End-member mixing analysis reveals divergent patterns of soil-stream connectivity during mid-winter runoff events between two catchments in the northeastern USA

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Key Points:

* Winter soil nutrient availability was comparable to the growing season, with potential transport from soils irrespective of forest cover or agricultural use.
* End-member mixing analysis of winter events revealed complexity of soil-stream connectivity that differed across agricultural and forested subcatchments.
* Winter in Vermont is far more dynamic and relevant to annual nutrient budgets than previously considered.

Abstract

More frequent and intense rain-on-snow events and mid-winter thermal thaws, as well as thinner and inconsistent snowpack have been observed in the northeastern USA. Yet the impact of changing winter conditions on flowpaths and consequences to nutrient cycles and budgets is unknown. To manage and predict water quality, it is critical to understand how warming winters mobilize water and nutrients. Here, we used three complementary approaches to investigate hydrologic connectivity and nutrient mobilization during winter runoff events: *in situ* stream nutrient data, soil nutrient availability, and event-level end-member mixing analysis (EMMA) to determine source contributions to streamflow during three separate mid-winter to spring melt events at two low-order streams – one forested, one agricultural in Vermont, USA. We found that soil available nitrate, phosphate, and ammonium were present throughout the winter for transport. EMMA identified three end-member sources to streamflow: groundwater, meltwater, and soil water. The agricultural catchment, where soils remained subfreezing for the winter, displayed consistent temporal flowpath dynamics for all runoff events, with pre-event groundwater successively replaced by meltwater, then soil water. In contrast, the forested catchment with consistent snowpack and above-freezing soils displayed a seasonal progression, from no apparent soil-stream connectivity during a February rain-on-snow event to increasing contributions of soil water to streamflow during a March thermal event and the spring melt. These analyses suggest that winter in this climate is far more dynamic and relevant to nutrient budgets than previously considered, and that landcover and snowpack behavior modulate soil/snow-stream connectivity and nutrient provenance during winter thaws.

**Plain Language Summary**

Changes in how water moves through a landscape can affect the timing, amount, and quality of water that flows into streams during snowmelt. However, we do not fully understand how changing winter conditions impact water runoff pathways to stream. In the northeastern USA, winters are expected to have more frequent and intense rain-on-snow events, mid-winter thaws, and thinner, less consistent snowpacks. These changes could affect the form water takes (snowpack vs. rain) and its capacity for soil infiltration and/or surface transport, potentially altering connections between soils and streams. Understanding how water and nutrients move during winter is important for planning and managing land and water resources for water quality and soil nutrient retention. We analyzed how meltwater, soil water, and groundwater contribute to stream flow during three different snowmelt events from mid-winter to spring. We focused on two small streams in the Lake Champlain Basin of northern Vermont: one in a forested area and one in an agricultural area. We found that soil nutrients including nitrate, ammonium, and phosphate could all be available for transport at each site. For all runoff events, streamwater could be explained as a mixture of three water sources: groundwater, meltwater, and water from shallow soils. The agricultural catchment, where soils remained below freezing for the winter months, had consistent flowpaths across the runoff events, with pre-event groundwater replaced by meltwater contribution, then soil water. In contrast, the forested catchment with consistent snowpack and above-freezing soils displayed a seasonal progression of no apparent soil-stream connectivity to increasing contributions of soil water to streamflow. These findings indicate we need to develop a model for winter runoff events that is specific to land use, soil type, and snowpack evolution to help us understand how changing winter conditions will affect downstream water quality in the future.

1 Introduction

In the northeastern USA, winters are losing the subfreezing and snowy conditions that ecosystems, human economies, and management practices are based upon (Casson et al. 2019; Contosta et al. 2019). As winters warm, the subfreezing temperatures and persistent snowpack that have historically reduced winter runoff and associated nutrient transport are disrupted by midwinter rain-on-snow (ROS) and thermal snowmelt events (Sebestyen et al. 2008; Contosta et al. 2019; Hale et al. 2025; Perdrial et al. 2014). Further, precipitation is predicted to increase throughout the 21st century in the northeastern USA, particularly in the winter and spring seasons (Picard et al. 2023) and corresponding increases in temperature are projected to grow the proportion of precipitation falling as rain rather than snow (Kunkel 2022). These progressive climatological shifts mean that the traditional paradigm of winter playing a limited role in biogeochemical cycling and transport in this climate is likely changing rapidly (Seybold et al., 2022).

Substantial winter hydrological changes in northern temperate regions have already been observed. For example, in the Midwest of the USA, cold season discharge (between November 1 and March 31) approximately doubled between 1928 and 2021 (Seybold et al. 2022). In New England, winter river discharge similarly increased (53-66%) over the same period (Figure 1, Table S1, and Vermont Climate Assessment, Clark et al. 2021). Such winter discharge increases are driven by increasing annual precipitation (Guilbert et al. 2014), winter precipitation, proportions of precipitation falling as rain vs. snow (Picard et al. 2023), and frequency of snowmelt events (Hale et al. 2025). These trends all illustrate increased water transport during the winter with likely corresponding increases in winter nutrient export (Seybold et al. 2022; Winter et al. 2022; Casson et al. 2012).

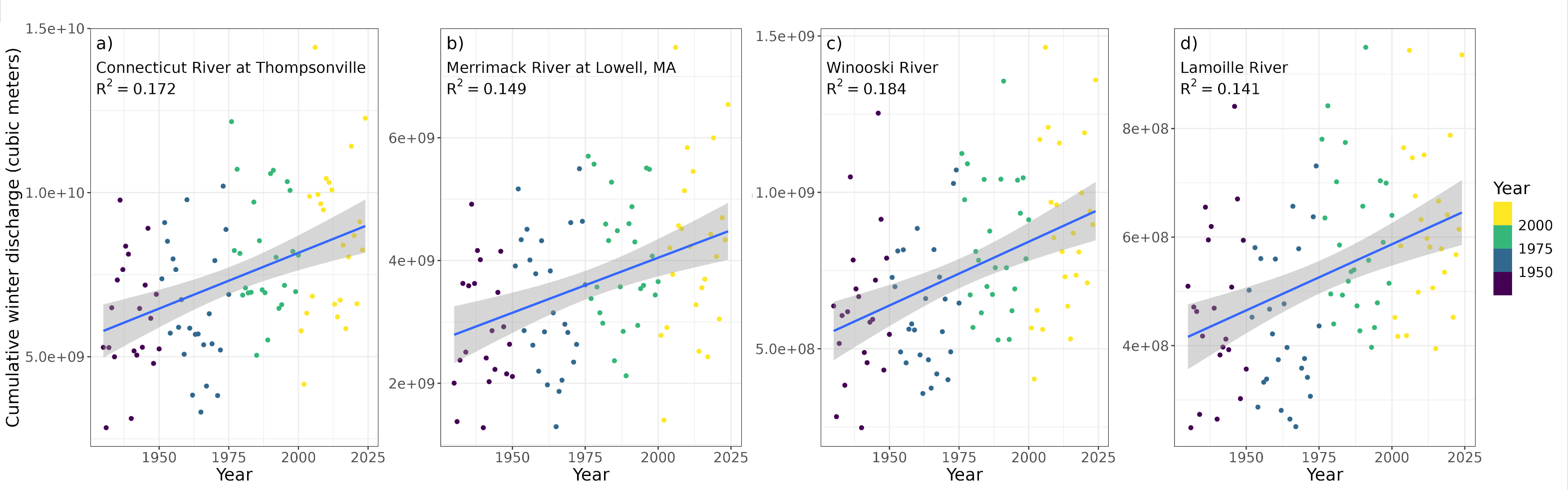


Figure 1. Increasing cumulative winter discharge (1 November–31 March), from 1928 to 2025 for (a) the Connecticut River at Thompsonville, Connecticut (USGS Gauge 01184000); (b) the Merrimack River at Lowell, Massachusetts (USGS Gauge 01100000); c) the Winooski River at Essex Junction, Vermont (USGS Gage 04290500); d) the Lamoille River at East Georgia, Vermont (USGS Gage 0492000). Shaded areas are 95% confidence intervals.

