Unprocessed Atmospheric Nitrate in Waters of the Northern Forest Region in the U.S. and Canada

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S *Supporting Information*

ABSTRACT: Little is known about the regional extent and variability of nitrate from atmospheric deposition that is transported to streams without biological processing in forests. We measured water chemistry and isotopic tracers (δ^{18}O and δ^{15}N) of nitrate sources across the Northern Forest Region of the U.S. and Canada and reanalyzed data from other studies to determine when, where, and how unprocessed atmospheric nitrate was transported in catchments. These inputs were more widespread and numerous than commonly recognized, but with high spatial and temporal variability. Only 6 of 32 streams had high fractions (>20%) of unprocessed atmospheric nitrate during baseflow. Seventeen had high fractions during stormflow or snowmelt, which corresponded to large fractions in near-surface soil waters or groundwaters, but not deep groundwater. The remaining 10 streams occasionally had some (<20%) unprocessed atmospheric nitrate during stormflow or baseflow. Large, sporadic events may continue to be cryptic due to atmospheric deposition variation among storms and a near complete lack of monitoring for these events. A general lack of observance may bias perceptions of occurrence; sustained monitoring of chronic nitrogen pollution effects on forests with nitrate source apportionments may offer insights needed to advance the science as well as assess regulatory and management schemes.
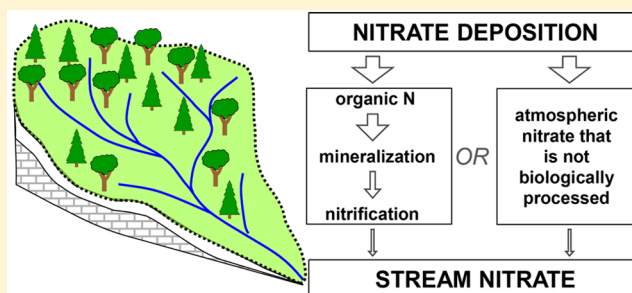
INTRODUCTION

There is a need to adopt a more comprehensive view of how atmospheric nitrogen pollution affects freshwaters in light of complex ecosystem processes that control how nitrogen is cycled and transported in forests. While temperate forests are typically nitrogen limited[1] and input−output budgets show high net annual retention of nitrogen deposited to forests,[2−6] some nitrate from atmospheric deposition is rapidly transported to streams without being retained or biologically transformed.[7−21] That evidence has emerged over nearly two decades, yet perceptions of how, when, and where nitrate from atmospheric deposition moves through catchments have not necessarily advanced. Importantly, empirical evidence of direct effects of atmospheric nitrate pollution on freshwater is not always acknowledged and ecosystem/biogeochemical models do not represent processes that drive the timing and places where rapid nitrate transport to streams bypasses processing in forests.

In temperate, low- to midelevation forests, most nitrate from atmospheric deposition infiltrates forest soils and passes through the organic nitrogen pool before some nitrate is eventually rereleased via mineralization and nitrification.[3,21−24] Biological processing, including denitrification, limits nitrate leaching from most nitrogen-polluted forests.[3,4,23,25,26] Chronic nitrogen deposition has multiple effects on forest productivity, soil nutrient status, and water chemistry.[2,4,27−31] Effects of chronic nitrogen deposition include tree mortality and enrichment of groundwater with nitrate in severely polluted (and nitrogen saturated) forests, increased ratios of inorganic to organic nitrogen in soil and stream waters of moderately polluted forests, and transport of inorganic nitrogen to higher order reaches downstream of headwater forests.[4,27,32,33] These conditions have often been used to assess nitrogen-saturation status of forests[2,4,21,27,30] (where stage 0 = no signs of saturation, stage 1 = initial effects, stage 2 = saturated, and stage 3 = saturated, with chronic nitrate leaching as a forest declines[2,34]). Consequently, knowing when, where, and how atmospheric nitrate moves is important for maintaining healthy forests and clean water as well as assessing the success of legislative and management policies intended to reduce nitrogen pollution impacts to water resources and forests.

Nitrate isotopes, particularly the natural abundance of oxygen-18 (^{18}O) relative to oxygen-16 in nitrate (δ^{18}O-nitrate), have been critical in the apportionment and detection of unprocessed nitrate from atmospheric deposition that has been transported to receiving waters.[16,35] The mass independent fractionation of delta oxygen-17 (δ^{17}O) relative to mass dependent fractionation of δ^{18}O (Δ^{17}O-nitrate) is increasingly used as a nitrate source tracer in catchment studies and provides insight on both transport and processing of atmospheric nitrate.[16,36] Nonetheless, more data for more sites are available for δ^{18}O-nitrate, and when used in conjunction with the relative abundance of nitrogen-15 (δ^{15}N), these isotopes provide insight on nitrate processing and transport. In the context of source tracing, δ^{15}N is useful in diagnosing effects of biogeochemical processing on nitrate concentration, δ^{18}O, and δ^{15}N.[35] Regardless of the particular tracer and compelling results from past studies, atmospheric nitrate is generally perceived to be efficiently processed in forests without much nitrate from atmospheric deposition reaching streams. We contend that this perception reflects a lack of recognition and observance of large proportions (>20%) of unprocessed atmospheric nitrate in waters, not a lack of occurrence.

The presence of large proportions of unprocessed atmospheric nitrate in streams may be perceived to be uncommon or go undetected for various reasons. (1) Despite technical advancements,[37−40] few laboratories analyze nitrate isotopes, costs remain fairly high per sample, and methods are labor intensive with low analytical throughput.[37] (2) Most studies focus on biological processing, not on transport through forests. Plus, most studies lack enough information to discern among the surface, shallow subsurface, or deep subsurface pathways along which water and nitrate are transported to streams. (3) Relatively few studies have samples from stormflow or snowmelt events, when high nitrate concentrations and the largest amounts of unprocessed atmospheric nitrate oftentimes occur.[7,9,16,18,19,22] Sampling during events has been critical to detecting unprocessed atmospheric nitrate in waters despite the difficulties of sampling short-duration events with sufficient resolution to capture rapid changes in flow, solute concentrations, and isotopic values.[7,19,41] (4) Additionally, some past source apportionments were premised on ^{18}O from water and air being incorporated at a fixed ratio into nitrate during nitrification.[35] That approach is now recognized to be inconsistent with process understanding[42−44] and the assumption sometimes provides an unrealistic δ^{18}O value for an end-

member that is needed for nitrate source apportionment.[13,16,18,45]

Overall, while nitrate source studies have informed the science, there has been relatively little information to document how common or widespread direct effects of nitrate pollution on forest streams have been, or enough information to extrapolate from particular sites to a broader knowledge of regional forests. What is known from individual nitrate isotope studies provides some expectations of how, when, and where nitrate from atmospheric deposition moves through forests. For example, many studies have identified individual stormflow or snowmelt events with high fractions of unprocessed atmospheric nitrate in stream waters.[7,9,16,18,19,22] There is evidence that most unprocessed atmospheric nitrate in streams originates from near-stream areas.[7,9,16,19] High proportions of unprocessed atmospheric nitrate in near-surface soil waters decrease with depth in soil or till, which has been attributed to biological processing along vertical, unsaturated flowpaths above groundwater tables or bypass of deeper flowpaths via near-surface lateral downslope movement to streams when saturated during stormflow or snowmelt events.[7,16,18,19,46,47] Nonetheless, there is relatively little information on soil waters or groundwaters to support assertions about how nitrate sourcing in those waters affects movement through the subsurface to surface waters. Despite one example of unprocessed atmospheric nitrate in spring waters (considered as a proxy of catchment groundwaters) of nitrogen saturated forests,[32] there is little evidence of widespread groundwater enrichment with nitrate, which is considered to be a bellwether of severely nitrogen-polluted forests.[2] Otherwise, relatively few forests have deep groundwater enriched in nitrate,[48,49] and extremely few samples of groundwater in forests have been analyzed for nitrate isotopes,[32,50] especially for nitrate source apportionment.

