesting that during snowmelt, nitrate has a greater influence on pH than DOC (Figure 9.a, c, d). In general, as the drainage network expands, it connects to include areas of high nitrate and DOC upslope. However, the DOC appears to be more persistent as it moves down the stream channel than the nitrate, which decreases in concentration moving toward the stream outlet. This decrease in concentration may indicate consumption of nitrate within the stream (Bernhardt et al., 2002, 2005) or transformation of nitrate along the flowpath (von Schiller et al., 2011). It is important to note that these maps represent a snapshot in time—although nitrate is high at points within the catchment, even at the highest flow (1 October 2010), nitrate concentration at the outlet is low. The importance of the timing of sample collection has been demonstrated previously (Ohte et al., 2004; Sebestyen et al., 2014). Given that nitrate concentration does increase rapidly at the stream outlet at certain moments (Figures 3 and 4), this suggests that the nitrate concentration peak, typically observed on the rising limb of the hydrograph (Duncan et al., 2017; Hornberger et al., 1994; Inamdar et al., 2004), has passed at the time of the sampling on 1 October 2010. Indeed, the peak discharge occurred prior to the collection of stream samples on 1 October 2010.

Synthesizing these data suggests several stages of drainage network expansion with increasing flow conditions. Figure 9, based, in part, on the model of Jensen et al. (2017) shows the implications of drainage network expansion for nitrate transport. Initially, when flow increases above baseflow (Figure 9.a), the connection to E podzol soil units is a result of stream length expansion (Figures 9.b and 9.c). At the highest flows, the expansion of the variable source area--when the near-stream zone saturates, and network length is maximized--leads to the largest nitrate export (Figure 9.d). This conceptual diagram shows the likely spatial extent of the stream network in the catchment. The ability to map connectivity of different soil units to the active stream channel and subsurface contributing area, and, ultimately, to the drainage network for a variety of flow conditions and points in the year would greatly enhance our ability to identify the source area of streamwater nitrate and model the expected nitrate and DOC export under different conditions. Figure 9 emphasizes that the bedrock-dominated upper portions of the catchment, hotspots for nitrate production (Pardo et al., 2015) and source areas of streamwater nitrate, are hydrologically connected to the catchment outlet during event flow.

These responses demonstrate that concepts like N saturation (Aber et al., 1989) and N retention must be understood in the context of spatial heterogeneity across a catchment. This would not alter the timing of N saturation for systems with very limited or extremely high excess N availability, or fundamentally change the concept. However, for intermediate stages of N saturation (Aber et al., 1989), considering the spatial arrangement of a catchment could introduce nuance to the cascade of N responses and the timing of expected N export. Since portions of a catchment can have a disproportionate influence on N export from the catchment, it can be misleading to base assessment of N saturation on input/output budgets. In addition, care must be taken in using input/output budgets to interpret within-catchment N dynamics; the controls on N cycling are numerous and are both biotic and abiotic.

5 Conclusions

By accounting for the spatial heterogeneity in soil type within a catchment and using fine temporal- and spatial-scale measurements, we were able to demonstrate that as stream flow increases and more of the catchment becomes hydrologically connected with the expanding active stream channel and subsurface contributing area, the source of streamwater nitrate shifts from near-stream sources (Bh podzol soil units and seeps) to sources further from the stream (Bhs-E podzol soil units). This study showed that bedrock-controlled E and Bhs podzol soil units, hotspots for nitrate production, are connected to the stream during events and represent the source of most nitrate export. This analysis represents an important shift in our understanding of where streamwater nitrate comes from at the HBEF, as the assumption in the past has been that the sources for streamwater nitrate were in the near-stream zone.

This finding has implications for future sampling approaches. Sampling of events is more important for understanding fluctuations in export--especially in response to disturbances and extreme events--than weekly samples, which are important for providing a baseline, but are likely to miss the peak event response. Using the sensor data, for example, we can evaluate the accuracy of the annual nitrate flux from W3 at the HBEF which is calculated using weekly chemistry samples (Aulenbach et al., 2016). As in other analyses (Pellerin et al., 2012), we found that the estimate using weekly chemistry samples captured about 83% (0.89 vs 1.07 kg N ha^{-1} yr^{-1}) of the 2015 annual flux (the year with the most complete sensor data).

In order to improve our understanding of the timing of export of nitrate and other solutes, additional sampling, field measurements, and data analysis are needed. These include (1) a network of sensors (chemistry and water table) coupled with groundwater chemistry; (2) further empirical modelling (machine learning) to predict high-frequency weathering-derived solutes that can provide further insight into how the catchment derives water and solutes (Green et al., 2020); (3) tracer studies to better define flowpaths and transport rates; (4) fine-scale microbial processing measurements to quantify the timing and extent of microbial N transformations, and (5) mechanistic modelling.

One of the most significant benefits of quantifying the systematic variation in soil units and linking soil units to biogeochemical function (i.e., nutrient cycling rates, microbial transformation rates) is that it becomes possible to scale up more accurately, first to the forest catchment scale, then to the landscape scale in forest ecosystems (Fraser, 2019; Fraser et al., 2020). Our data suggest that bedrock outcrops and associated shallow soils are critical in estimating N flux. With the high level of accuracy (~86%) in predictions of these features in the Hubbard Brook Valley and the nearby Wild Ammonoosuc catchment, a broader scale mapping effort is currently underway in similar ecosystems within the White Mountain National Forest. The soils in our watershed are typical of glaciated uplands where bedrock exposed ridges, interspersed with shallow soils, transition downslope into areas of deeper soil developed in deeper glacial drift. Soil surveys indicate that such features are prevalent in glaciated uplands in the northeastern US, with bedrock-controlled soils (< 1 m depth to bedrock) occupying approximately 9 million ha (NRCS, SSURGO database). They are also common in other midlatitude, glaciated regions worldwide. This approach, thus, holds promise for improving regional soil maps for similar mountainous areas in the northeastern US and may be applicable to other mountainous regions with a humid climate.

The ability to map connectivity of different soil units to the drainage network for a variety of flow conditions and points in the year would greatly enhance our ability to identify the source of streamwater nitrate and predict the expected nitrate and DOC export under different conditions. Given our understanding of the impacts of temperature and moisture on microbial transformations producing nitrate (e.g., Booth et al., 2005; He et al., 2008; Stark & Firestone, 1995) and potential for increased soil C mineralizability under cyclic wetting and drying conditions (Possinger et al., 2020), shifting climate, including projections in this region for increased temperature, precipitation, and storm intensity (Hayhoe et al., 2008), is likely to alter the export patterns for both DOC and NO_3^-. This study could provide a springboard for linking soil C and N cycling to catchment or landscape-scale mechanistic models and enhancing our ability to predict the effects of changing climate on forested catchments in the northeastern U.S.

Acknowledgments

We thank Jane Hislop and Jeff Merriam, USFS, Durham, NH for water analyses; Tammy Wooster for field collections and sample analysis; Lisle Snyder and Jody Potter, UNH, for sensor analyses; and Maggie Burns for fieldwork and data analysis; Leah Charash for preliminary data analysis and data management; and J.P. Gannon for providing data for this analysis. We appreciate the reviews of K. Lohse, D. Ross, and S. Sebestyen on an earlier version of this manuscript. The Hubbard Brook Experimental Forest is maintained and operated by Northern Research Station, USDA Forest Service, Madison, WI.

FUNDING

Funding for this study was provided by the Northern Research Station, USDA Forest Service and the National Science Foundation through the Hydrological Sciences (EAR-1014507) and Geobiology and Low-Temperature Geochemistry (EAR-1643415/1643327) and Long-Term Ecological Research Programs. Funding was provided by the National Science Foundation's Research Infrastructure Improvement Awards EPS 1101245 and IIA-1330641. MBG was supported by Joint Venture Agreements between the Northern Research Station (NRS) and Plymouth State University, and NRS and Case Western Reserve University

Data availability

All data are available via the Environmental Data Initiative (EDI) including precipitation (doi.org/10.6073/pasta/c64ad38eef4f56d9e34749f166f64caa ; USDA Forest Service, 2019b); streamwater discharge (doi.org/10.6073/pasta/282953c2290b1f00d9326ffd9a7e9668 ; USDA Forest Service, 2019a); water table data (doi.org/10.6073/pasta/a7b6b61df98b65244eba64d8bc391582; McGuire et al., 2016); synoptic survey data from 2009-2010 (doi.org/10.6073/pasta/886612f65609a28eebcd5f4d74032012; (Bailey, S. and K. McGuire. 2019); synoptic survey data from 2015 (https://doi.org/10.6073/pasta/fafd7b2334e34a633577764bc36cbb66; Bailey et al. 2019a);

subsurface water chemistry (doi.org/10.6073/pasta/ed3c561b4a15364bf9172f2cc7d7911c; Bailey et al. 2021); water chemistry sample data (doi.org/10.6073/pasta/4022d829f3a1fa4057b63b5db8b1a172; Bernhardt et al., 2019). Streamwater sensor data are available at the HydroShare (http://www.hydroshare.org/resource/8217eab0997d493782ff321ca5f95f28; Potter et al., 2020) and were originally published in Potter et al. (2018).