Seybold et al. (2022) showed, through the coincidence of rain-on-snow frequency and nutrient sources, that there is large-scale potential for high wintertime nutrient export for 53% of the contiguous USA. The authors present a conceptual model of winter runoff events under warmer and wetter conditions to highlight five primary hydrological and biogeochemical drivers that may control winter event flowpaths and export: 1) Event conditions including the frequency, intensity, duration, and precipitation composition, that lead to winter runoff events involving snowmelt and rain-snowpack interactions. 2) Soil nutrients remain available for mobilization due to reduced or no plant uptake during the winter season. 3) Snowpack conditions preceding and evolving during the event, including snowpack onset timing, duration, depth, ripeness and consistency through the season; 4) Soil conditions which may include effects of insulation by snow, bare and frozen ground, or freeze-thaw cycles on infiltration capacity and moisture (Shanley et al. 2002; Fuss et al. 2016), microbial activity (Schimel et al. 2004; Nobrega and Grogan 2007), and plant root mortality dynamics or soil physical disturbances (Fitzhugh et al. 2001; Kreyling et al. 2020; Fuss 2016) that may modulate nutrient availability and mobilization in soils. 5) Effects of management practices, particularly where fertilizers are abundant (Basu et al. 2010; Seybold et al. 2022) and may be subject to freeze-thaw cycles that enhance soluble nutrient transport (Kreyling et al. 2020). The complex interactions of these hydrobiogeochemical drivers mean that little is known about dominant flowpaths or the range of sources and flowpaths that may result from warm winter events. Indeed, winter runoff events generated by rain, thermal melt, and ROS may foster meltwater and rain-snowpack-soil interactions with complex flowpath activations possible (Winter et al., 2022); importantly, the role of subsurface or soil flowpaths and soil-stream connectivity are unknown.

As noted by Seybold et al. (2022), few wintertime studies exist to test the conceptual model and the importance of its potential drivers. We seek to integrate soil, meltwater and in-stream winter biogeochemical and physical time series data to mechanistically explore nutrient mobility and changes in provenance during winter runoff generation events. As primary questions, we ask: 1) What are the dominant flowpaths of winter runoff events between two sites in northern Vermont with contrasting land uses and site properties?; 2) How and when are streams connected to soils, if at all, during the varied winter runoff event types and antecedent conditions observed in recent winters?; And 3) If soils and streams are connected during winter thaws, does stream response during winter runoff events demonstrate mobilization of soil nutrients?

We investigated water flowpaths and soil nutrient availability during several mid-winter events and the final spring melt over a single winter. Using sub-daily measurements of stream geochemistry before, during and after winter melt events, we separated the hydrographs using event-level end-member mixing analysis (EMMA), where we allowed end-member selection to evolve throughout the winter-to-spring period to account for changing geochemistry of soil water and meltwater (McDonnell et al. 1990; Harris et al. 1995; Rice and Hornberger 1998). We also evaluated soil nutrient availability over the course of fall through spring. By conducting our study at both a forested catchment and an agricultural one, we documented a range of conditions that influence both the availability of nutrients for transport and the routing of runoff through hydrologic flowpaths during winter melt events. Our objective was to address the above questions by identifying and quantifying hydrologic flowpaths across different melt event types and contrasting land use regimes as well as determining soil available nutrients, thus providing a novel window into the extent to which soils connect to streams during winter, as well as initial insight into the potential impacts of changing winters on water quality and ecosystem function.

2 Methods

2.1 Study site description

We studied two low-order streams within the Lake Champlain basin with distinct land use/land cover regimes (Figure 2). Wade Brook (WB, forested) and Hungerford Brook (HB, agricultural) are both located in the greater Missisquoi River basin and are influenced by winter snowpack accumulation and spring snowmelt (Table 1). Mean annual wintertime temperatures range from 4 to 8 °C but vary according to topography and elevation. Winter temperatures are variable and frequently lower than 0 °C (Kunkel 2022). Average annual precipitation (rain and snow) also varies as a function of elevation and topography; for HB, 973 mm of total precipitation with 2029 mm of snowfall; for WB, 1036 mm of total precipitation with 2115 mm of snowfall (30 year-mean for 1991-2020, NOAA, 2021). The vegetation at HB is mixed red maple (*Acer rubrum*), northern red oak (*Quercus rubra*), and eastern cottonwood (*Populus deltoides*) with varied ferns (group *Pteridophytes*), nettles (*Urtica dioca*) (Landsman-Gerjoi et al. 2020), and increasing abundance of invasive phragmites (*Phragmites australis*). The primary agricultural use is dairy and corn silage. Vegetation at WB is dominated by northern hardwood species including American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.). Soil types at HB are Inceptisols (Aquic Dystric Eutrudepts) and Entisols from glaciolacustrine and glaciofluvial material. Soil types at WB are Inceptisols (Fluvaquentic Dystrudepts and Fluvaquentic Endoaquepts) (Soil Survey Staff, 2022).

Approximate snowpack depths at HB were estimated from the National Snowfall Analysis observed data product available from the National Weather Service National Operational Hydrologic Remote Sensing Center for Station ENFV1 (Enosburg Falls 2, 129 m elevation and 18 km east of the HB site). Approximate snowpack depths at WB were estimated from daily measurements at the Community Collaborative Rain, Hail, and Snow Network (CoCoRaHS) station VT-FR-30 (1.5 km northwest of the WB site and equivalent to the lowest elevation in the catchment).

Table 1. Summary of catchment attributes for study sites in Vermont. Precipitation data from the latest 30-year (1991 to 2020) release for NOAA station #s USC00437032 (St Albans Radio, VT, for Hungerford Brook); and USC00432769 (Enosburg Falls, VT, for Wade Brook.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Subcatchment name | Stream site coordinates | Subcatchment area [km2] | Primary focal land use [%] | Max. catchment elevation [m] | Mean catchment slope | Mean annual temp [°C] | Mean annual precipitation [mm] | Mean annual snowfall [mm] |
| Forested: Wade Brook | 44° 51’N, 72° 33’W | 16.7 | 95.1 | 981 | 26 | 7 | 1036 | 2115 |
| Agricultural: Hungerford Brook | 44° 54’N, 73° 30’W | 48.1 | 44.8 | 354 | 5.6 | 7 | 973 | 2029 |

2.2 Streamwater and end-member sampling

During rain, ROS, or thermal snowmelt events, stream samples were collected at 2-6-hour intervals using Teledyne ISCO (Lincoln, NE, USA) 6712 automated samplers into 1-L polyethylene terephthalate bottles. The samplers were programmed to begin collection prior to hydrograph rise, though logistical constraints precluded capturing the pre-event conditions during certain events. Freezing conditions and low power to the samplers resulted in some coverage loss, typically between midnight and 9:00 am. Bottles were removed from the samplers within 24 hours of collection and divided for separate analyses: 50-100 mL were filtered immediately through 0.45 µm polyethersulfone (PES) membranes and frozen at -20 °C prior to major cation and anion analyses; 60 mL were filtered through GF/F glass microfiber filters (0.7 µm nominal pore size) and refrigerated at 4 °C for dissolved organic carbon (DOC) analysis; and unfiltered streamwater was collected without headspace in 20 mL glass vials and refrigerated before stable water isotope analysis.