Data from disparate studies have not previously been compiled to assess emergent patterns for a broad geographic region. We collected samples and compiled existing data to document where large fractions (>20%, up to 100%) of unprocessed atmospheric nitrate occurred within a region that spanned the range (up to 30 kg total nitrogen ha^{-1} y^{-1}) of chronic nitrogen deposition over the northern and eastern U.S. and southern Canada.[4,51,52] Our main goal was to determine the magnitudes and geographic variation of inputs of unprocessed atmospheric nitrate to stream waters, soil waters, and groundwaters across this regional forest through a meta-analysis of nitrate δ^{18}O and δ^{15}N data. We hypothesized that the proportion of nitrate that is unprocessed nitrate from atmospheric sources would sometimes be larger in soil waters in response to rainfall or snowmelt events than in stream waters. The presence of large fractions of unprocessed nitrate from atmospheric sources in subsurface waters would reflect a potential for transport to a stream. In contrast, the absence or the lack of plausible pathways of transport would indicate that any unprocessed atmospheric nitrate in surface waters would have solely come from direct atmospheric inputs or adjacent saturated surfaces. High proportions of unprocessed atmospheric nitrate in soil waters may also be a source of elevated proportions of unprocessed atmospheric nitrate in groundwater, if that occurs. Rapid transport from near-stream areas during particular stormflow or snowmelt events may drive inputs of unprocessed atmospheric nitrate to streams. For that reason, we explored the relative importance of baseflow, stormflow, and snowmelt as well as near-stream vs hillslope areas. In those landscape areas, we considered the vertical distribution of nitrate isotopes, nitrate

sources in the subsurface, and inundation frequencies to assess how flowpath routing and catchment wetness affect nitrate cycling and transport. To frame those results, we considered other environmental factors. For example, sites encompassed variability in mean annual air temperature (MAT from 1 to 11 °C), precipitation amount (MAP from 680 to 1330 mm), elevation (30 to 1000 m asl), forest type (coniferous, deciduous, or mixed), geology, lithology, and the nitrate depositional gradient (~0.5 to 8 kg nitrate ha^{-1} y^{-1} in wet deposition[53]).

■ MATERIALS AND METHODS

We collected surface and subsurface water samples from existing catchment study sites, as well as compiled data from published studies to document spatial variation in forests that span Minnesota, New Hampshire, New York, Connecticut, Massachusetts, Vermont, and Maine (sites are listed in Supporting Information (SI) Table S1 and mapped in SI Figure S1). We adopt the broad term of Northern Forest Region corresponding to an ecoclimatic zone,[54] administrative units (e.g., USDA Forest Service, U.S. Environmental Protection Agency, and USDA Climate Hubs), and a region that has been highly scrutinized in past assessments of nitrogen pollutant effects on forests and streams.[53,55−57] We include sites in Ontario, Pennsylvania, West Virginia, and Maryland to give a broader perspective on regional nitrogen pollution effects. All included catchments are predominantly, though not exclusively, forest. None of the catchments has high-density residential, expansive industry, or large confined animal feedlots as land cover or land use, each of which affects the efficacy of nitrate source tracers.[35] The forest types include deciduous, coniferous, and mixed overstory types (SI Table S1). Elevations where samples were collected range from just about sea level to about 1000 m, but none of our study sites are primarily alpine or subalpine catchments where exposed bedrock, permafrost, glaciers, or shallow soils may have pronounced effects on water and nitrate transport though catchments.[58−62]

In the field sampling component of our study, we collected waters for measurement of concentration and natural-abundance isotopic composition of nitrate in variably saturated soil waters ($n = 13$ samplers) and perennial stream waters ($n = 15$ stream catchments) for snowmelt and rainfall-runoff events from 2010 to 2011. Shallow soil waters were collected at some ($n = 4$), but not all catchments, from samplers that were 5−15 cm deep (SI Table S2). We opportunistically sampled existing monitoring infrastructure, with soil waters collected from tension or zero-tension samplers, and having various depths that were established for other studies at individual sites. More streamwater than soil water samples were collected because soil waters were only sometimes available and could only be collected after sufficient accumulation in samplers. We considered soil waters to be broadly representative of source areas in riparian areas and on hillslopes that may hydrologically connect to streams via lateral subsurface flowpaths when soil/till profiles wet up with rainfall during events or snowmelt.[63] We sometimes sampled deeper soil or till waters (30−110 cm depths) to assess the fate of atmospheric nitrate that vertically infiltrated the profile, along the flowpath of recharge to deeper soils/tills and groundwater. At some sites we collected precipitation (SI Table S3). We measured nitrate concentrations using automated colorimetric analysis after cadmium-column reduction[64] and prepared samples for nitrate isotope (δ^{18}O and δ^{15}N) analysis using the bacterial denitrifier method.[39,40,65] with more details in SI S1.

We compiled $\delta^{18}O$ and $\delta^{15}N$ values from other studies, whether published or previously unpublished. The compiled data include samples of precipitation, throughfall, snow cores, snowmelt, seeps, streams, soil/till waters, and groundwaters. Some of the compiled data originated from different studies at our sampled sites, some streams clustered in nearly adjacent catchments, and some streams were sampled at multiple sub-basins within a larger encompassing catchment. The number of sites and samples by water type are listed in SI Table S4, with sample collection spanning two decades (1995–2016). The timespan of the compiled data set corresponds to a general decline in atmospheric deposition from recorded highs during the 1980s.[4,53] In total, our data set included 1829 values for $\delta^{18}O$ and 1642 values for $\delta^{15}N$ of nitrate. At a minimum, one value, and, at most, 244 values were available for any particular stream. Most were stream samples, with fewer samples of other water types. For the limited catchments ($n = 10$) with data, we include groundwaters (SI Table S5). We distinguish among source areas in riparian areas (0.3–1.8 m depths) and on hillslopes (0.03–4 m depths) from which nitrate may have been transported. Soil water sampling depths were known and depths to the groundwater table were sometimes measured in wells where groundwaters were sampled.[15,66,67] We plotted soil water and groundwater (whenever possible) concentration and isotopic values by depth.