References

Abbott, B. W., Gruau, G., Zarnetske, J. P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S., Pierson-Wickmann, A.-C., Davy, P., & Pinay, G. (2018). Unexpected spatial stability of water chemistry in headwater stream networks. *Ecology Letters*, *21*(2), 296–308. https://doi.org/10.1111/ele.12897

Aber, J. D., Goodale, C. L., Ollinger, S. V., Smith, M.-L., Magill, A. H., Martin, M. E., Hallett, R. A., & Stoddard, J. L. (2003). Is Nitrogen Deposition Altering the Nitrogen Status of Northeastern Forests? *BioScience*, *53*(4), 375. https://doi.org/10.1641/0006-3568(2003)053[0375:INDATN]2.0.CO;2

Aber, J. D., Nadelhoffer, K. J., Steudler, P., & Melillo, J. M. (1989). Nitrogen Saturation in Northern Forest Ecosystems. *BioScience*, *39*(6), 378–386. https://doi.org/10.2307/1311067

Andersson, L., & Lepistö, A. (1998). Links Between Runoff Generation, Climate and Nitrate-N Leaching from Forested Catchments. *Water, Air, & Soil Pollution*, *105*, 227–237. https://doi.org/DOI:10.1023/A:1005093223246

Asano, Y., Uchida, T., Mimasu, Y., & Ohte, N. (2009). Spatial patterns of stream solute concentrations in a steep mountainous catchment with a homogeneous landscape. *Water Resources Research*, *45*(10). https://doi.org/10.1029/2008WR007466

Aulenbach, B. T., Burns, D. A., Shanley, J. B., Yanai, R. D., Bae, K., Wild, A. D., Yang, Y., & Yi, D. (2016). Approaches to stream solute load estimation for solutes with varying dynamics from five diverse small watersheds. *Ecosphere*, *7*(6). https://doi.org/10.1002/ecs2.1298

Austin, B. J., & Strauss, E. A. (2011). Nitrification and denitrification response to varying periods of desiccation and inundation in a western Kansas stream. *Hydrobiologia*, *658*(1), 183–195. https://doi.org/10.1007/s10750-010-0462-x

Ávila A., Piñol J., Rodà F., & Neal C. (1992). Storm solute behaviour in a montane Mediterranean forested catchment. *Journal of Hydrology* 140 (1-4), 143 – 161. https://doi.org/10.1016/0022-1694(92)90238-Q

Bäckman, J. S. K., & Klemedtsson, Å. K. (2003). Increased Nitrification in Acid Coniferous Forest Soil Due to High Nitrogen Deposition and Liming. *Scandinavian Journal of Forest Research*, *18*(6), 514–524. https://doi.org/10.1080/02827580310017466

Bailey, A. S., Hornbeck, J. W., Campbell, J. L., & Eagar, C. (2003). *Hydrometeorological database for Hubbard Brook Experimental Forest: 1955-2000*. US Department of Agriculture, Forest Service, Northeastern Research Station. http://www.fs.fed.us/ne/newtown_square/publications/technical_reports/pdfs/2003/gtrne305.pdf

Bailey, S. (2019). Hubbard Brook Experimental Forest: Pedon locations, 1995-present ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/a7bffc2c0be8052e83b2145993ffa46c. Accessed 2020-04-01

Bailey, Scott W., Brousseau, P. A., McGuire, K. J., & Ross, D. S. (2014). Influence of landscape position and transient water table on soil development and carbon distribution in a steep, headwater catchment. *Geoderma*, *226–227*, 279–289. https://doi.org/10.1016/j.geoderma.2014.02.017

Bailey, Scott W., Buso, D. C., & Likens, G. E. (2003). Implications of sodium mass balance for interpreting the calcium cycle of a forested ecosystem. *Ecology*, *84*(2), 471–484. https://doi.org/10.1890/0012-9658(2003)084[0471:IOSMBF]2.0.CO;2

Bailey, S.W., Gannon, J.P., McGuire, K.J. & Pardo, L.H. (2021. Hubbard Brook Experimental Forest: Watershed 3 Subsurface Water Chemistry ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/ed3c561b4a15364bf9172f2cc7d7911c (Accessed 2021-07-20)

Bailey, S. & McGuire, K. 2019. Hubbard Brook Experimental Forest: W3 Surface Water Sampling Sites – 2009-2010 ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/886612f65609a28eebcd5f4d74032012 (Accessed 2021-07-02).

Bailey, S., McGuire, K., Ross, D., & Green, M. (2019a). Hubbard Brook Experimental Forest: Synoptic Surface Water Chemistry, 2015 ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/fafd7b2334e34a633577764bc36cbb66 (Accessed 2020-11-10)

Bailey, S.W., McGuire, K. J., Ross, D. S., Green, M. B., & Fraser, O. L. (2019b). Mineral Weathering and Podzolization Control Acid Neutralization and Streamwater Chemistry Gradients in Upland Glaciated Catchments. *Frontiers in Earth Science*, *7*, 296.

Benettin, P., Bailey, S. W., Campbell, J. L., Green, M. B., Rinaldo, A., Likens, G. E., McGuire, K. J., Botter, G. (2015). Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA. *Water Resources Research*, 51, 9256– 9272.

Benton, Joshua R. (2020). Temporal dynamics of groundwater flow direction in a glaciated, headwater catchment, MS Thesis, Department of Geosciences, Virginia Tech, 48 p.

Bernal, S., Butturini, A., & Sabater, F. (2002). Variability of DOC and nitrate responses to storms in a small Mediterranean forested catchment. *Hydrology and Earth System Sciences Discussions*, *6*(6), 1031–1041.

Bernal, S., Butturini, A., & Sabater, F. (2005). Seasonal Variations of Dissolved Nitrogen and DOC:DON Ratios in an Intermittent Mediterranean Stream. *Biogeochemistry*, *75*(2), 351–372. https://doi.org/10.1007/s10533-005-1246-7

Bernhardt, E. S., Hall, Jr., R. O., & Likens, G. E. (2002). Whole-system Estimates of Nitrification and Nitrate Uptake in Streams of the Hubbard Brook Experimental Forest. *Ecosystems*, *5*(5), 419–430. https://doi.org/10.1007/s10021-002-0179-4

Bernhardt, E. S., & Likens, G. E.. 2002. Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. *Ecology* 83:1689-1700.

Bernhardt, E. S., Likens, G. E., Hall, R. O., Buso, D. C., Fisher, S. G., Burton, T. M., Meyer, J. L., Mcdowell, W. H., Mayer, M. S., Bowden, W. B., Findlay, S. E. G., Macneale, K. H., Stelzer, R. S., & Lowe, W. H. (2005). Can't See the Forest for the Stream? In-stream Processing and Terrestrial Nitrogen Exports. *BioScience*, *55*(3), 219. https://doi.org/10.1641/0006-3568(2005)055[0219:ACSTFF]2.0.CO;2

Bernhardt, E., G. Likens, & E. Rosi. (2019). Continuous precipitation and stream chemistry data, Hubbard Brook Ecosystem Study, 1963 – present. ver 2. Environmental Data Initiative. https://doi.org/10.6073/pasta/4022d829f3a1fa4057b63b5db8b1a172. Accessed 2020-04-01.

Blaurock, K., Beudert, B., Gilfedder, B. S., Fleckenstein, J. H., Peiffer, S., & Hopp, L. (2021). Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment. Hydrology and Earth System Sciences, 25(9), 5133-5151.

Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.-W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., & De Vries, W. (2010). Global assessment of nitrogen deposition effects on terrestrial plant diversity: A synthesis. *Ecological Applications*, *20*(1), 30–59. https://doi.org/10.1890/08-1140.1

Booth, M. S., Stark, J. M., & Rastetter, E. (2005). Controls on nitrogen cycling in terrestrial ecosystems: A synthetic analysis of literature data. *Ecological Monographs*, *75*(2), 139–157. https://doi.org/10.1890/04-0988

Bourgault, R. R., Ross, D. S., & Bailey, S. W. (2015). Chemical and morphological distinctions between vertical and lateral podzolization at Hubbard Brook. *Soil Science Society of America Journal*, *79*, 428–439.

Bourgault, R. R., Ross, D. S., Bailey, S. W., Bullen, T. D., McGuire, K. J., & Gannon, J. P. (2017). Redistribution of soil metals and organic carbon via lateral flowpaths at the catchment scale in a glaciated upland setting. *Geoderma*, *307*, 238–252. https://doi.org/10.1016/j.geoderma.2017.05.039

Bracken, L. J., Wainwright, J., Ali, G. A., Tetzlaff, D., Smith, M. W., Reaney, S. M., & Roy, A. G. (2013). Concepts of hydrological connectivity: Research approaches, pathways and future agendas. *Earth-Science Reviews*, *119*, 17–34. https://doi.org/10.1016/j.earscirev.2013.02.001

Brooks, P. D., Chorover, J., Fan, Y., Godsey, S. E., Maxwell, R. M., McNamara, J. P., & Tague, C. (2015). Hydrological partitioning in the critical zone: Recent advances and opportunities for developing transferable understanding of water cycle dynamics. *Water Resources Research*, *51*(9), 6973–6987. https://doi.org/10.1002/2015WR017039

Burns, D. A., Hooper, R. P., McDonnell, J. J., Freer, J. E., Kendall, C., & Beven, K. (1998). Base cation concentrations in subsurface flow from a forested hillslope: The role of flushing frequency. *Water Resources Research*, *34*(12), 3535–3544.