Candidate end-members included precipitation (rain and new snow), soil water, meltwater, and groundwater. Rain was sampled in acid-washed polycarbonate funnels and 250-mL bottles attached to 0.5-m high stakes in open areas at each site and collected within 24 hours. Fresh snow from each event was collected into plastic bags using clean nitrile gloves and melted. Soil water was sampled approximately monthly from zero-tension lysimeters with three collection trays at 30-cm depth (two lysimeters at each site). Meltwater was collected after events using passive capillary samplers similar to those described in Penna et al. (2014) that sample the ground-snowpack interface (one meltwater sampler per site). Just before the onset of snowpack accumulation, 45 x 45 cm plastic collection sheets with attached fiberglass wicks were set on the ground. Prior to anticipated snowmelt events, 2-L high-density polyethylene bottles were set in buried boxes and placed to receive drainage from the wicks. Meltwater samples were collected within 48 hours of being set and were emptied after each event. Prior to deployment, meltwater sampling bottles and sheeting were acid-washed and fiberglass wicks were soaked with deionized water. Groundwater was sampled as baseflow and pre-event streamwater, and also from homeowner wells within each subcatchment twice yearly. All end-member samples were subsampled into PES, GF/F, and stable isotope fractions as with collected streamwater.

2.3 Laboratory analysis

Concentrations and water isotopes were measured in each sample of streamwater and in candidate end-members – precipitation, soil water, meltwater, and groundwater. We measured solutes that have been used in previous hydrograph separation studies (Sebestyen et al. 2008; Fuss et al. 2016; Porter et al. 2022). The concentrations of aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), potassium (K), manganese (Mn), magnesium (Mg), sodium (Na) , phosphorus (P), silicon (Si), and zinc (Zn) were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 3000DV, Perkin Elmer Corp, Norwalk, CT, USA). The precision and accuracy of the method was determined by duplicate samples (RPD = 5% ± 5%), and analysis of an external standard (NIST 1643f standard reference material recovery = 94 ± 2%); concentrations of fluoride (F-), chloride (Cl-), bromide (Br-), sulfate (SO4-2), nitrite (NO2-) and nitrate (NO3-) were measured using ion chromatography (Dionex, Sunnyvale, CA, USA). Ion chromatography accuracy determined with external standards (NIST 3180 series standard reference materials (recovery = 93 ± 4%). The DOC concentration was measured using persulfate oxidation followed by infrared CO2 detection (Teledyne Tekmar, Mason, OH, USA). The natural abundances of stable isotopes of hydrogen (H) and oxygen (O) were analyzed by laser absorption spectrometry using a Los Gatos Research T-LWIA 45-EP Liquid-Water Isotope Analyzer (Los Gatos Research, Inc, Mountain View, CA, USA) with machine precision of 0.5% for δD and 0.1% for δ18O (Stelling et al. 2021). Isotopic values were scaled relative to the Vienna Standard Mean Ocean Water (VSMOW). Values for deuterium (D) and oxygen 18 (18O) are reported in delta-notation (δ) in permil (‰) relative to VSMOW (Craig 1961).

2.4 In situ data collection

We used s::can spectro::lyser UV-Vis spectrophotometers (s::can Messtechnik GmbH, Vienna, Austria) to estimate DOC, NO3—N, and total phosphorus (TP) concentrations (Vaughan et al. 2017; Kincaid et al. 2020). Nitrate, total phosphorus (TP), and dissolved organic carbon (DOC) yields for each event were determined using the *in situ* sensor-derived concentrations (hereafter referred to as ‘sensor stream data’). Here we define nutrient losses as removal in streamwater (as opposed to biological uptake). We calculate yields of nutrient loss as mass per time divided by subcatchment drainage area. Each stream site was also equipped with a HOBO pressure transducer (Onset Computer Corporation, Bourne, MA, USA) to monitor stage. We previously developed stage-discharge rating curves for each catchment to estimate continuous time series for stream discharge using barometrically corrected stage measurements (Vaughan et al. 2017). Rating curves were developed using a combination of velocity-area calculations from stream velocity measurements (Turnipseed and Sauer 2010) and tracer dilution gauging (Kilpatrick and Cobb 1985).

Soil temperature and volumetric water content (VWC) were monitored using *in situ* sensors (Meter Environmental, Pullman, WA, USA) at three soil depths: 15, 30, and 45 cm at HB. Sensors were installed in two hillslopes to near-stream transects per subcatchment, with 2-5 sensors at each transect coincident with soil ion exchange resins. We used comparable soil sensor temperature and moisture sensors (TMS4, TOMST, Prague, Czech Republic) deployed at 6-cm soil depth at a similar and nearby (45-km) montane site (Ranch Brook, 44.50 N, -72.75 W) as a proxy for WB due to failure of the Meter sensors at that site. Each site was equipped with a HOBO RX3000 weather station (Onset Computer Corporation, Bourne, MA, USA) that measured rainfall, air temperature, atmospheric pressure, wind speed and wind direction.

To quantify available soil mineral nitrogen and phosphorus, we deployed ion exchange resin capsules (Unibest, Kennewick, WA, USA) year-round in 30-cm deep access tubes installed at a 30° angle in the soils at two riparian transects, the same wet and dry transects as the soil sensor transects described above, in both subcatchments following an upland-to-riparian gradient. For the purposes of this study, we combine the data from both wet and dry transects in our analysis (HB *n* = 6; WB *n* = 10). Capsules were collected and replaced monthly, rinsed free of loose soil or debris with deionized water, air dried for one week, and serially extracted into 2 mol/L potassium chloride. The extractant was filtered through Whatman #42 filter paper and frozen at -20 °C until colorimetric analysis for ammonium (NH4+), nitrate (NO3-), and phosphate (PO43-)using a microplate version of the phenol hypochlorite method (NH4+, Weatherburn 1967); vanadium/Griess method (NO3-, Doane and Horwáth 2003) and malachite green method (PO43-, Lajtha et al. 1999). Nutrient adsorption was blank-corrected using resin capsules that were not deployed in soils, and adsorption was standardized per unit area of capsule surface (11.4 cm2) for 30-day intervals, similar to Iversen et al. (2022).

2.5 Hydrologic flowpath determination via end-member mixing analysis

We used EMMA to estimate event streamflow contributions from distinct sources, or end-members, the potentials of which included precipitation (rain and snow), meltwater, soil water, and groundwater (or baseflow). The two assumptions underlying the EMMA approach are 1) that different sources to the streamwater are geochemically distinct from one another and 2) that source geochemical signatures are stable within the time and spatial consideration of the EMMA application, e.g., a runoff event (Hooper et al. 1990; Hooper 2003). Based on the approach of Hooper (2003), the tracer selection guidelines developed by Barthold et al. (2011), and workflow of Dwivedi et al. (2019), we selected conservative tracers for EMMA and determined the minimum dimensionality of the mixing space to explain the variability of the sample set.

We started with 18 possible tracers for each subcatchment (DOC, F, Cl, Br, SO4, Na, Mg, Al, Si, K, Ca, Fe, Mn, P, Cu, Zn, δ2H, and δ18O) and created a Pearson’s correlation table and corresponding bivariate tracer-tracer plots to evaluate evidence of conservative mixing, that is minimal adsorption or biological reactivity (Figure S1, S2). Conservative tracers were selected by co-linearity criteria of R2 > 0.50, p-value <0.01. In several cases, additional tracers that had slightly lower than 0.50 co-linearity were used because they had been demonstrated as conservative tracers for EMMA in similar catchments (Sebestyen et al. 2008; Fuss et al. 2016; Porter et al. 2022).