We included values from the most used, contemporary methods (bacterial denitrifier[39,40] and column[11,37,68,69]) for preparation and analysis of nitrate isotopes. We also include unpublished data for ten samples that were prepared using the chemical denitrifier method.[70] The column method was largely used from the 1990s to the mid-2000s. The bacterial denitrifier method,[39,40] which emerged during the early 2000s, has largely supplanted the column method since then. The chemical denitrifier method emerged during the mid-2000s and is less used. Due to several possible biases of the column method[37,38,40,71] (SI S2 and S3), $\delta^{18}O$ values from the column method are not directly comparable to values from the denitrifier methods. Therefore, we consider $\delta^{18}O$, $\delta^{15}N$, and associated concentrations of nitrate that were measured with the column method separately from the denitrifier methods.

As much as possible we apportioned amounts of nitrate that were unprocessed from atmospheric deposition (% unprocessed atmospheric nitrate) using a two-component, $\delta^{18}O$ mixing model approach. We summarize our approach here, with more detail on the approach and assumptions in SI S3 and an associated data publication.[72] The mixing model requires $\delta^{18}O$ of nitrate values for both atmospheric[35] (about +60‰ to +100‰) and nitrification[35] (about −10‰ to +10‰) end-members as well as water in which nitrate from those two end members mixed[8,32,35] (soil water, groundwater, or streamwater; about −10‰ to +90‰). Sources of nitrate can be interpreted and apportioned for the column method because that method results in a compressed range of values as compared to the denitrifier methods, but relative separation among the mixed and end-member values is preserved.

The selection of $\delta^{18}O$-nitrate values for the nitrification end-member is an important consideration.[19,37,71] Studies have shown that a common way to estimate $\delta^{18}O$-nitrate values for nitrification, which was premised on water and atmospheric oxygen (O_2) being ^{18}O sources for nitrate and the supposed constant relationship between those two sources, is too simplistic.[42–44,73–76] Consequently, the estimate of $\delta^{18}O$-nitrate of a nitrification source may be improved by using our approach:

assigning the nitrification end-member to a measured $\delta^{18}O$-nitrate value of soil water, groundwater, or pre-event stream-water, and at a time close to the mixed sample that is being apportioned. In total, we apportioned % unprocessed atmospheric nitrate for 1237 water samples. Of those apportionments, 886 were for 103 different streams; the others were for seeps or subsurface waters. Both end-members for each sample and an apportioned value are provided in the data publication.[72]

The lack of spatial replication and our estimation of atmospheric $\delta^{18}O$-nitrate for some times and places introduce uncertainty to source apportionments. Therefore, apportionments that are less than 10% unprocessed atmospheric nitrate are unlikely to be distinguishable within methodological uncertainty, as elaborated upon in SI S3. Nonetheless, these small values are less important to addressing our goals than knowing if large (>20%) values occur.

Streamflow data were available for some sites (SI Table S1), whether monitored and reported at fixed intervals (5 min to daily), or as instantaneous observations at the time of sampling. In addition to the relative metric (% unprocessed atmospheric nitrate), we also calculated areal yields of unprocessed atmospheric nitrate in units of mg nitrogen m^{-2} d^{-1} by multiplying concentration times % unprocessed atmospheric nitrate times streamflow. When fixed interval streamflow data were available from monitored sites, we apportioned a quick flow fraction[77] using a hydrograph separation[78] (SI S4). We consider apportioned streamflow values to be an index of runoff that occurred in response to rainfall or snowmelt, with a quick flow value of 0 cm d^{-1} equaling a period of baseflow and quick flow >0 cm d^{-1} equaling a period of stormflow or snowmelt runoff. We differentiate values (concentrations, $\delta^{18}O$-nitrate, $\delta^{15}N$-nitrate, and % unprocessed atmospheric nitrate) between stormflow or snowmelt events and baseflow when possible. For stream samples that were apportioned for both unprocessed atmospheric nitrate and streamflow, we have 607 apportioned values from 32 catchments. We show undifferentiated values ($n = 269$) for stream waters when we have no estimate of apportioned streamflow.

Depth to groundwater has been monitored at a site[66] (Sleepers River Watershed) where water level measurements have been made at three different elevations along a hillslope transect since 1993, and for a shorter duration (between August 2002 and October 2004) in the stream riparian zone.[66] We use these data to plot depth exceedance curves that we broadly and heuristically interpret to establish: (1) the saturation frequency of different soil depths by hillslope position (riparian, toeslope, midslope, and upslope), and (2) plausible links between soil water chemistry and solute transport to streams.

■ RESULTS AND DISCUSSION

Of the 1237 nitrate-source apportioned samples from 103 stream catchments across the Northern Forest Region, unprocessed atmospheric nitrate ranged from 0% to 96% of nitrate in streamwater ($n = 876$), 0% to 9% of nitrate in seep water ($n = 7$), 0% to 100% of nitrate in soil water ($n = 206$), 0% to 64% of nitrate in shallow (<1 m deep) groundwater ($n = 49$), and 0% to 11% of nitrate in deep (>1 m deep) groundwater ($n = 12$; Figure 1). While 469 of the samples from 57 of the catchments had 0%, 182 of the samples from 42 of the catchments had >20% unprocessed atmospheric nitrate. The large number of catchments with >20% unprocessed atmospheric nitrate is a strong indication that many waters in the
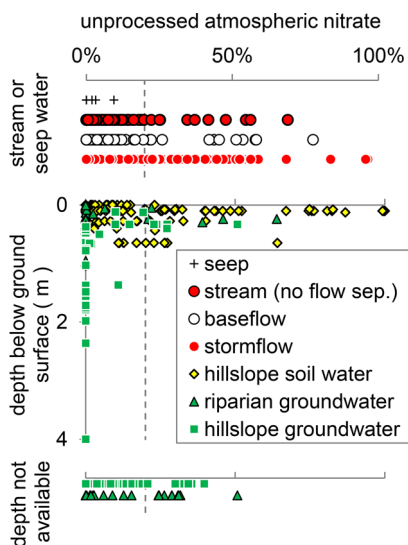
Figure 1. Fractions of unprocessed atmospheric nitrate for all apportioned samples and catchments, shown by water type. Circular symbols for streamwater show: stormflow or snowmelt (red dot), baseflow (O), or undifferentiated stormflow/baseflow (red dot with black border). Soil waters are shown by sampling depth and groundwater values are shown by water table depth below the surface at the time of sampling when known, or as "depth not available". Two streams in Minnesota, one in Ontario, two in West Virginia, and one in New York account for all values ($n = 11$) > 20% unprocessed atmospheric nitrate during baseflow. All other values ($n = 109$) during baseflow were ≤20%. Vertical hashed lines denote 20% unprocessed atmospheric nitrate.

Northern Forest Region at many times have substantial fractions of unprocessed atmospheric nitrate.