Burt, T. P., & Pinay, G. (2005). Linking hydrology and biogeochemistry in complex landscapes. *Progress in Physical Geography: Earth and Environment*, *29*(3), 297–316. https://doi.org/10.1191/0309133305pp450ra

Burton, W. C., Walsh, G. J., & Armstrong, T. R. (2000). *Bedrock geologic map of the Hubbard Brook Experimental Forest, Grafton County, New Hampshire* [Map]. US Geological Survey.

Cedarholm, D. (1994), Dominant soil water pathways on a northern New England forested hillslope, M.S. thesis, 177 pp., Univ. of N. H., Durham

Cirmo, C. P., & McDonnell, J. J. (1997). Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: A review. *Journal of Hydrology*, *199*(1–2), 88–120. https://doi.org/10.1016/S0022-1694(96)03286-6

Compton, J.E.; Boone, R.D.; Motzkin, G.; Foster, D.R. (1998). Soil carbon and nitrogen in a pine-oak sand plain in central Massachusetts: Role of vegetation and land-use history. *Oecologia*, 116 (4), 536-542, https://doi.org/10.1007/s004420050619

Covino, T. (2017). Hydrologic connectivity as a framework for understanding biogeochemical flux through watersheds and along fluvial networks. *Geomorphology*, *277*, 133–144. https://doi.org/10.1016/j.geomorph.2016.09.030

Creed, I. F., & Band, L. E. (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*(11), 3105–3120. https://doi.org/10.1029/98WR01924

Creed, I. F., Band, L. E., Foster, N. W., Morrison, I. K., Nicolson, J. A., Semkin, R. S., & Jeffries, D. S. (1996). Regulation of Nitrate-N Release from Temperate Forests: A Test of the N Flushing Hypothesis. *Water Resources Research*, *32*(11), 3337–3354. https://doi.org/10.1029/96WR02399

De Boer, W. D., & Kowalchuk, G. A. (2001). Nitri®cation in acid soils: Micro-organisms and mechanisms. *Soil Biology*, 14.

Detty, J. M., & McGuire, K. J. (2010). Threshold changes in storm runoff generation at a till-mantled headwater catchment. *Water Resources Research*, *46*(7). https://doi.org/10.1029/2009WR008102

Ducharme, A. A., Casson, N. J., Higgins, S. N., & Friesen-Hughes, K. (2021). Hydrological and catchment controls on event-scale dissolved organic carbon dynamics in boreal headwater streams. Hydrological Processes, 35(7), e14279.

Duncan, J. M., Band, L. E., & Groffman, P. M. (2017). Variable nitrate concentration-discharge relationships in a forested watershed. *Hydrological Processes*, *31*(9), 1817–1824. https://doi.org/10.1002/hyp.11136

Egusa, T., Ohte, N., Oda, T., & Suzuki, M. (2013). Relationship between catchment scale and the spatial variability of stream discharge and chemistry in a catchment with multiple geologies. Hydrological Research Letters, 7(2), 12-17.

Fierer, N., & Schimel, J. P. (2002). Effects of drying–rewetting frequency on soil carbon and nitrogen transformations. *Soil Biology and Biochemistry*, *34*(6), 777–787. https://doi.org/10.1016/S0038-0717(02)00007-X

Fraser, O.L., Bailey, S. W., Ducey, M. J., & McGuire, K. J. (2020). Predictive modeling of bedrock outcrops and associated shallow soil in upland glaciated landscapes. *Geoderma*. https://doi.org/10.1016/j.geoderma.2020.114495

Fraser, Olivia L. (2019). *Long-term forest growth and decadal soil chemistry change across the white mountain national forest*. University of New Hampshire.

Gannon, John P., McGuire, K. J., Bailey, S. W., Bourgault, R. R., & Ross, D. S. (2017). Lateral water flux in the unsaturated zone: A mechanism for the formation of saptial soil heterogeneity in a headwater catchment. *Hydrological Processes*, *31*, 3568–3579.

Gannon, J.P., Bailey, S. W., & McGuire, K. J. (2014). Organizing groundwater regimes and response thresholds by soils: A framework for understanding runoff generation in a headwater catchment. *Water Resources Research*, *50*, 8403–8419.

Gannon, J.P., Bailey, S. W., McGuire, K. J., & Shanley, J. B. (2015). Flushing of distal hillslopes as an alternative source of stream dissolved organic carbon in a headwater catchment. *Water Resources Research*. https://doi.org/10.1002/2015WR016927

Germann, P. F., Pierce, R. S., & Beven, K. (1986). Kinematic wave approximation to the initiation of subsurface storm flow in a sloping forest soil. *Advances in water resources*, *9*(2), 70-76

Gillin, C. P., Bailey, S. W., McGuire, K. J., & Gannon, J. P. (2015). Mapping of hydropedologic spatial patterns in a steep headwater catchment. *Soil Science Society of America Journal*, *79*(2), 440–453.

Goodale, C. L., & Aber, J. D. (2001). The long-term effects of land-use history on nitrogen cycling in northern hardwood forests. *Ecological Applications*, *11*(1), 15.

Green, M. B., Pardo, L. H., Bailey, S. W., Campbell, J. L., McDowell, W. H., Bernhardt, E. S., Rosi, E. (2020). Predicting high-frequency variation of streamwater solute concentrations *Hydrological Processes*

Hayhoe, K., Wake, C., Anderson, B., Liang, X.-Z., Maurer, E., Zhu, J., Bradbury, J., DeGaetano, A., Stoner, A. M., & Wuebbles, D. (2008). Regional climate change projections for the Northeast USA. *Mitigation and Adaptation Strategies for Global Change*, *13*(5–6), 425–436. https://doi.org/10.1007/s11027-007-9133-2

Hedin, L.O., von Fischer, J.C., Ostrom, N.E., Kennedy, B.P., Brown, M.G., & Robertson, G.P. (1998). Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79**,** 684-703

Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, *25*(3), 147–165. https://doi.org/10.1007/BF00024390

Inamdar, S. P., Christopher, S. F., & Mitchell, M. J. (2004). Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes*, *18*(14), 2651–2661. https://doi.org/10.1002/hyp.5572

Inamdar, S. P., & Mitchell, M. J. (2006). Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales. Water Resources Research, 42(3).

Inamdar, S. P., O'leary, N., Mitchell, M. J., & Riley, J. T. (2006). The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA. *Hydrological Processes: International Journal*, *20*(16), 3423–3439. https://doi.org/10.1002/hyp.6141

Jackson, C. R., Bitew, M., & Du, E. (2014). When interflow also percolates: downslope travel distances and hillslope process zones. *Hydrological Processes*, *28*(7), 3195-3200.

Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., & Marshall, L. A. (2009). Hydrologic connectivity between landscapes and streams: Transferring reach-and plot-scale understanding to the catchment scale. *Water Resources Research*, *45*(4), W04428.

Jensen, C. K., McGuire, K. J., & Prince, P. S. (2017). Headwater stream length dynamics across four physiographic provinces of the Appalachian Highlands. *Hydrological Processes*, *31*(19), 3350–3363. https://doi.org/10.1002/hyp.11259

Johnson D.W., Cheng W. & Burke I.C. (2000). Biotic and abiotic nitrogen retention in a variety of forested soils. *Soil Sci. Soc. Am. J.* 64: 1503–1514.

Kiewiet, L., Meerveld, I. V., Stähli, M., & Seibert, J. (2020). Do stream water solute concentrations reflect when connectivity occurs in a small, pre-Alpine headwater catchment?. Hydrology and Earth System Sciences, 24(7), 3381-3398.

Klaus, J., & Jackson, C. R. (2018). Interflow is not binary: A continuous shallow perched layer does not imply continuous connectivity. *Water Resources Research*, *54*(9), 5921-5932.

Koenig, L. E., Shattuck, M. D., Snyder, L. E., Potter, J. D., & McDowell, W. H.. 2017. Deconstructing the Effects of Flow on DOC, Nitrate, and Major Ion Interactions Using a High-Frequency Aquatic Sensor Network. *Water Resources Research 53*:10655-10673.

Lohse, K.A., Brooks, P.D., McIntosh, J.C., Meixner, T., & Huxman, T.E. (2009). Interactions Between Biogeochemistry and Hydrologic Systems. *Annual Review of Environment and Resources* 34**,** 65–96. doi: 10.1146/annurev.environ.33.031207.111141.

Lohse, K. A., Sanderman, J., & Amundson, R. (2013). Identifying sources and processes influencing nitrogen export to a small stream using dual isotopes of nitrate. *Water Resources Research*, *49*(9), 5715–5731. https://doi.org/10.1002/wrcr.20439

Lovett, G. M., Weathers, K. C., & Arthur, M. A. (2002), Control of nitrogen loss from forested watersheds by soil carbon:nitrogen ratio and tree species composition, Ecosystems, 5, 712-718. https://doi.org/10.1007/s10021-002-0153-1

Lovett, G. M., Weathers, K. C., Arthur, M. A., & Schultz, J. C. (2004), Nitrogen cycling in a northern hardwood forest: do species matter?, Biogeochemistry, 67(3), 289-308.