The tracer data were standardized to ensure that solutes with greater variability could not influence the model more than solutes with lesser variability (Christophersen and Hooper 1992). We standardized using *z*-scoring, whereby the mean of each column in the streamwater solute data is subtracted from the values in the column and then divided by the standard deviation of that column. After standardization, we then performed a principal components analysis (PCA) of the correlation matrix composed of the normalized conservative streamwater tracer data. For both subcatchments, we selected from the tracer matrices the dimensionality of the mixing space (number of eigenvectors to retain) based on the guidelines of Hooper (2003), namely: a) the retention of only as many eigenvectors as necessary to explain 80-90% of the observed dataset variability (Christophersen and Hooper 1992) and b) the retention of a minimum number of eigenvectors so that the pattern between observed and residuals for the conservative tracers is random (Hooper 2003).

The selected tracer concentrations for each potential end-member were normalized with the streamwater scalers and projected into the principal component space (or *U*-space) defined by the PCA. For individual events, three end-members were selected based on the primary criteria described by Dwivedi et al. (2019) and Barthold et al. (2011), that end-members should form the vertices of the mixing space and circumscribe most of or all the streamwater tracer observations within the principal component space. We selected end-members for each event-level EMMA from a pool of candidates that included soil water lysimeters from the wet and dry transect at each site, meltwater lysimeters, and groundwater wells or baseflow samples.

We used the same PCA-based method of Christophersen and Hooper (1992) to estimate the fractional contribution of each end-member to streamwater based on the PC scores. The following mass balance equations were solved:

(1)

(2)

(3)

Where *U1* and *U2* are the first and second principal components of the PCA, respectively, and *f* is the fraction of streamflow assigned to each end-member denoted as *fg* for groundwater, *fsm* for meltwater, and *fsw* for soil water with similar subscripts for component assignments. Using the SciPy Python package (Virtanen et al. 2020), we used the sequential least squares programming method (SLSQP) for constrained nonlinear optimization, with the sum of fractional contributions constrained to equal 1 and each contribution constrained between 0 and 1 (Dwivedi et al. 2019). We evaluated the error for each event-level EMMA by comparing the model-predicted tracer concentrations with the observed values (Supplementary Information Figure 5) (Fuss et al. 2016; Inamdar and Mitchell 2006).

2.6 Runoff event type determination

We classified runoff events as rain-on-snow (ROS) events, midwinter thermal events, and the final spring melt by the following metrics: We defined ROS events as 3 mm of rain over six days on any snowpack depth, similar to Freudiger et al. (2014) and a median metric compared to previous ROS studies which range from 1 mm d-1 (Il Jeong and Sushama 2018) to 10 mm d-1 (Seybold et al. 2022). We defined midwinter thermal events as periods when discharge rose above site-specific stormflow threshold when there was no rain-on-snow within a three-day period. Finally, we defined the final spring melt as the last melt event without snowfall of the year at each site, regardless of precipitation. Three events were sampled at each subcatchment for EMMA in the winter of 2023. These include a ROS event in February, a thermal event in March, and the final spring melt in March-April.

**3 Results**

3.1 Winter characteristics

Winter of 2023 was characterized by intermittent snowpack between January and April. The snowpack first developed at HB beginning January 10, 2023, reached a seasonal peak of 25-cm on February 3, and final snowmelt occurred by April 1 (Figure 3b). The snowpack at WB began to develop on November 16, 2022 and peaked at 57-cm on March 15, 2023. Final snowmelt occurred in the second week of April and snowpack was fully melted by April 14 (Figure 3i). At HB, the March thermal event had the largest water and nitrate yield of the winter-to-spring melt period, though TP yield was highest during the final spring melt (Table 2). At WB, while the final spring melt event had the greatest nitrate and TP yields, a ROS and winter rain event were also observed to have yields nearly as great (Table 2).

Table 2. Winter event nutrient water-normalized yields at Hungerford Brook (HB) and Wade Brook (WB) in the winter of 2023 with total source contributions from end-members groundwater, soil water, and meltwater.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Subwatershed | Event type | Event start date/time | Event end date/time | Event duration [hrs] | Water yield [mm] | Nitrate yield [kg NO3-N km-2/ mm water yield] | Total phosphorus yield [kg P km-2/ mm water yield] | DOC yield [kg DOC km-2/ mm water yield] | Event total baseflow [%] | Event total soil water [%] | Event total meltwater [%] |
| Hungerford | ROS | 02/9/2023 5:15 | 02/19/2023 4:00 | 236.75 | 56.9 | 3.70 | 0.11 | 7.00 | 35.4 | 31.5 | 33.1 |
| Hungerford | Thermal | 03/21/2023 6:00 | 03/23/2023 23:30 | 64 | 14.0 | 3.95 | 0.18 | 11.01 | 36.9 | 25.5 | 37.6 |
| Hungerford | Spring melt | 03/31/2023 6:00 | 04/11/2023 17:15 | 272.75 | 49.7 | 2.28 | 0.29 | 6.62 | 35.2 | 32.6 | 32.2 |
| Wade | ROS | 02/9/2023 5:15 | 02/19/2023 4:00 | 236.75 | 59.1 | 0.28 | 0.01 | 2.14 | 64.0 | 0.0 | 35.9 |
| Wade | Thermal | 03/21/2023 6:00 | 03/27/2023 3:45 | 139.75 | 30.5 | 0.30 | 0.01 | 2.29 | 58.8 | 34.1 | 7.1 |
| Wade | Spring melt | 03/31/2023 6:00 | 04/12/2023 6:00 | 285.25 | 120.9 | 0.32 | 0.01 | 2.91 | 21.3 | 36.8 | 41.9 |

3.2 Soil characteristics and nutrient availability

Soil temperatures at 6-cm depth were ~2 °C lower at HB than at WB. Soils at HB were less insulated by snowpack (Figure 3c,j;). Soil volumetric water content at 6-cm depth (VWC) was also lower at HB (~37-41%) than at WB (~45-70%) throughout the winter-to-spring sampling period, with greater seasonal variation in soil VWC at WB. At HB during the February ROS event, soil VWC at 6-cm depth rose rapidly from 36 to 42% after rainfall (Figure 5d). For the March thermal event and the final spring melt, soil VWC at 6-cm depth fluctuated less, though it still increased concurrently with the hydrograph without lag (Figure 5h,l). At WB, soil VWC was stable during the February ROS event and more dynamic during the March thermal event, increasing ~5% during the hydrograph peak (Figure 6d,h).

In general, soil mineral nitrogen and phosphate availability were highly variable in both subcatchments (Figure 3), but overall soil nutrient availability was higher for HB than WB. At HB, where chemical fertilizers were applied in the spring and manure was applied in the fall, the site had the highest levels of soil available ammonium during November and December 2022 (Figure 3e). Soil available nitrate at HB was highly variable in the winter, with overall greatest mean site availability during October (post-manure spreading), January, February, and March (Figure 3f). At HB, soil available phosphate was relatively stable throughout October 2022 to April 2023, with slightly more available phosphate in October followed by low levels with no significant changes between November and April (Figure 3g). At the forested WB site, where there is no agricultural activity, soil available mineral N and P were generally stable from October to April. Soil available nutrients were more dynamic throughout the study period and had more variability both across the transects and over the course of the year at HB (*n* = 6) compared with WB (*n* = 10).