Most large fractions only occurred during stormflow or snowmelt runoff. When both % unprocessed atmospheric nitrate and streamflow were apportioned, 61 of the 72 fractions that were >20% unprocessed atmospheric nitrate occurred during stormflow or snowmelt, and that happened at 17 of 32 streams (Figure 2). Furthermore, fractions >30% during stormflow or snowmelt were observed 34 times at 10 streams; fractions >40% were observed 24 times at eight streams; and fractions >50% were observed 12 times at five streams. Observation of larger fractions at fewer sites may reflect limitations of the assembled data and studies. Large fractions may be elusive because most studies lack samples and isotopic values when the highest proportions occur, typically on the rising limb of stormflow or snowmelt events[7,17,19] (SI Figure S2). In general, waters are rarely sampled with enough resolution during events to document changing nitrate concentrations and sources.[7,16,19] Additionally, we only had monitored streamflow data from 32 of

122 streams, which was needed for stormflow/snowmelt and baseflow apportionment.

Knowing the amounts of unprocessed atmospheric nitrate in streams is important to understanding how nitrogen pollution affects temperate forests and highlights a need to reframe a common perspective that atmospheric nitrate is efficiently processed in catchments. Oftentimes, annual input−output budgets and multiyear isotopic mass balances show that 80% or more of the nitrate that is deposited from the atmosphere is not exported in stream waters of forested catchments.[4−6] Likewise, many nitrate isotope studies show processing of atmospheric nitrate over hours to weeks.[7,16,22,26,79,80] Nonetheless, occasional large proportions (>20%) of unprocessed atmospheric nitrate in surface and shallow subsurface waters show that (1) atmospheric nitrate is transported through many forests with little to no time for biological processing, and (2) nitrate from atmospheric deposition has direct effects on surface waters throughout and surrounding the Northern Forest Region.

Interactions among sources, transformations, and transport processes explain why % unprocessed atmospheric nitrate values vary with flow conditions and over time (Figure 3). We acknowledge that factors such as geology, lithology, geomorphology, climate, vegetation, intrastorm variation of nitrate deposition, and how much atmospheric deposition is wet or dry[2,4,16,57,81−84] have superimposed effects on a framework of interacting sources and transport processes as drivers of nitrate movement from the atmosphere to surface waters. These factors certainly contribute to variation among nearly adjacent catchments, as well as variation across the entire region. We further explore the concept of sourcing and transport effects on % unprocessed atmospheric nitrate in waters after broadly discussing general and geographic patterns.

Magnitudes and ranges of nitrate concentrations were largest in stream waters and near-surface (<1 m) soil waters, both of which were > meteoric waters > near-surface (<1 m) groundwaters > deep groundwaters (SI Figure S3). Maximum values of % unprocessed atmospheric nitrate in stream waters and near-surface soil waters were > near-surface groundwaters ≫ deep groundwaters (Figure 1). In general, % unprocessed atmospheric nitrate values in stream waters and groundwaters were inversely related to concentration, with no >20% values at nitrate concentrations >50 μmol L^{-1} (Figure 4). Soil waters, with several 30% to 40% values with up to ~200 μmol nitrate L^{-1}, deviated somewhat from that pattern, yet the largest fractions (40−100%) still occurred when soil water nitrate concentrations were ≤50 μmol nitrate L^{-1}. The inverse relationship is indicative of a greater relative effect of atmospheric deposition when and where deposition is lower. The pattern corresponds to observed positive correlations between nitrification rates[4,85] and inorganic nitrogen leaching[86]
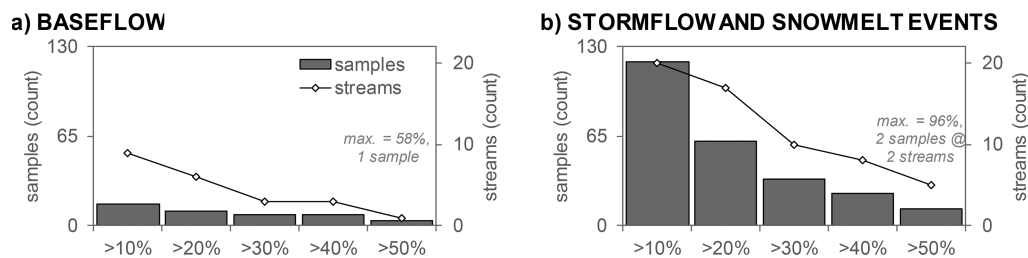