Luo, Y., Ahlström, A., Allison, S. D., Batjes, N. H., Brovkin, V., Carvalhais, N., Chappell, A., Ciais, P., Davidson, E. A., Finzi, A., Georgiou, K., Guenet, B., Hararuk, O., Harden, J. W., He, Y., Hopkins, F., Jiang, L., Koven, C., Jackson, R. B., … Zhou, T. (2016). Toward more realistic projections of soil carbon dynamics by Earth system models. *Global Biogeochemical Cycles*, *30*(1), 40–56. https://doi.org/10.1002/2015GB005239

McGuire K., S. Bailey, J. Gannon. (2016). Water level recordings from wells in Watershed 3 at the Hubbard Brook Experimental Forest, 2007 - present. Environmental Data Initiative. https://doi.org/10.6073/pasta/a7b6b61df98b65244eba64d8bc391582. Dataset accessed 4/01/2020

McHale, M. R., McDonnell, J. J., Mitchell, M. J., & Cirmo, C. P. (2002). A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed. Water Resources Research, 38(4), 2-1.

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., & Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, *450*(7169), 537–540. https://doi.org/10.1038/nature06316

Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, *86*, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026

Nadelhoffer, K. J., & Fry, B. (1994). Nitrogen isotopes in forest ecosystems. In *Stable isotopes in ecology and environmental science* (pp. 22–44). Blackwell Scientific Publications.

Nippgen, F., McGlynn, B. L., & Emanuel, R. E. (2015). The spatial and temporal evolution of contributing areas. Water Resources Research, 51(6), 4550-4573.

Ohte, N., Sebestyen, S. D., Shanley, J. B., Doctor, D. H., Kendall, C., Wankel, S. D., & Boyer, E. W. (2004). Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique. *Geophysical Research Letters*, *31*(21), n/a-n/a. https://doi.org/10.1029/2004GL020908

Pardo, Linda H., Fenn, M. E., Goodale, C. L., Geiser, L. H., Driscoll, C. T., Allen, E. B., Baron, J. S., Bobbink, R., Bowman, W. D., Clark, C. M., Emmett, B., Gilliam, F. S., Greaver, T. L., Hall, S. J., Lilleskov, E. A., Liu, L., Lynch, J. A., Nadelhoffer, K. J., Perakis, S. S., … Dennis, R. L. (2011). Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecological Applications*, *21*(8), 3049–3082. https://doi.org/10.1890/10-2341.1

Pardo, L H, Hemond, H. F., Montoya, J. P., Fahey, T. J., & Siccama, T. G. (2002). Response of the natural abundance of 15N in forest soils and foliage to high nitrate loss following clear-cutting. *Canadian Journal of Forest Research, 32*, 1126-1136.

Pardo, L. H., Green, M. B., Bailey, S. W., McGuire, K. J., Goodale, C. L., Groffman, P. M. (2015) Using a hydropedological framework to identify carbon and nitrogen cycling hotspots in a forested catchment. Presented at the 100th Ecological Society of America Annual Meeting, Baltimore, MD.

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., & Bergamaschi, B. A. (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*(1–3), 183–198. https://doi.org/10.1007/s10533-011-9589-8

Pinay, G., Peiffer, S., De Dreuzy, J.-R., Krause, S., Hannah, D. M., Fleckenstein, J. H., Sebilo, M., Bishop, K., & Hubert-Moy, L. (2015). Upscaling Nitrogen Removal Capacity from Local Hotspots to Low Stream Orders' Drainage Basins. *Ecosystems*, *18*(6), 1101–1120. https://doi.org/10.1007/s10021-015-9878-5

Possinger, A. R., Bailey, S. W., Inagaki, T. M., Kögel-Knabner, I., Dynes, J. Z., Arthur, Z. A., Lehmann, J. (2020). Organo-mineral interactions and soil carbon mineralizability with variable saturation cycle frequency. *Geoderma 375*, 114483. https://doi.org/10.1016/j.geoderma.2020.114483.

Potter, J. D., Koenig, L. McDowell, W. H., & Snyder, L. (2018). New Hampshire EPSCoR Intensive Aquatic Network continuous Discharge, Nitrate, fDOM, Temperature, and Specific Conductance Data, HydroShare, http://www.hydroshare.org/resource/8217eab0997d493782ff321ca5f95f28

Potter, J. D., Koenig, L. McDowell, W. H., & Snyder, L. (2020). New Hampshire EPSCoR Intensive Aquatic Network continuous Discharge, Nitrate, fDOM, Temperature, and Specific Conductance Data, HydroShare, https://doi.org/10.4211/hs.8217eab0997d493782ff321ca5f95f28

Rose, L. A., Sebestyen, S. D., Elliott, E. M., & Koba, K. (2015). Drivers of atmospheric nitrate processing and export in forested catchments. *Water Resources Research*, *51*(2), 1333-1352.

Rusjan, S., Brilly, M., & Mikoš, M. (2008). Flushing of nitrate from a forested watershed: An insight into hydrological nitrate mobilization mechanisms through seasonal high-frequency stream nitrate dynamics. *Journal of Hydrology*, *354*(1–4), 187–202. https://doi.org/10.1016/j.jhydrol.2008.03.009

Sebestyen, S. D., Boyer, E. W., Shanley, J. B., Kendall, C., Doctor, D. H., Aiken, G. R., & Ohte, N. (2008). Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. *Water Resour. Res*, *44*, W12410.

Sebestyen, Stephen D., Boyer, E. W., & Shanley, J. B. (2009). Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States. *Journal of Geophysical Research: Biogeosciences*, *114*(G2), n/a-n/a. https://doi.org/10.1029/2008JG000778

Sebestyen, S. D., Ross, D. S., Shanley, J. B., Elliott, E. M., Kendall, C., Campbell, J. L., Dail, D. B., Fernandez, I. J., Goodale, C. L., Lawrence, G. B., Lovett, G. M., McHale, P. J., Mitchell, M. J., Nelson, S. J., Shattuck, M. D., Wickman, T. R., Barnes, R. T., Bostic, J. T., Buda, A. R., Burns, D. A., Eshleman, K. N., Finlay, J. C., Nelson, D. M., Ohte, N., Pardo, L. H., Rose, L. A., Sabo, R. D., Schiff, S. L., Spoelstra, J., & Williard, K. W. J. (2019), Unprocessed atmospheric nitrate in waters of the Northern Forest Region in the U.S. and Canada, Environ. Sci. Technol., 53(7), 3620-3633. https://doi.org/10.1021/acs.est.9b01276

Sebestyen, S. D., Shanley, J. B., Boyer, E. W., Kendall, C., & Doctor, D. H. (2014), Coupled hydrological and biogeochemical processes controlling variability of nitrogen species in streamflow during autumn in an upland forest, Water Resour. Res., 50(2), 1569-1591. https://doi.org/10.1002/2013WR013670

Siccama, T. G., Fahey, T. J., Johnson, C. E., Sherry, T. W., Denny, E. G., Girdler, E. B., Likens, G. E., & Schwarz, P. A. (2007). Population and biomass dynamics of trees in a northern hardwood forest at Hubbard Brook. *Canadian Journal of Forest Research*, *37*(4), 737–749. https://doi.org/10.1139/X06-261

Sklash, M.G. & Farvolden, R.N. (1979). The role of groundwater in storm runoff. In: W. Back & D.A. Stephenson (Guest-Editors), *Contemporary Hydrogeology — The George Burke Maxey Memorial Volume. J. Hydrol*., 43: 45-65.

Snyder, L., Potter, J. D., & McDowell, W. H. (2018). An Evaluation of Nitrate, fDOM, and Turbidity Sensors in New Hampshire Streams. *Water Resources Research*, *54*(3), 2466–2479. https://doi.org/10.1002/2017WR020678

Soil Survey Staff. 2014. Keys to Soil Taxonomy, 12th ed. USDA-Natural Resources Conservation Service, Washington, DC.

Stark, J. M., & Firestone, M. K. (1995). Mechanisms for soil moisture effects on activity of nitrifying bacteria. *Applied and Environmental Microbiology*, *61*(1), 218–221. https://doi.org/10.1128/AEM.61.1.218-221.1995

Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J., & Kling, G. W. (2003). An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. *Global Biogeochemical Cycles*, *17*(4), n/a-n/a. https://doi.org/10.1029/2003GB002041

Tian, H., Lu, C., Yang, J., Banger, K., Huntzinger, D. N., Schwalm, C. R., Michalak, A. M., Cook, R., Ciais, P., Hayes, D., Huang, M., Ito, A., Jain, A. K., Lei, H., Mao, J., Pan, S., Post, W. M., Peng, S., Poulter, B., … Zeng, N. (2015). Global patterns and controls of soil organic carbon dynamics as simulated by multiple terrestrial biosphere models: Current status and future directions. *Global Biogeochemical Cycles*, *29*(6), 775–792. https://doi.org/10.1002/2014GB005021

USDA Forest Service, Northern Research Station. (2019a). Hubbard Brook Experimental Forest: Instantaneous Streamflow by Watershed, 1956 – present. Environmental Data Initiative. https://doi.org/10.6073/pasta/282953c2290b1f00d9326ffd9a7e9668. Dataset accessed 4/01/2020.