3.3 Event hydrograph separation by end-member mixing analysis

For HB, we selected tracers Mg, Na, Ca, Cl, Si, δ2H, and δ18O; for WB, Mg, Na, Ca, δ2H, and δ18O. The first two principal components described 80.2-98.9% of the variance in streamwater geochemistry for each event during the study period (Figure 4). For all sampled events, we best explained streamwater composition using groundwater/baseflow, meltwater and soil water chemistries sampled closest in time to the event (Figure 4). End-member geochemical variability was high during the winter-to-spring snowmelt period, particularly for groundwater/baseflow and meltwater samples (Table 3 and Supplementary Figures S3, S4). Several outlier streamwater data points, especially for the ROS events at both WB and HB, fell outside the mixing space bound by the three selected end-members (Figure 4). Especially in these cases and for events with few streamwater samples, the error for our EMMA models, obtained by comparison of model-predicted and observed solute values, could be high (Supplementary Figure S5).

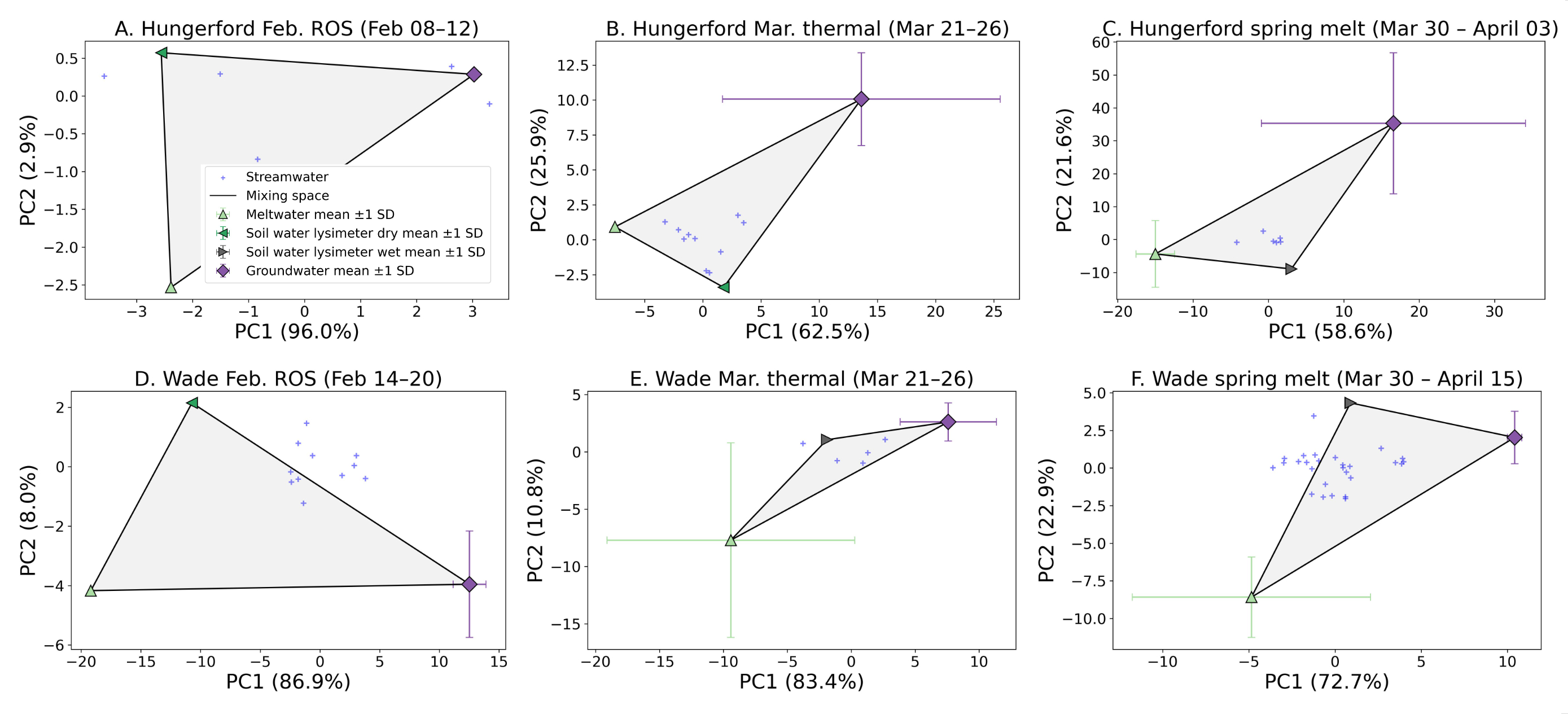


Figure 4. Two-dimensional mixing space (U-space) plots for event-level end-member mixing analysis (EMMA) comprised of the first two principal components of geochemical tracer datasets for winter runoff events in the winter of 2023 at Hungerford Brook (A, B, C) and Wade Brook (D, E, F). End-member error bars represent one standard deviation of mean end-member samples when replicate measurements were available for the event.

Table 3. Mean concentration values of potential hydrologic ﬂowpath tracers in each end-member type for Hungerford and Wade Brook subcatchments.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Subcatchment | Endmember type | Si [mg/L] | Mg [mg/L] | Na [mg/L] | Ca [mg/L] | Cl [mg/L] | δD | δ18O |
| Hungerford | Soil water – Dry transect | 5.00 ± 0.95 (2) | 3.75 ± 0.29 (2) | 2.21 ± 0.31 (2) | 27.65 ± 1.37 (2) | 5.56 ± 0.09 (2) | 80.32 ± 1.15 (2) | 12.41 ± 0.53 (2) |
|  | Soil water - Wet transect | 1.88 ± NA (1) | 0.753 ± NA (1) | 0.241 ± NA (1) | 3.51 ± NA (1) | 3.04 ± NA (1) | 77.61 ± 17.01 (2) | 11.18 ± 2.03 (2) |
|  | Meltwater | 3.69 ± 2.83 (3) | 2.11 ± 1.68 (3) | 1.66 ± 1.26 (3) | 12.60 ± 14.3 (3) | 4.29 ± 2.19 (2) | 81.88 ± 7.61 (2) | 12.64 ± 1.26 (2) |
|  | Groundwater/baseflow | 3.73 ± 2.65 (4) | 12.4 ± 9.3 (4) | 18.3 ± 3.0 (4) | 64.9 ± 27.8 (4) | 41.9 ± 14.5 (4) | 71.9 ± 4.0 (4) | 10.7 ± 0.6 (4) |
| Wade | Soil water – Dry transect | 0.505 ± 0.089 (3) | 0.335 ± 0.061 (3) | 1.12 ± 0.10 (3) | 0.568 ± 0.028 (3) | 1.90 ± 0.02 (3) | 91.29 ± 1.89 (2) | 13.28 ± 0.05 (2) |
|  | Soil water - Wet transect | 1.279 ± NA (1) | 0.328 ± NA (1) | 0.858 ± NA (1) | 1.446 ± NA (1) | 1.736 ± NA (1) | 78.10 ± NA (1) | 11.58 ± NA (1) |
|  | Meltwater | 0.114 ± 0.123 (3) | 0.137 ± 0.059 (3) | -1.03 ± 0.17 (3) | 0.58 ± 0.14 (3) | 1.76 ± 0.22 (3) | 94.78 ± 8.57 (4) | 13.14 ± 1.24 (4) |
|  | Groundwater/baseflow | 1.49 ± 0.575 (4) | 0.541 ± 0.202 (4) | 1.58 ± 0.22 (4) | 4.80 ± 1.84 (4) | 1.39 ± 0.42 (4) | 77.5 ± 4.3 (4) | 11.7 ± 0.4 (4) |

At HB during all three observed events (February ROS, March thermal, and the final spring melt), we observed a similar pattern of hydrograph and source evolution (Figure 5). In each event, groundwater-dominated streamflow was replaced by a pulse of meltwater entering the stream during the peak of the hydrograph, followed within several hours by a pulse from soil water which made up 60-75 % of streamflow (Figure 5b,e,h). Stream DOC concentration rose coincidently with soil water contribution to streamflow, though we note that the stream sensor was buried during peak discharge of the March thermal event and data after that point were lost (Figure 5f). Stream nitrate concentration fell during the hydrograph peak and rose again, particularly during the February ROS event (Figure 5c).