Figure 2. Numbers of stream samples and catchments with >10% unprocessed atmospheric nitrate during (a) baseflow and (b) stormflow and snowmelt events.
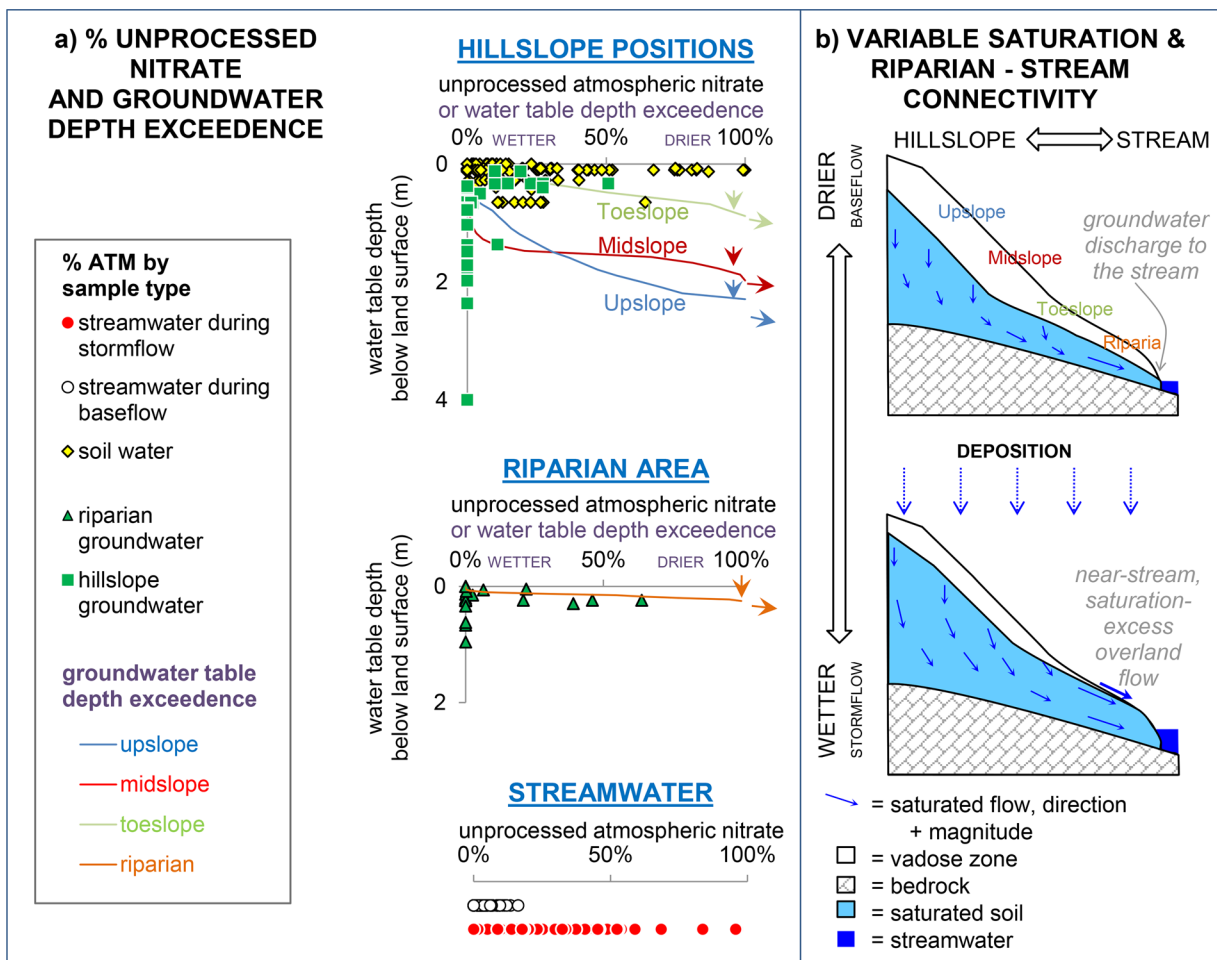
Figure 3. Most forests in our regional study were symptomatic of stage 0−1 nitrogen saturation, which fits a conceptual model of high fractions of unprocessed atmospheric nitrate in streams originating from direct atmospheric inputs to a stream or to a near-stream area. (a) % unprocessed atmospheric nitrate (ATM) values are shown by depth and source area (riparian or hillslope) relative to the stream within (b) a framework of lowered water tables during baseflow (upper) and higher water tables during stormflow when surface saturation expands into riparian areas (lower). With the exception of 6 of 32 particular streams (data shown in Figure 1), % unprocessed atmospheric nitrate was distinctly higher during stormflow (up to 96%) as compared to baseflow (up to 16%). The water table exceedance curves in (a) demonstrate how most soils on hillslopes rarely saturate to the surface where unprocessed atmospheric nitrate is a substantial percentage of the nitrate pool. In contrast, riparian water tables tend to fluctuate near the surface coinciding with the zone where % unprocessed atmospheric is high because atmospheric nitrate from rain or snowmelt infiltrates during events. The arrows in (a) depict vertical flow above saturation (in the vadose zone) and lateral flow when water saturated.
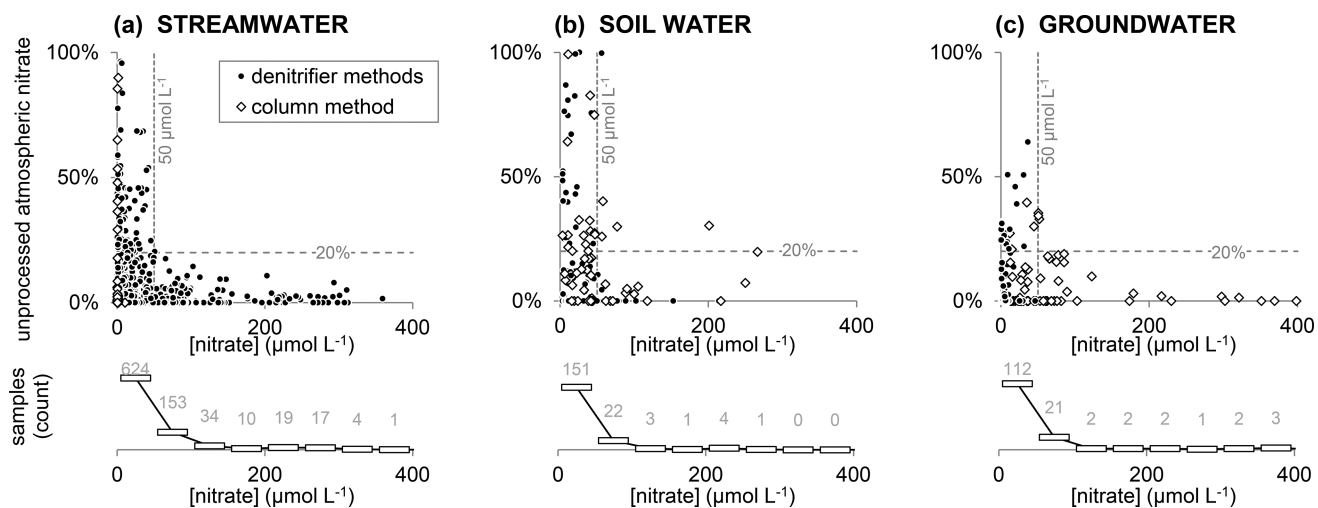