USDA Forest Service, Northern Research Station. (2019b). Hubbard Brook Experimental Forest: Total Daily Precipitation by Watershed, 1956 - present. Environmental Data Initiative. https://doi.org/10.6073/pasta/c64ad38eef4f56d9e34749f166f64caa. Dataset accessed 4/01/2020.

USDA Forest Service, Northern Research Station. (2019). USFS Durham Lab water analysis method detection limit (MDL) limit of quantification (LOQ), 2010 - present ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/890b1fadb61d3e86dc6f3d9afea79705 (Accessed 2020-08-10).

Vitousek, PeterM., & Howarth, RobertW. (1991). Nitrogen limitation on land and in the sea: How can it occur? *Biogeochemistry*, *13*(2). https://doi.org/10.1007/BF00002772

von Schiller, D., Acuña, V., Graeber, D., Martí, E., Ribot, M., Sabater, S., Timoner, X., & Tockner, K. (2011). Contraction, fragmentation and expansion dynamics determine nutrient availability in a Mediterranean forest stream. *Aquatic Sciences*, *73*(4), 485–497. https://doi.org/10.1007/s00027-011-0195-6

Warby, R. A. F., Johnson, C. E., & Driscoll, C. T. (2005). Chemical Recovery of Surface Waters Across the Northeastern United States from Reduced Inputs of Acidic Deposition: 1984−2001. *Environmental Science & Technology*, *39*(17), 6548–6554. https://doi.org/10.1021/es048553n

Welter, J. R., & Fisher, S. G. (2016). The influence of storm characteristics on hydrological connectivity in intermittent channel networks: Implications for nitrogen transport and denitrification. *Freshwater Biology*, *61*(8), 1214–1227. https://doi.org/10.1111/fwb.12734

Whittaker, R. H., Bormann, F. H., Likens, G. E., & Siccama, T. G. (1974). The Hubbard Brook Ecosystem Study: Forest Biomass and Production. *Ecological Monographs*, *44*(2), 233–254. https://doi.org/10.2307/1942313

Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., & Fleckenstein, J. H. (2021). Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to longterm time scales. *Water Resources Research*, *57*, e2020WR027992. https://doi.org/10.1029/2020WR027992

Wollheim, W. M., Mulukutla, G. K., Cook, C., & Carey, R. O. (2017). Aquatic nitrate retention at river network scales across flow conditions determined using nested in situ sensors. Water Resources Research, 53(11), 9740-9756.

Zimmer, M. A., Bailey, S. W., McGuire, K. J., & Bullen, T. D. (2013). Fine scale variations of surface water chemistry in an ephemeral to perennial drainage network. *Hydrological Processes*, *27*, 3438–3451.

Zimmer, Margaret A., & McGlynn, B. L. (2018). Lateral, Vertical, and Longitudinal Source Area Connectivity Drive Runoff and Carbon Export Across Watershed Scales. *Water Resources Research*, *54*(3), 1576–1598. https://doi.org/10.1002/2017WR021718

Tables

Table 1

Percent Area, Carbon and Nitrogen Content by Soil Unit in Watershed 3 at the Hubbard Brook Experimental Forest

Soil Unit (HPU)	Percent of watershed covered by HPU[a]	C kg/m^2 for profile[b]	N kg/m^2 for profile[c]	Fraction of time with water table (median)[d]	Low end of interquartile range [d]	Low end of interquartile range [d]	Standard deviation [d]
E	3.2	20.9	1.1	0.525	0.240	0.538	0.25
Bhs	26.4	27.8	1.4	0.574	0.417	0.606	0.16
Typical	41.3	18.6	0.9	0.033	0.012	0.110	0.15
Bimodal	7.0	28.8	1.5				
Bh	16.5	21	1.2	0.996	0.993	0.997	0.01
Bedrock Histosol (O)	5.6						

[a]Based on Gillin et al (2015). [b]Bailey et al. (2014). [c]Based on Bailey et al. (2014); Supplemental information 2. [d]Gannon et al. (2014).

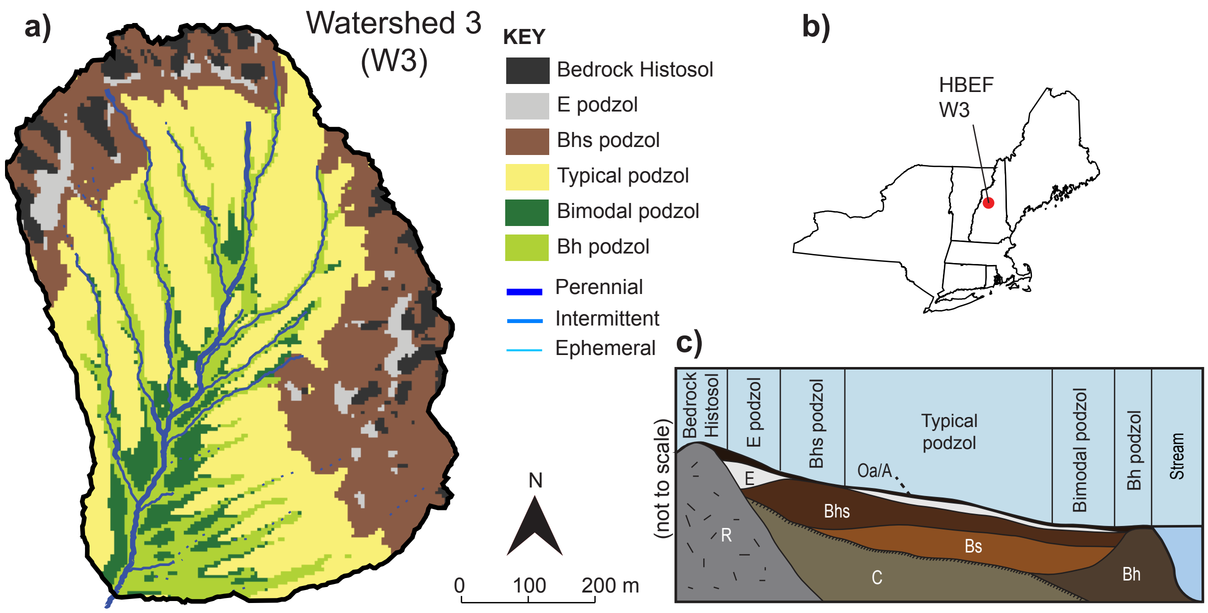


Figure 1: Soil unit map and schematic of Watershed 3 at the Hubbard Brook Experimental Forest

a) Map showing soil units: bedrock Histosol (organic on bedrock), E podzol, Bhs podzol, Typical podzol (typical spodosol), Bimodal podzol, Bh podzol (near stream) with perennial, intermittent, and ephemeral streams; b) Northeastern U.S. regional map; c) Conceptual model showing the distribution of soil groups along a representative hillslope.