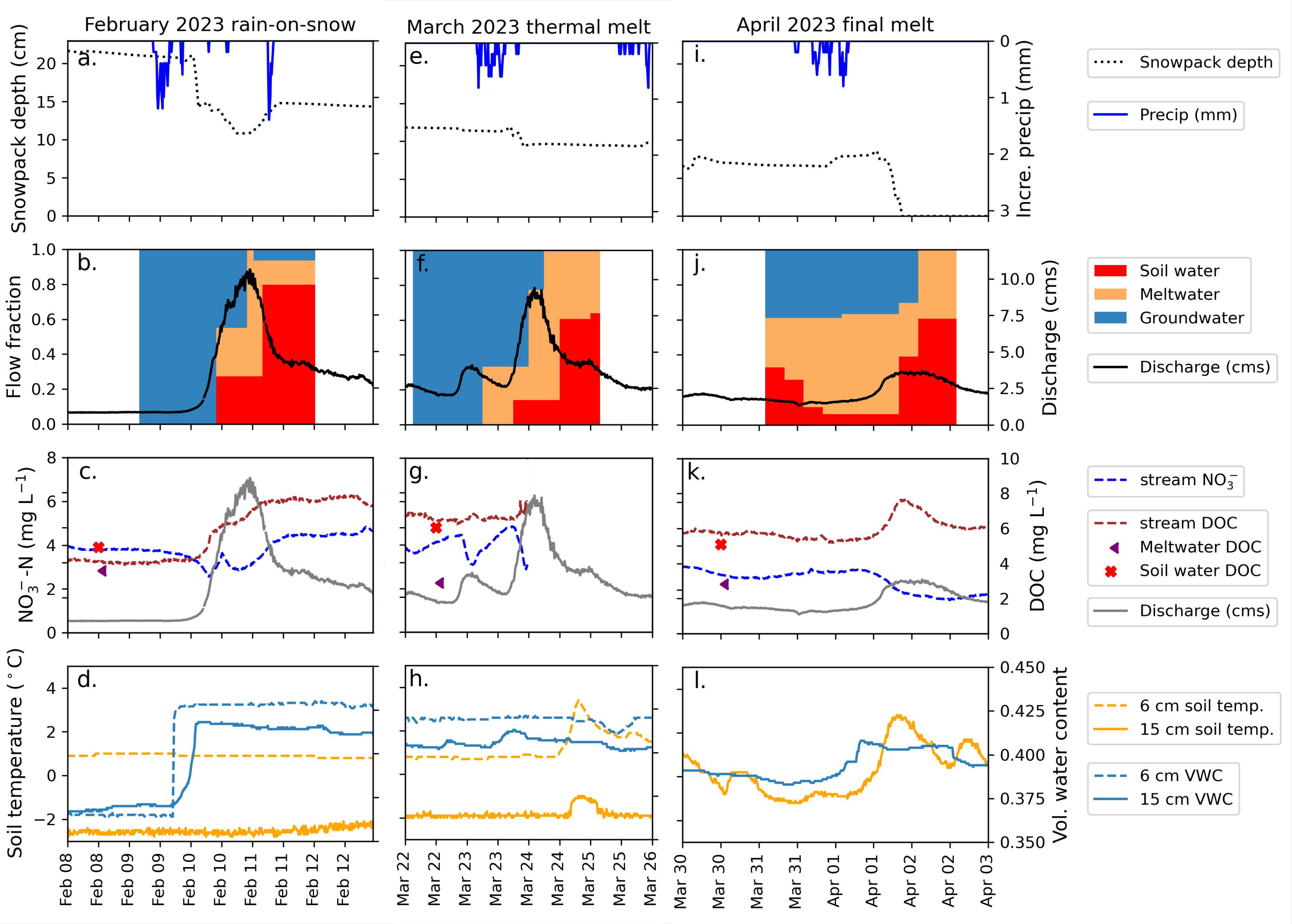


Figure 5. Hungerford Brook hydrograph separation (HB) with end-member mixing analysis for a February ROS event (a-c); a mid-March thermal melt (d-f); and during the April final snowmelt (g-i) in 2023. Upper panels show the incremental precipitation and approximate snowpack depth. Middle panels indicate fraction of ﬂow through ﬂowpaths during the events superimposed on the hydrograph. Lower panels indicate stream sensor nitrate and DOC and grab sampled nitrate and DOC for soil water and meltwater end-members with the hydrograph in grey. Bottom panels show 6-cm and 15-cm soil temperature and moisture readings. Stream sensor nitrate and DOC data are missing for the March thermal melt discharge peak.

At WB, each observed event’s combination and timing of sources (i.e., EMMA separation) was distinct (Figure 6). During the February ROS, when snowpack declined dramatically (Figure 6a), meltwater was the primary contributor to streamflow (60-66%). Beginning at about 12 hours before the hydrograph peak until the snowpack was nearly entirely depleted, meltwater replaced groundwater as the dominant contributor (Figure 6b). During this first monitored event we observed little shift in 6-cm depth soil moisture and temperature (Figure 6d).