Figure 4. (top) Percent unprocessed atmospheric nitrate in (a) streamwater, (b) soil water, and (c) groundwater vs nitrate concentration. (bottom) Numbers of samples.
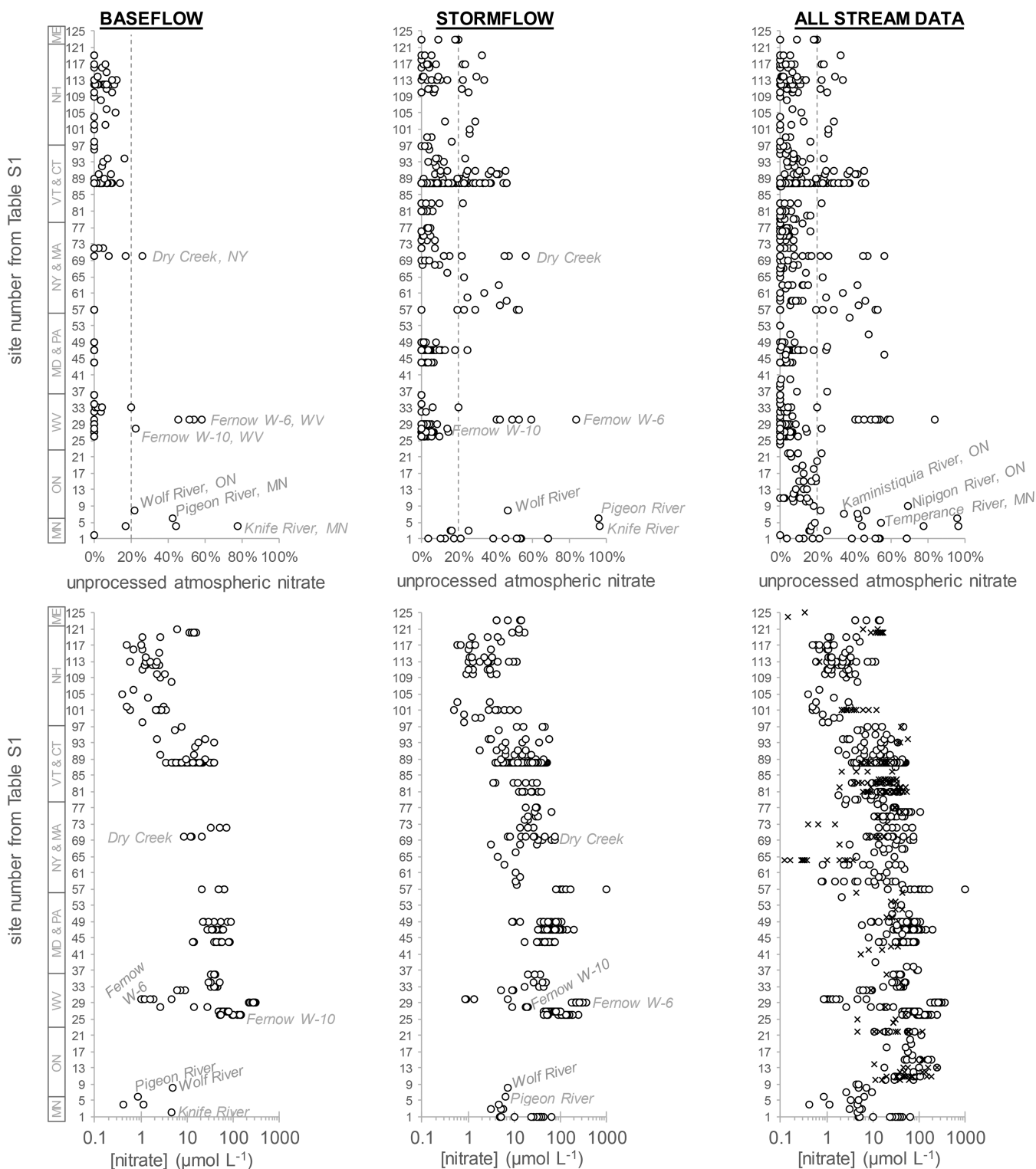
Figure 5. Percent unprocessed atmospheric nitrate (top panels) and nitrate concentration (bottom panels) in streamwater during baseflow (left) and stormflow (center), or irrespective of flow condition (right panels). Site names and location information are provided in SI Table S1. State or province abbreviations appear on the *y*-axis of the far left panel. Seeps are included (right panels). Streams with >20% unprocessed nitrate from atmospheric deposition during baseflow are named (left and center) for comparisons between baseflow and stormflow. In the right panel, several streams are referenced relative to the narrative or SI. × symbols (bottom right panel) show nitrate concentrations for samples that were not apportioned.

with increased nitrogen deposition, resulting in more nitrate from nitrification than atmospheric deposition that is available for transport in more polluted forests. Given this information, use of $\delta^{18}O$ to trace unprocessed atmospheric nitrate movement to streams may prove futile when nitrate is >50 μmol L^{-1}. Higher

stream nitrate concentrations (Figure 5) generally occurred where chronic nitrogen deposition was most severe from West Virginia and Maryland to Pennsylvania and New York, with lowest concentrations in Minnesota, western Ontario, and

Maine where chronic nitrate deposition was smaller in magnitude.[53,87]

Though uncommon, little processing of nitrate from atmospheric deposition occurs at some forests, causing >20% unprocessed atmospheric nitrate even during baseflow (6 of 32 streams with apportioned streamflow). Overall, % unprocessed atmospheric nitrate ranges in baseflow and stormflow were similar (Figure 1), which is attributable to high values during baseflow at three western tributary streams to Lake Superior in Minnesota and western Ontario, two streams in the Fernow Experimental Forest of West Virginia, and one stream in the Catskill Mountains of New York. At five of those six streams, maximum % unprocessed atmospheric nitrate values were higher during some stormflow or snowmelt events than during baseflow (Figure 5). Percent unprocessed atmospheric nitrate values were >40% at two Minnesota streams (Knife River: 2 of 3 baseflow values; Pigeon River: 1 baseflow value) and Fernow W-6 (5 of 6 baseflow samples), with only one baseflow value >20% at Wolf River (Ontario; 22%), Fernow W-10 (22%) and Dry Creek (New York; 26%). Of the streams with >20% unprocessed atmospheric nitrate during baseflow, we focus on the Minnesota/Ontario rivers and Fernow W-6 (West Virginia), which several times had >40% unprocessed atmospheric nitrate and where nitrogen cycling processes are relatable from studies of similar landscapes or site-specific studies. Unprocessed nitrate from atmospheric deposition was sometimes a particularly large fraction of stream nitrate (ranging from 0% to 96%) in the Lake Superior tributaries, where concentrations (<10 μmol L^{-1}) were low relative to most streams in our study. These catchments have lowland areas in peatlands,[88] with conifer cover, perennially high water tables,[67] low water pH,[89] seasonally frozen soils,[90] and little nitrification relative to high denitrification potential.[91,92] Those features and associated nitrogen cycling processes affect the relationship between time needed for nitrate to accumulate in soil waters relative to the frequency of hydrological events during which nitrate moves.[93] Denitrifiers require both a source of nitrate and enough time to reduce that nitrate,[94] whether from atmospheric deposition or nitrification. In contrast, high percentages of unprocessed atmospheric nitrate indicate transport that is more rapid than nitrogen transformations. With various limits on nitrification and denitrification in peatlands,[91,92] extensive peatlands may result in nitrate from the atmosphere being transported to, and detected in those streams, including several Minnesota streams that had <20% during baseflow and >20% during stormflow (Figure 5). In West Virginia, the upland Fernow W-6 catchment had conifer cover, low soil pH, low nitrification rates, and low (<10 μmol L^{-1}) stream nitrate concentrations.[95] In contrast to W-6, streams at nearly adjacent[82] and nearby catchments,[8,17] with deciduous or mixed deciduous/hardwood cover types, followed the general pattern of low % unprocessed atmospheric nitrate during baseflow and elevated % unprocessed atmospheric nitrate during stormflow. Consequently, conifer cover and associated nitrogen cycling processes seem to be a reason why particular streams had >20% unprocessed atmospheric nitrate during baseflow.

There was no clear patterning of δ^{18}O-nitrate or % unprocessed nitrate with catchment size, mean annual temperature (MAT), mean annual precipitation (MAP), or elevation (SI Figures S9 and S10). A lack of association is not surprising given the nearly identical MAT and MAP for nearby catchments that had considerable differences in % unprocessed atmospheric nitrate dynamics. For example, particular Fernow catchments variously show high (>50%) or low (<10%) % unprocessed

atmospheric nitrate during baseflow though there is little variation in elevation, soils, or geology among catchments. As previously shown,[16] annual wet deposition of total nitrogen and nitrate in precipitation (commonly available through national[96] or other monitoring programs) did not correlate with % unprocessed atmospheric nitrate. That study showed that nitrate deposition amount during discrete stormflow or snowmelt events, which is a time scale on which deposition is rarely quantified, was highly correlated[16] ($R^2 = 0.90$) with the volume-weighted % unprocessed atmospheric nitrate per event. The event-scale data (for several rainfall and snowmelt events at a single site) demonstrate rapid transport of atmospheric deposition irrespective of the magnitude of annual deposition or annual precipitation. Though not evident at the regional scale, more localized analysis of MAT, MAP, and atmospheric deposition may reveal stronger associations of these factors with % unprocessed atmospheric nitrate in stream waters.