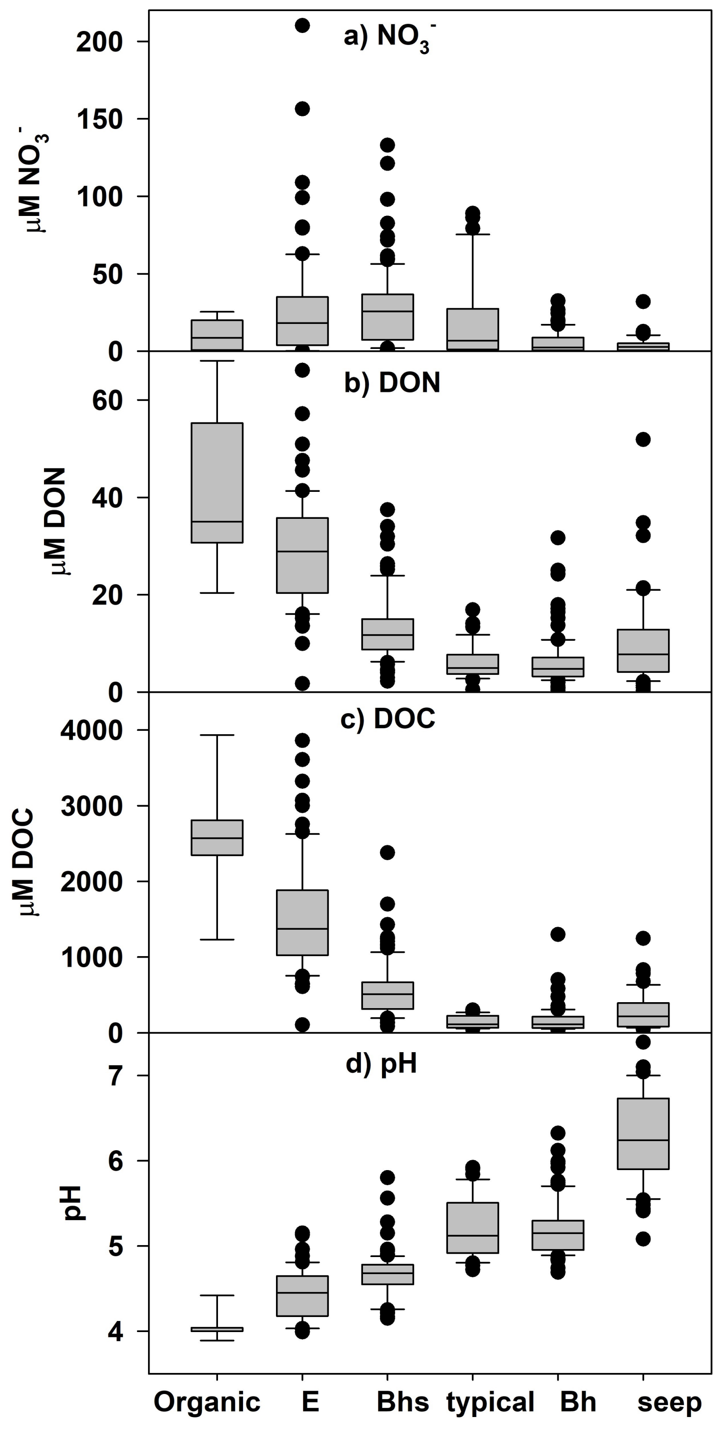


Figure 2: Distribution of concentrations of (a) nitrate, (b) dissolved organic nitrogen, (c) dissolved organic carbon, and (d) pH in groundwater samples

Organic (bedrock Histosol), E, Bhs, typical, and Bh podzols refer to soil units as shown in Figure 1. Seeps are natural groundwater discharge points adjacent to the stream channel. Boxes show the median, 25th and 75th percentiles. Whiskers show the 10th and 90th percentiles.

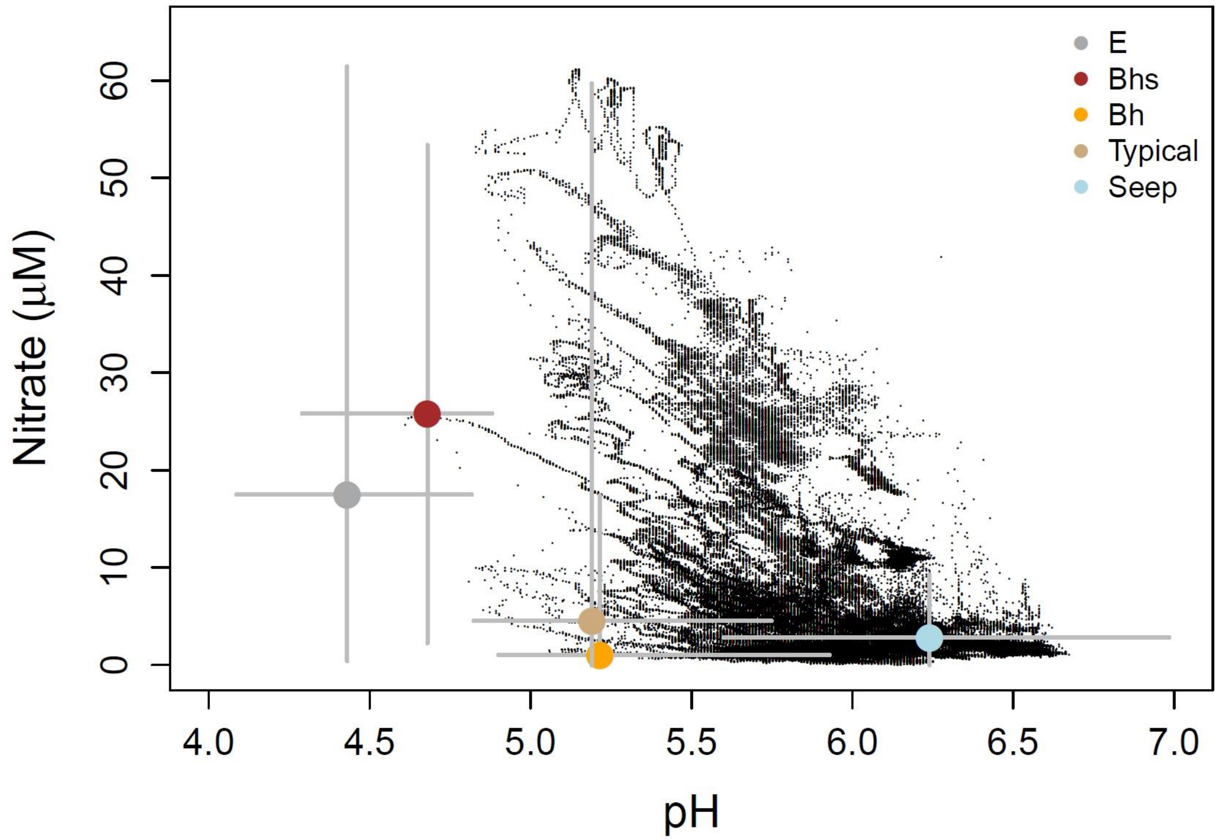


Figure 3: Nitrate concentration versus pH by soil unit for groundwater and streamwater sensor
Median and 10th and 90th percentiles for groundwater in soil units E, Bhs, typical, and Bh podzols (as shown in Figure 1). Sensor streamwater data are shown as black points. Some individual events are discernable beginning when nitrate is high and pH is low and moving toward lower nitrate concentration and higher pH. The high nitrate-low pH spiraling values occur during a snowmelt event.

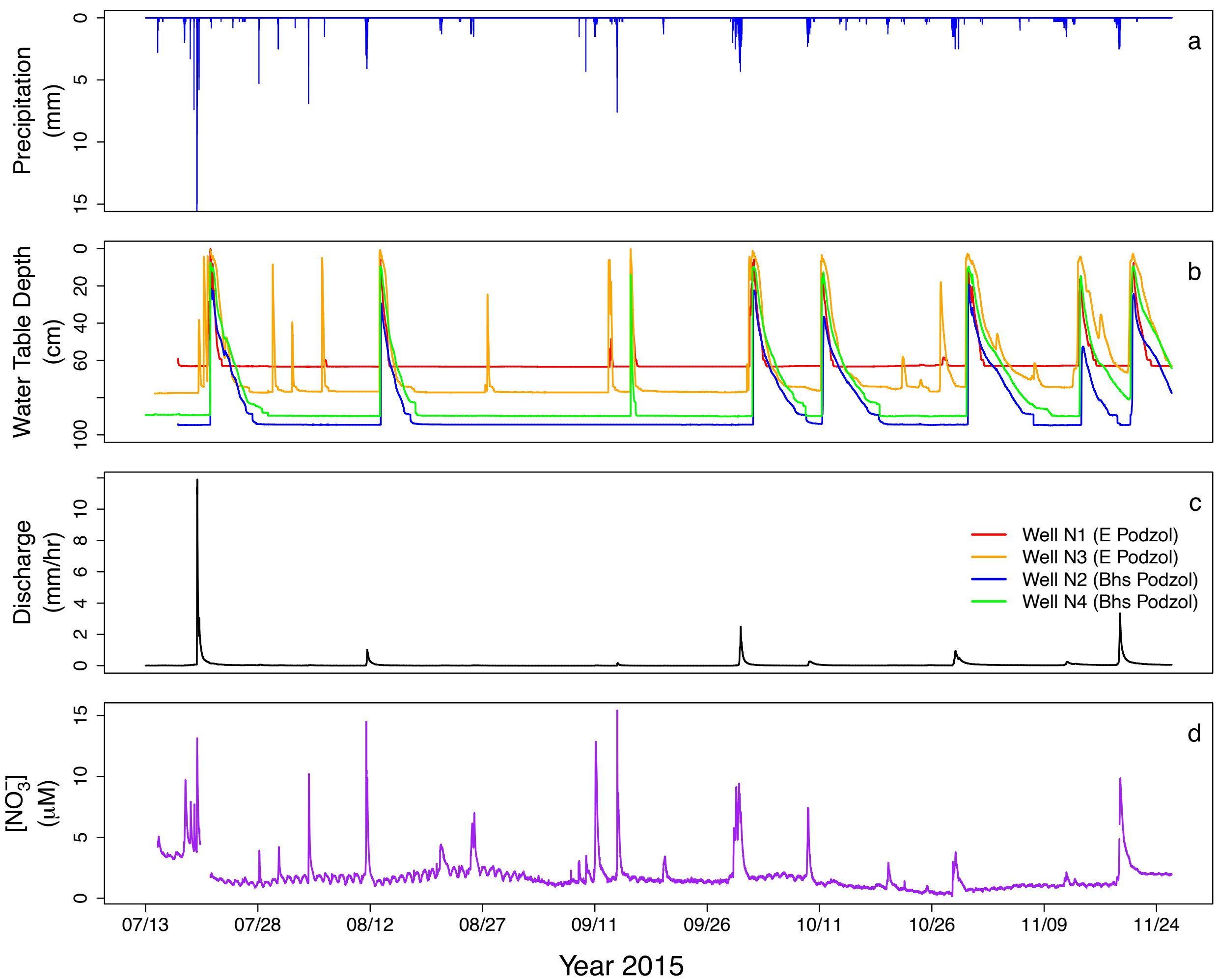


Figure 4: Hydrograph with Precipitation, depth to water table, discharge, and nitrate concentration for July-December 2015 at W3 at the HBEF

Type 1 events occur when there is water table only in the E podzol solum; Type 2 events occur when there is water table in both E and Bhs podzol solum. In Type 1 events, the increases in precipitation and water table height coincides with nitrate concentration, although the increase in discharge is negligible. In Type 2 events, precipitation, water table, discharge, and nitrate concentration all increase and lead to elevated nitrate flux. Wells N1, N2, N3, are N4 are shown as illustrations of the dynamics in paired E/Bhs podzol wells.