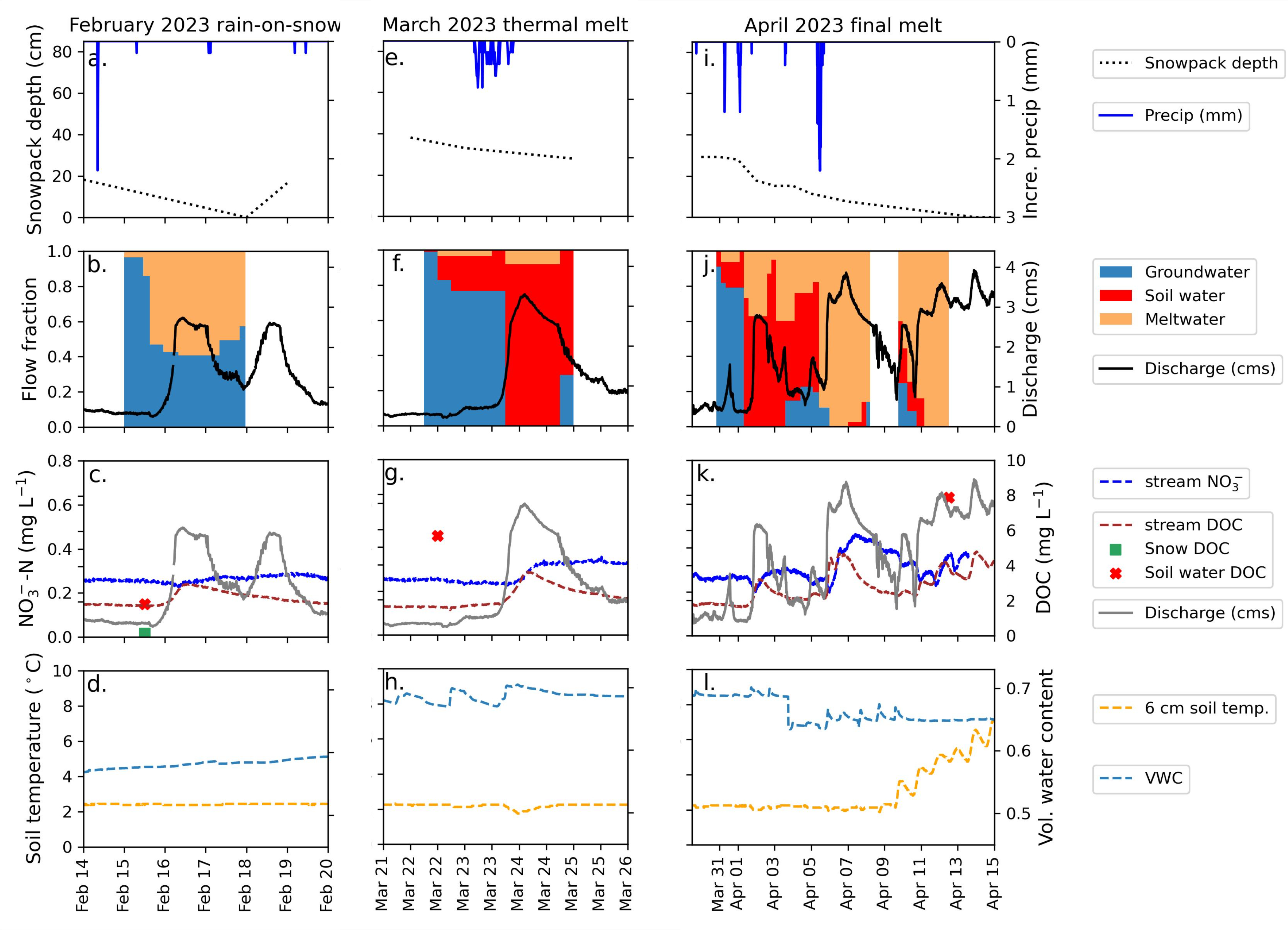


Figure 6. Wade Brook hydrograph separation (WB) with end-member mixing analysis for a February ROS event (a-c); a mid-March thermal melt (d-f); and during the April final snowmelt (g-i) in 2023. Upper panels show the incremental precipitation and approximate snowpack depth. Middle panels indicate fraction of ﬂow through ﬂowpaths during the events superimposed on the hydrograph.  Lower panels indicate stream sensor nitrate and DOC and grab sampled nitrate and DOC for soil water and meltwater end-members with the hydrograph in grey. Bottom panels show 6-cm soil temperature and moisture readings for three sensors at Ranch Brook in Stowe, Vermont, US. Snowpack depth data are missing for the beginning and end of the March thermal melt event.

Such stability in soil temperature and moisture was not the case in events later in the season at WB, however: during a March thermal event, where the snowpack received some rain but fell below our threshold for ROS events, soil volumetric water content increased from ~57 to 64% over the 12 hours concurrent with the stream reaching peak discharge (Figure 6h). At the same time, EMMA results show that soil water contribution to streamflow increases from <10% at the beginning of monitoring to almost 90% during the hydrograph peak (Figure 6f), along with concurrent increases of stream sensor DOC and nitrate (Figure 6g).

During the final spring melt at WB the snowpack receded entirely from the stream corridor even though snow likely remained at high catchment elevations (Figure 6i). At the onset of the final spring melt, we observed the highest 6-cm depth soil VWC values for our sampled events, ~70% (Figure 6l). The high soil VWC period coincides with high soil water contribution to streamflow, ~50-80% (Figure 6j). Subsequently, high rainfall drove rapid snowpack loss that coincided with up to 100% meltwater contribution to streamflow (Figure 6j). Over the final spring melt, stream nitrate and DOC concentrations, like EMMA contributions, were more dynamic than the February ROS or March thermal melt events. At the onset of the final spring melt with rain and snowpack depth decline, an initial hydrograph peak was composed primarily of soil water (83%) and both stream DOC and nitrate concentration rose with discharge, though nitrate showed more of a lag (Figure 6k). In the subsequent hydrograph peak of the final spring melt, several days later and after heavier rainfall with continued snowpack depth decline, both stream DOC and nitrate reached their highest concentrations observed during the winter-to-spring study period. During this hydrograph peak, meltwater dominated streamflow, briefly reaching 100% contribution. As with the soil water dominated hydrograph peak, the peak nitrate concentration showed a greater temporal lag compared to DOC concentration.

4 Discussion

Winter runoff events are becoming more common in seasonally snow-covered watersheds of the northeastern USA and it is unlikely that the sources, flowpath types and magnitudes for these events will be similar to those for growing season events, when soils are warmer and have active plant uptake, snow and soil frost are absent, and soil moisture may be lower (Seybold et al. 2022). Yet, the difficulties inherent with stream and end-member monitoring and sampling under winter conditions mean that there is relatively less known about how individual winter runoff events influence water and nutrient flowpaths than during spring, summer, and autumn. Our data show that 1) Soil nutrient availability is highly dynamic during winter but always comparable to the growing season, suggesting ample potential for winter nutrient transport from soils irrespective of forest cover or agricultural use; 2) Catchment soil-stream connectivity can be significant during winter, meaning that shallow soils can be both a substantial source of water and nutrients during winter runoff events; 3) Source contributions to streams during winter runoff events vary with antecedent and event conditions; and 4) Winter DOC and nitrate yields during winter can be high during winter events when flowpaths from soil and meltwater sources exist, and event dynamics and yields vary by catchment landcover and also between events. Taken together, our findings demonstrate that developing one conceptual model to predict winter thaw effects on nutrient source areas and receiving waters is difficult. A new paradigm is needed as a consequence of the increasing frequency of winter thaws that results in stream runoff events.

Soils at both the agricultural and forested sites had nutrients available for transport during mid-winter, often on par with those available during the spring runoff period and the growing season (Figure 3). Neither lab incubations or previous studies predict soil nutrient availability for our subcatchments or soil types, but our results point to winter nitrate sources at both subcatchments which is either soil and/or snowpack derived and is not exhausted over the course of seasonal progression, similar to the results of earlier winter runoff event nitrate export work (Winter et al. 2022). Snowpack can be both a source of nutrients (Casson et al. 2012; 2014) and also insulates soils so that they remain above freezing (Groffman et al. 2001), allowing microbial processes to continue during the winter and for carbon and nutrients to accumulate in riparian and hillslope soils (Groffman et al. 2001; 2006; Schimel et al. 2004; Brooks et al. 2011). Our observations of soil available ammonium, nitrate and phosphate do not indicate winter accumulation at WB, where snowpack was consistent and soil temperature at 6-cm depth was consistently above freezing. This could be due to the hydrologic connectivity evidenced by EMMA, particularly during the March thermal melt event (Figure 6). At HB, where snowpack was less consistent during the winter of 2023 and soil temperatures were below freezing, we also did not see a clear indication of soil available nutrient accumulation over the winter season, though soil available nitrate was as high in January-March as it was after manure spreading in October (Figure 3). In all, the mobilization potential of soil nutrients in winter at WB and HB points to winter being an important period for annual nutrient budgets, meriting further quantification, as has been examined for the spring, summer, and fall in these subcatchments (Vaughan et al. 2017; Kincaid et al. 2020).