Overall, we focus on event-driven inputs of unprocessed atmospheric nitrate to streams and non- or minimally nitrogen-saturated forests[2,34] (stages 0 and 1). Most of the 122 catchments were minimally nitrogen-saturated based on our site knowledge or previous diagnoses. One of the Fernow Experimental Forest catchments, unique among our study sites, has been diagnosed as stage-3 nitrogen saturated.[82] However, other Fernow catchments span the stages of nitrogen saturation[82,97] (W-6 = stage 0, W-5 and W-10 = stage 1, W-4 = stage 2, W-7 = stage 3).

Stream δ^{18}O-nitrate and % unprocessed nitrate were quite variable across a broad range of streamflow (10^{-3} to 7 cm d^{-1}; SI Figure S11). A pattern of some of the highest % unprocessed atmospheric nitrate values at moderate sized stormflow events (quick flow = ~10^{-3} to 10^{-1} cm d^{-1}), may be indicative of thresholds that affect transport of nitrate from atmospheric deposition. Moderate levels of quick flow may link the optimal conditions of sourcing (atmospheric deposition), proximity of certain landscape contributing areas, and wetness that induce water and unprocessed atmospheric nitrate movement. At times of no quick flow (i.e., baseflow), nitrate is not entering a catchment from wet atmospheric deposition or snowmelt. When quick flow is only a small fraction of streamflow after some rainfall or snowmelt, there may be insufficient connectivity of landscape areas that are sources of water and unprocessed atmospheric nitrate. Above a certain threshold, most unprocessed atmospheric nitrate may have already moved to a stream prior to peak flow, or a relatively larger proportion from nitrification may effectively dilute nitrate from atmospheric deposition.[17] Yields of unprocessed atmospheric nitrate increased to a high of 2.1 mg nitrogen m^{-2} d^{-1}, though yields were highly variable at high flow. Fractions of unprocessed atmospheric nitrate did not similarly increase with quick flow as a fraction of streamflow. Together, the patterns of unprocessed atmospheric nitrate (% and yields) with quick flow (cm d^{-1} or as a fraction of streamflow) provide evidence that nitrate from nitrification becomes the dominant nitrate source with increasing quick flow. A finite input of atmospheric nitrate during any particular storm or snowmelt event relative to a large pool from nitrification may be part of the reason. Hillslopes are a much larger portion of the areas of most catchments than riparian areas, and nitrification is enhanced relative to denitrification during prolonged periods when near-surface hillslope soils are not water saturated.[95,98] Another factor may be rapid runoff during stormflow or snowmelt events from riparian areas.[7,9] Persistent denitrification with limited nitrification in

riparian areas with near-surface inundation[99,100] during baseflow periods may cause nitrate from the atmosphere during rainfall or melt events to be large relative to the pool from nitrification. Consequently, highest proportions of unprocessed atmospheric nitrate may only occur as quick flow initiates and mobilizes nitrate from atmospheric deposition on near-stream areas, yet proportions decrease if nitrate from nitrification on hillslopes connects during wetter conditions.[7,9,93]

We explored vertical patterns of nitrate concentration, nitrate isotopes, and water table levels in soils and tills to further elucidate mechanisms of nitrate processing, transport in landscapes, and connectivity of unprocessed atmospheric nitrate to streams. Namely, soil water may be stationary or flow vertically with gravity to a deeper groundwater when unsaturated. As water tables rise, shallow subsurface stormflow initiates along near-surface lateral flowpaths down hill-slopes[93,101] and shallow subsurface flowpaths transmit more water, more rapidly than deeper flowpaths.[102] Our overarching premise is that nitrate deposition affects stream nitrate dynamics during stormflow or snowmelt events if the water table intersects layers where unprocessed nitrate from atmospheric deposition is available to be mobilized[7,9,19,24,93] (Figure 3).

When % unprocessed atmospheric nitrate, δ^{18}O-nitrate, and δ^{15}N-nitrate of subsurface waters were stratified by depth of sampling (soil waters) or depth to water table (groundwater), patterns with depth were similar between the methods (denitrifier and column) for concentrations and isotopic values (Figure 1 and SI Figure S3). Concentration (up to 860 μmol L^{-1}) and δ^{18}O values (-14‰ to $+86$‰) of nitrate were most variable and highest in samples from the near surface and decreased with depth in the top 1 m of soil profiles for soil waters and groundwaters (see Section S5 for discussion of δ^{15}N values and nitrate processing in soils). Values of δ^{15}N were wide ranging in shallow soil waters (-10‰ to $+40$‰) and fairly stable in shallow groundwater (most values -2‰ to $+6$‰, with one value of -10‰). Below 1 m, values in groundwaters remained fairly stable: up to 60 μmol nitrate L^{-1}, -5‰ to $+10$‰ for δ^{18}O and $+2$‰ to $+5$‰ for δ^{15}N. The depth patterns and isotopic values are indicative of the loss of nitrate from atmospheric deposition and de novo nitrate produced in situ via nitrification. Overall, when surficial soils are not water saturated, atmospheric nitrate appears to be consumed by biological processing along vertical flowpaths through hillslope soils or tills.[7,46,47,80]

Without near-surface saturation, there is no mechanism for nitrate transport on the time scale of a stormflow or snowmelt event from near-surface soil waters to streams. Water tables rise first in riparian areas before rising, if at all, in hillslopes during any particular event.[1,3,10] In surficial soil waters and shallow groundwater (and only shallow) in both near-stream and upslope areas, % unprocessed atmospheric nitrate was at times higher than in stream waters (Figure 3), highlighting these soils as potential sources of stream nitrate. Nonetheless, water tables are typically too deep to intersect near-surface soil waters on hillslopes (Figure 3). In contrast, fluctuations of the shallow water table near streams do intersect and mobilize soil waters[63,103] that sometimes during events have large fractions of unprocessed atmospheric nitrate.

Higher elevation catchments (in other regions) may have more bedrock exposure, talus fields, shallow soils, large seasonal inputs of nitrate-laden snow, permafrost, and glacial stores of nitrate from atmospheric deposition. These features, along with flow over bedrock or frozen ground (including more distal

hillslopes), are important drivers of how nitrogen is processed and how unprocessed atmospheric nitrate is transported in certain high-elevation catchments.[59−62] Though seemingly different in landscape features, a similar concept of nitrate from atmospheric deposition entering a catchment and movement from hydrologically connected landscapes areas prevails for both alpine and temperate forests.