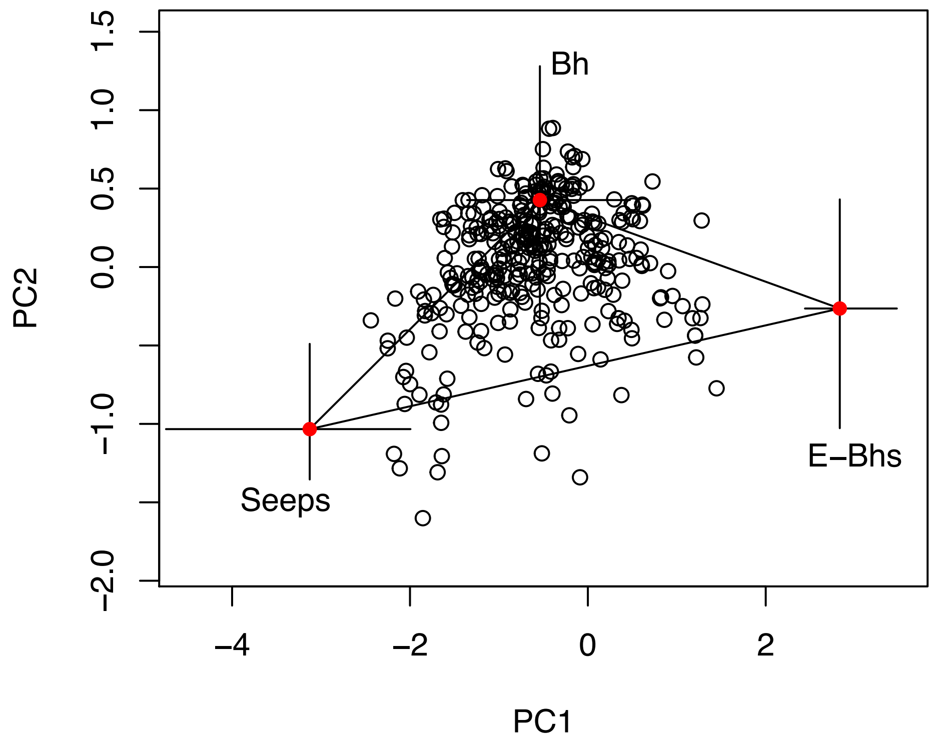


Figure 5: End-member mixing analysis using principal component analysis
The end member mixing model traced the contribution of end member HPUs to stream water during each grab sample. The mixing model used principal components of total Al, Ca, Na, DOC, and pH from seeps, Bh podzols, combined E and Bhs podzols, and streamwater (open circles). The end members show the median principal component values (filled circles) and the inter-quartile ranges as error bars. The medians are connected with lines to show the triangular mixing space for our analysis.

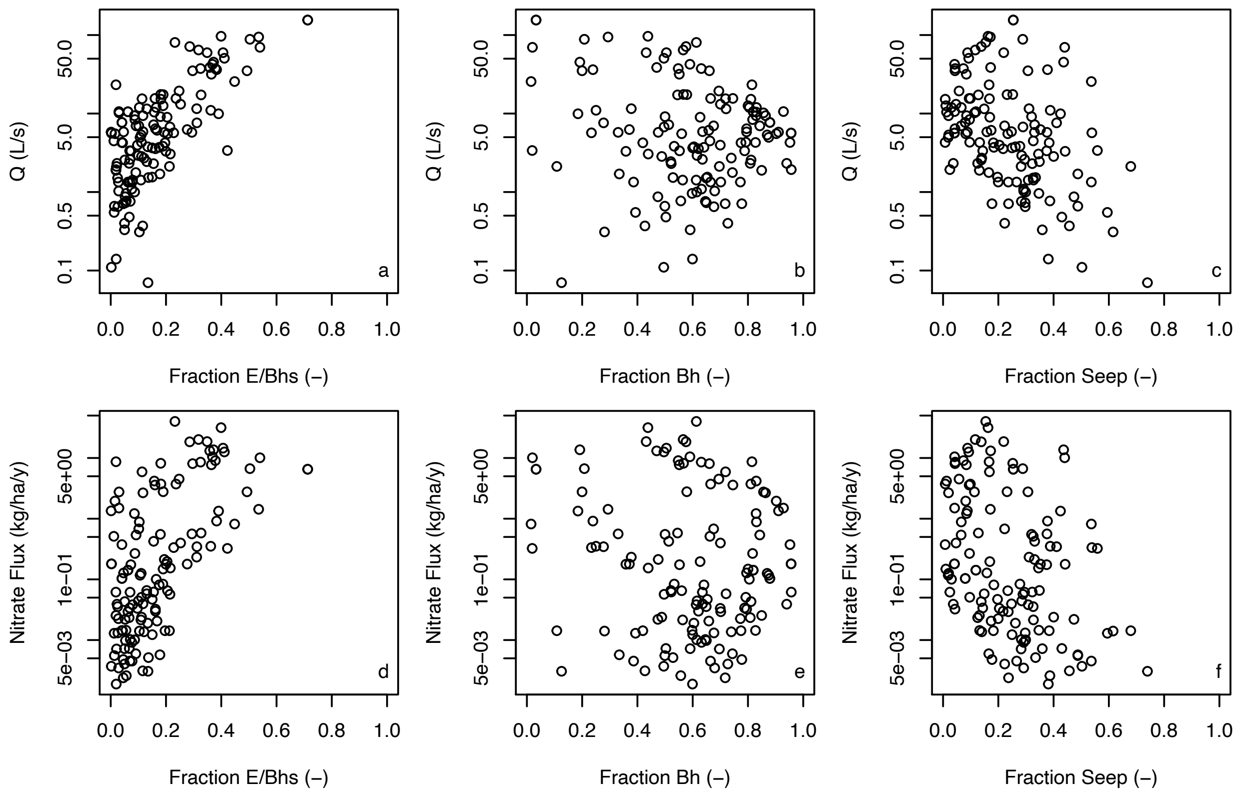
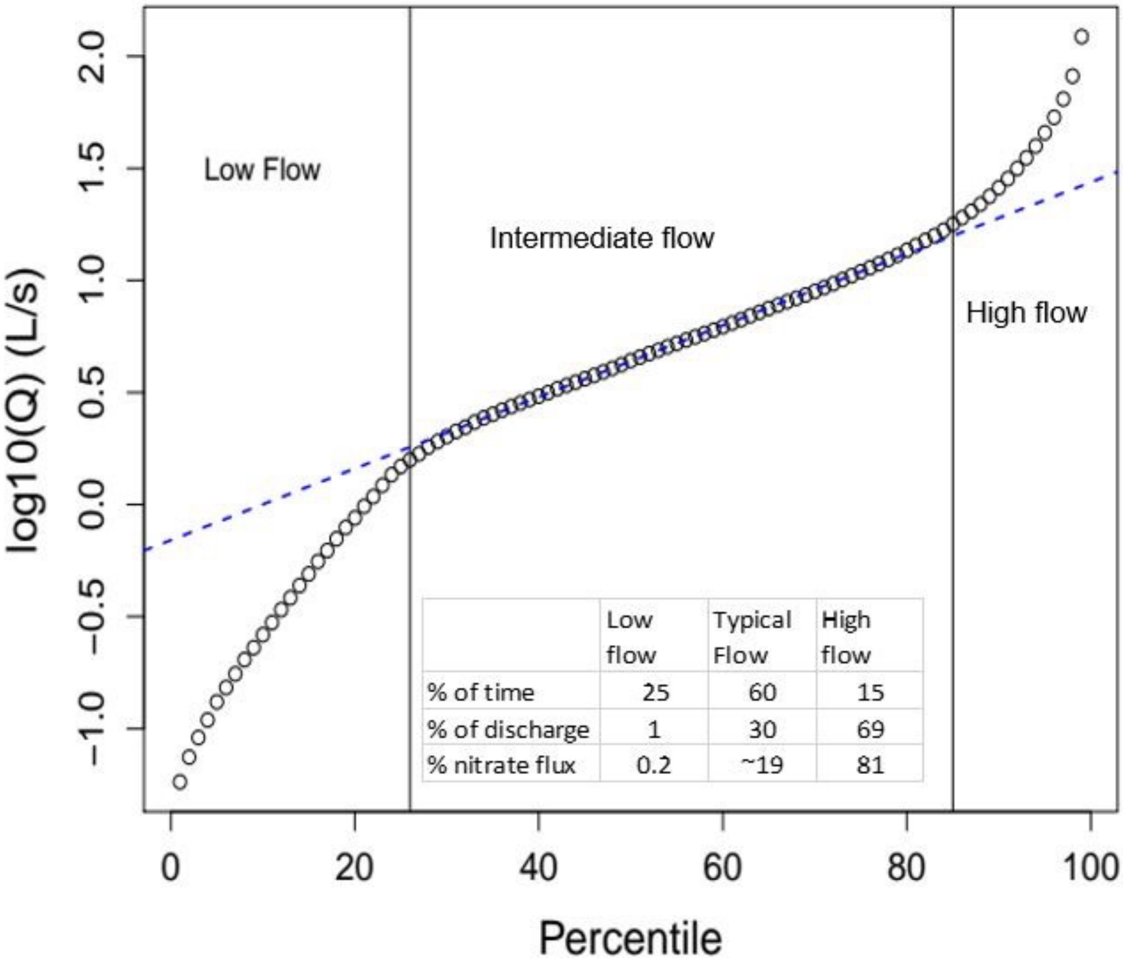