Concurrently with measurements of available soil nutrients in winter, event-level EMMAs revealed that our two catchments have strong soil-stream connectivity during mid-winter runoff events and that high soil water contributions align with increases in stream DOC and nitrate (Figures 5,6). Our results show a consistent signal of soil water contribution during all winter runoff events at HB, even though soils were consistently subfreezing (January through early April at 6-cm). Depending on initial soil water content and soil texture, subfreezing soil temperatures can result in soil frost or freezing, the extent of which has been shown in snow-influenced regions to be a key predictor of spring streamflow magnitude in headwater catchments (Jones et al. 2023; Bayard et al. 2005). In some cases, frozen soils increase surface runoff, but this can vary with the type of soil frost, for example granular vs. concrete freezing (Shanley and Chalmers 1999; Shanley et al. 2002). Limited wintertime research in the northeastern USA suggests that while granular frost can allow infiltration, widespread concrete frost prevents infiltration and increases runoff (Shanley et al. 2002; Fuss et al. 2016; Pellerin et al. 2012). Further, soil freezing and concrete frost are more likely to form in open or agricultural areas, especially if soil moisture is high, soil texture is fine, or soils are tilled (Shanley and Chalmers 1999; Kane and Stein 1983). Although we did not explicitly measure soil frost depth or type and we lack information about the percentage of the catchment with snow cover or snowpack morphology (e.g., the presence of impeding layers like basal ice), any soil frost that was present in HB failed to impede routing through shallow soils. Although there were periods of bare ground at HB between initial snowpack development and the final snowmelt during the final spring melt in the winter of 2023 (Figure 3b), the events we evaluated with EMMA were consistent in that they all had snowpack depths at the onset of the thaw that did not fully deplete over the course of the sampled event until the tail end of the final spring melt. Our event-level EMMAs indicate that there was soil-stream connectivity during runoff events in HB, suggesting that, if soil frost was present in HB’s consistently subfreezing soils (Jan-early April), it may have been granular (Fuss et al. 2016) or else concrete but discontinuous (Shanley and Chalmers, 1999), allowing for infiltration. However, it is possible that continuous concrete ground frost may develop in this agricultural drainage when there is no antecedent snowpack and bare ground prior to winter rainfall, or perhaps with certain antecedent conditions such as a wet fall season preceding subfreezing temperatures. Further research that includes a wider range of winter runoff events and antecedent conditions will reveal how soil conditions affect both nutrient accumulation patterns and water and nutrient flowpath dynamics.

At WB, where soil frost formation during the observed winter was unlikely due to relatively consistent snowpack and sustained above-freezing soil temperatures, there was a lack of apparent soil-stream connectivity during the February ROS event as evidenced by static soil VWC and no contribution from soil water in the EMMA (Figure 6). In contrast, during the March thermal event, soil VWC was more responsive and dynamic, and soil water contribution to streamflow was high as indicated by EMMA, perhaps reflecting differences between the events in snowpack melt rate and/or infiltration into soil. Our three event-level EMMAs at WB along with soil sensor and stream sensor monitoring indicate increasing connectivity between snow, soils and the stream over the course of winter as moisture increases beneath a relatively deep and sustained snowpack. At HB, in contrast, with thinner and less consistent snowpack, soil-stream connectivity was relatively consistent across the three event-level EMMAs. Snowpack storage and structure may also control some of the observed differences between soil-stream connectivity in the two subcatchments and, at WB, across events (Webb et al. 2019; Würzer et al. 2017; Eiriksson et al. 2013). Overall, the disparate seasonal progressions in streamflow source dynamics in our two systems point to winter being a hydrologically complex and varied period for which we recommend further sensor and tracer-based investigations to distinguish mechanistic controls related to meteorological, snowpack, and soil dynamics preceding and during winter runoff events, particularly in systems where high vulnerability to winter nutrient runoff has been shown to be likely (Seybold et al. 2022).

We found that spring snowmelt events were not, as a rule, the most important in terms of nutrient yield, especially for nitrate yield at HB, where the highest event yields of the study period occurred during February and March (Table 2). This finding is in line with the results of long-term event classification across six mesoscale sub-catchments of varying land use in Germany, which identified that along with high-rainfall events during the growing season, snowmelt-induced events with high antecedent wetness exported the greatest nitrate concentrations and loads across all catchments, without exhibiting source limitation (Winter et al. 2022). Similarly, a meta-analysis of ROS events in Ontario and the northeastern USA revealed that ROS events at all but a northernmost site contributed a significant proportion of annual and winter nitrate export (average of 12 and 42%, respectively) (Crossman et al. 2016).

To establish frameworks for understanding the controls on water and nutrient flowpaths during winter melt events in HB and WB, we present a conceptual model of winter catchment dynamics (Figure 7) based on the soil nutrient availability, event-level EMMA, and stream and soil sensor results of this work. In our model, 1) Ample labile nutrients in the soil are primed for transport; 2) Soils can become connected to the stream during winter and thus facilitate nutrient transport and loading, but landcover and snowpack exert some control on this by modulating water/nitrate infiltration and storage; and 3) Winter events can be particularly efficient at exporting nitrate irrespective of land use due to connectivity to both snow and soil nitrate sources and lack of vegetative uptake.

Critical to interrogating this conceptual model are stream, soil, and snowpack datasets that allow for the comparison of individual winter runoff events. Our study highlights variability of end-member chemistry throughout the winter-to-spring period and demonstrates a justification for frequent source sampling for winter event-level EMMAs that can allow for a comprehensive analysis of end-member variability and its influence on calculated source contributions (Inamdar et al. 2013). Further research beyond the scope of the soil condition monitoring of this work, including soil frost depth determinations, would allow us to better understand and predict soil infiltration in winter for integration into this model (Fuss et al. 2016). Additionally, determining the snowpack source of nitrate through experiments or natural isotopic tracers (Sebestyen et al. 2008; Rollinson et al. 2021; Novak et al. 2025) could advance a source-to-stream understanding of the consequences of winter runoff events across catchments.

6 Conclusions

This work produced high-resolution water chemistry datasets during mid-winter and spring melt events at two catchments in northern Vermont to compare end-member contributions (soil water, meltwater, groundwater, precipitation) to streamflow. Overall, our findings suggest an underrecognized complexity of soil-stream connectivity during winters in this climate and landscape. We establish that winter soil nutrient pools are comparable in magnitude to those of the spring and are relatively consistent across land use, elevation, snow cover, and soil temperature, demonstrating that ample potentially labile nutrient pools exist in the soils under snowpack. Importantly, we show that during select winter runoff events, these robust potentially labile soil pools are highly connected to streams and not ‘static’ as assumed in the classic, hydrological dormant winter paradigm (Seybold et al., 2022). Yet interesting site-specific differences also emerged, with connectivity to soils being consistent across events in the agricultural lowland watershed with more transient snowpack, whereas soils became more connected to the stream over the course of winter as soil moisture increases under consistent snowpack with warmer soil temperatures in the mountains. This finding suggests that a more nuanced conceptual model that incorporates how variable land use and snowpack conditions impact nutrient transport during winter thaws is needed, and our findings provide a novel window into these drivers that could be expanded upon with future studies.

Mechanistic understandings of flowpath variation and contributions during mid-winter melt events have been elusive. However, sub-daily knowledge of water and nutrient flowpaths is particularly important as warmer, wetter winters are projected for the future. We used three powerful tools: high frequency stream sensors, monthly soil nutrient measurements, and event-level EMMAs that is, our selected end-members were sampled frequently throughout the winter-to-spring sampling period close in time to each event, rather than averaged across the season. Allowing the end-member composition to evolve through the winter-to-spring period allowed us to best account for seasonal hydrogeochemical progression of streamflow sources and ultimately to gain insight into how different runoff event types, catchments, and conditions correspond with different flowpath and nutrient yield outcomes. As we gain more knowledge of winter processes, colder and snowier historical conditions can be contrasted with warmer, wetter winters like that of 2022-2023. These findings are important for the assessment of downstream effects of stream nutrient and organic matter export into the future, and the monitoring of water quality responses to land and water management and climate resilience in a changing Northeast.

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**Conflicts of Interest**

The authors declare no competing interests.

**Open Research**

The raw data and R and Python code that support the findings and figures of this study are openly available at the following Github repository: https://github.com/MeganEDuffy/LCBP-EMMAs.

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