Finally, our data offer insight on groundwater enrichment with nitrate. A pathway of groundwater transport does not appear to be common in or around the Northern Forest Region. Fractions of unprocessed atmospheric nitrate were similar in shallow (<1 m) riparian groundwater and stormflow in the stream (Figure 3). Values were similar among deep groundwater from hillslope wells (>1 m deep), stream baseflow (when the majority of streams with >20% unprocessed atmospheric nitrate only during stormflow or snowmelt are considered), and seep water samples. With the caveats that (1) groundwaters were only collected from ten of our study catchments (SI Table S5), and (2) those rare streams with >20% unprocessed atmospheric nitrate in baseflow did not have associated soil or groundwater samples, we found no deep soil/till water or groundwater (>1 m deep) enriched in unprocessed atmospheric nitrate. Although we had few seeps in our study and seeps have been considered a proxy of groundwater discharge to streams,[32,48] none had >10% unprocessed atmospheric nitrate. Patterns of decreasing and less variable nitrate concentrations with depth, and smaller and less variable proportions of unprocessed atmospheric nitrate in deep soils and tills (Figure 1 and SI Figure S3) show (1) nitrate processing with vertical drainage to groundwater; and (2) evidence that nitrate from atmospheric deposition does not move along deep flowpaths to streams.

Overall, our results confirm that a direct relationship of atmospheric pollution to the variation of stream nitrate concentrations known for single sites[7,9] applies across a broad range of forestlands in the northern and eastern U.S. and southern Canada. Our synthesis of nitrate isotope studies provides a clear message for and around the Northern Forest Region that may broadly apply to other temperate forests that are affected by elevated nitrate deposition: nitrate from atmospheric deposition that enters forests sometimes rapidly moves to streams without processing. Deposition to riparian areas and transport along shallow subsurface flowpaths during stormflow are particularly important to yields of up to several mg unprocessed atmospheric nitrogen m^{-2} d^{-1} in streams. Knowledge of unprocessed atmospheric nitrate in waters is important to an assessment of forest health, the provisioning of clean water, and assessments of nitrogen reduction legislation and management policies. For example, the fraction of unprocessed atmospheric nitrate in stream waters may be a more relevant indicator of how atmospheric deposition affects minimally polluted forests and times when biogeochemical processes are ineffective in the processing of atmospheric nitrate,[104] as well as providing a more useful criteria for the establishment of critical loads, than the more simple approach of using stream nitrate concentration.[105] Reductions to nitrate deposition would reduce the amount of nitrate from atmospheric deposition that is transported through forests to streams if the climate of recent decades persists. In contrast, if nitrate deposition is not further reduced and extreme precipitation events continue to increase in frequency and magnitude,[106] the importance of unprocessed atmospheric nitrate may be amplified. The fractions of unprocessed atmospheric nitrate inputs to streams substantially varied among nearly adjacent catchments as well as

the region, which indicates a continued need to assess nitrogen pollution effects at sites having different depositional, physical, and biological characteristics. However, there are no funded or sustained programs for long-term monitoring of nitrate isotopes, which could also include $\Delta^{17}O$. Monitoring with nitrate source apportionments may provide vital information that is needed to assess the status and trends of atmospheric nitrogen pollution effects on forests and streams.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01276.

> Introduction. S1: Field and laboratory methods (narrative with Figure S1 and Figure S2). S2: Use of multiple laboratories (narrative and Figures S3 and S4). S3: Establishing nitrification and atmospheric end-members (narrative, Figures S5−S7, and equations). S4: Apportionment of quick flow (narrative). S5: Nitrate processing in subsurface waters (narrative). Other Supporting Information Figures: Figure S8: % unprocessed atmospheric nitrate in stormflow and baseflow. Figure S9: Bivariate plots of $\delta^{18}O$-nitrate and % unprocessed atmospheric nitrate vs catchment area and elevation. Figure S10: Bivariate plots of $\delta^{18}O$ of nitrate and % unprocessed atmospheric nitrate vs MAP and MAT. Figure S11: Bivariate plots of nitrate concentration or flux, $\delta^{18}O$ of nitrate, and unprocessed atmospheric nitrate vs streamflow or quick flow. Tables: Table S1: Site information. Full table is the file "SiteInformation.xlsx." Table S2: Soil water information. Table S3: Meteoric water information. Table S4: Numbers of sampling locations and sample numbers by water type. Table S5: Groundwater information. Associated data publications: Sebestyen, S. D., Kendall, C., Elliott, E. M., Schiff, S. L., Barnes, R. T., Bostic, J. T., Buda, A. R., Burns, D. A., Campbell, J. L., Dail, D. B., Eshleman, K. N., Fernandez, I. J., Finlay, J. C., Goodale, C. L., Griffiths, N. A., Hall, S. J., Lawrence, G. B., Lovett, G. M., McHale, P. J., Mitchell, M. J., Nelson, D. M., Nelson, S. J., Ohte, N., Pardo, L. H., Rose, L. A., Ross, D. S., Sabo, R. D., Shanley, J. B., Shattuck, M. D., Spoelstra, J., Weintraub, S. R., Wickman, T. R., & Williard, K. W. J. (2019), Nitrate isotope database for meteoric waters, surface waters, soil waters, and groundwaters, Forest Service Research Data Archive, Fort Collins, CO; DOI 10.2737/RDS-2019−0003. Shanley, J. B., Sebestyen, S. D., Smith, T. E., Chalmers, A. T., Clark, S. F., & Denner, J. C. (2019), Groundwater level data for Watershed-9 (W-9) in the Sleepers River Research Watershed (Vermont), Forest Service Research Data Archive, Archive, Forest Service Research Data Archive, Fort Collins, CO; DOI 10.2737/RDS-2018−0064. Sources of streamflow data are listed in Table S1 (PDF)
> IsotopesByLab-Column.pdf (PDF)
> TableS1_SiteInformation.xlsx (XLSX)
> TableS1_Attributes.txt (TXT)
> TableS1_References.txt (TXT)

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S.D.S. coordinated the project with J.B.S., D.S.R., and cooperators. S.D.S., D.S.R., and J.B.S. wrote the proposal that funded new sampling for this study. D.S.R. or S.D.S. oversaw lab analyses of nitrate and ammonium at laboratories. S.D.S. compiled data and wrote the manuscript. E.E.M. oversaw nitrate isotope analyses at the University of Pittsburgh. C.K. oversaw nitrate isotope analyses for many of the included data sets. D.S.R., J.B.S., J.L.C., D.B.D., M.D.S., I.J.F., C.L.G., G.B.L., G.M.L., P.J.M., M.J.M., and S.J.N. provided water samples from their research sites. T.R.W. coauthored a grant that funded analysis of some samples. R.T.B., J.T.B., A.R.B., D.A.B., K.N.E., J.C.F., C.L.G., C.K., D.M.N., N.O., L.H.P., L.A.R., R.D.S., S.L.S., J.S., and K.W.J.W. provided data from their studies. All authors contributed to manuscript editing. After the first four authors, the authors are ordered alphabetically within two groups: those that contributed samples, and then those who shared data.

Notes

The authors declare no competing financial interest.
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