Figure 6: Stream discharge as a function of fraction of E/Bhs podzol soil unit, Bh podzol soil unit and Seep water contribution

Discharge and nitrate flux are shown versus the fractional contribution of each soil unit to each streamwater sample. The positive relationship with the E/Bhs podzol soil unit fraction suggests that these soils are important contributing areas to high flows and high nitrate fluxes, while seep fraction decreases in importance as discharge increases. Bh soil unit fractional contribution is not clearly related to discharge or nitrate flux.



	Low flow	Typical Flow	High flow
% of time	25	60	15
% of discharge	1	30	69
% nitrate flux	0.2	~19	81

Figure 7 Cumulative frequency distribution of streamwater discharge for W3 at the HBEF
Low flow conditions occur 25% of the time; intermediate flow conditions occur 60% of the time; high flow conditions occur 15% of the time. Sixty-nine per cent of the annual stream discharge occurs during high flow, along with 81% of nitrate export from the catchment. The total range of discharge is 0-995 L/s

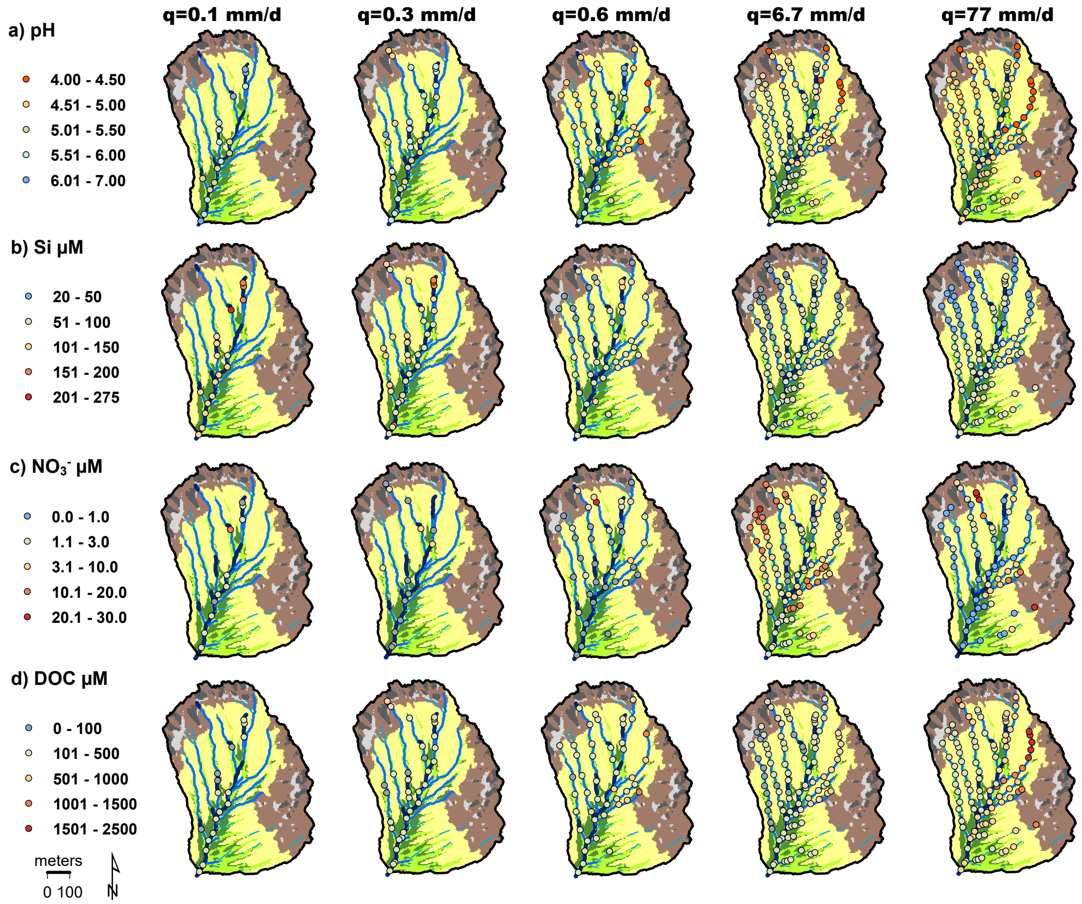


Figure 8: Stream chemistry spatial patterns as stream flow increases
Catchment maps showing how stream chemistry changes as stream flow increases and more of the catchment becomes hydrologically connected with the expanding active stream channel and subsurface contributing area. For sampling dates: 21 Aug 2010; 6 Aug 2010; 22 Jul 2015; 1 April 2010; 1 Oct 2010. Based on data from Bailey & McGuire (2019) for 2010 dates; Bailey et al. (2019a) for 2015 date. a) pH; b) Si; c) nitrate; d) DOC
Map colors follow Figure 1: Bedrock histosol (black), E podzol (gray), Bhs podzol (brown), Bimodal podzol (dark green), Bh podzol (light green), perennial stream (heavy royal blue line), intermittent stream (medium blue line), ephemeral stream (fine, light blue line).

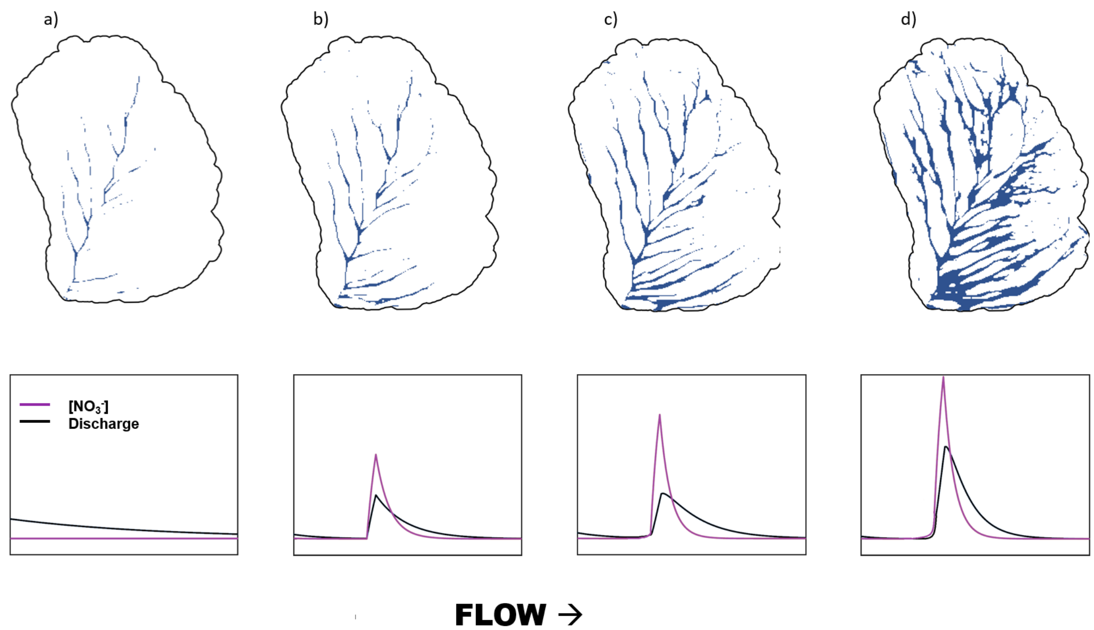


Figure 9: Schematic showing how the drainage network might expand with increasing flow The upper panels show hypothetical drainage network expansion corresponding to increasing flow scenarios. The lower panel indicates how discharge and nitrate concentration might vary from a) baseflow discharge and nitrate concentration, to b) low brief discharge and a small spike in nitrate concentration of short duration on the rising limb of the hydrograph; to c) moderate discharge and a moderate spike in nitrate concentration of short duration on the rising limb of the hydrograph; to d) higher, longer duration discharge and a large increase in nitrate concentration on the rising limb of the hydrograph leading to considerable nitrate export.