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Key Points:
- Percent atmospheric nitrate is low during baseflow in many forested catchments
- Percent atmospheric nitrate may be high during stormflow
- Catchment hydrology and topography influence atmospheric nitrate in streams

Correspondence to:
L. A. Rose,
lab125@pitt.edu

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Drivers of atmospheric nitrate processing and export in forested catchments

Lucy A. Rose[1], Stephen D. Sebestyen[2], Emily M. Elliott[1], and Keisuke Koba[3]

[1]Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania, USA, [2]USDA Forest Service, Grand Rapids, Minnesota, USA, [3]Institute of Agriculture, Tokyo University of Agriculture and Technology, Tokyo, Japan

Abstract Increased deposition of reactive atmospheric N has resulted in the nitrogen saturation of many forested catchments worldwide. Isotope-based studies from multiple forest sites report low proportions (mean = ~10%) of unprocessed atmospheric nitrate in streams during baseflow, regardless of N deposition or nitrate export rates. Given similar proportions of atmospheric nitrate in baseflow across a variety of sites and forest types, it is important to address the postdepositional drivers and processes that affect atmospheric nitrate transport and fate within catchments. In a meta-analysis of stable isotope-based studies, we examined the influence of methodological, biological, and hydrologic drivers on the export of atmospheric nitrate from forests. The $\delta^{18}O\text{-}NO_3^-$ values in stream waters may increase, decrease, or not change with increasing discharge during stormflow conditions, and $\delta^{18}O\text{-}NO_3^-$ values are generally higher in stormflow than baseflow. However, $\delta^{18}O\text{-}NO_3^-$ values tended to increase with increasing baseflow discharge at all sites examined. To explain these differences, we present a conceptual model of hydrologic flowpath characteristics (e.g., saturation overland flow versus subsurface stormflow) that considers the influence of topography on landscape-stream hydrologic connectivity and delivery of unprocessed atmospheric nitrate to streams. Methodological biases resulting from differences in sampling frequency and stable isotope analytical techniques may further influence the perceived degree of unprocessed atmospheric nitrate export. Synthesis of results from numerous isotope-based studies shows that small proportions of unprocessed atmospheric nitrate are common in baseflow. However, hydrologic, topographic, and methodological factors are important drivers of actual or perceived elevated contributions of unprocessed atmospheric nitrate to streams.

1. Introduction

Deposition of atmospheric nitrogen (N) exceeds critical N loads in some ecosystems [*Ågren and Bosatta*, 1988; *Fenn et al*., 2008; *Galloway et al*., 2008; *Pardo et al*., 2011], and has been linked to elevated N export from forests worldwide [*Aber et al*., 1998; *Galloway et al*., 2003]. Nitrogen saturation is the theory that excess nitrate will leach from soils and landscapes when vegetation and soil sinks do not assimilate additional N inputs [*Ågren and Bosatta*, 1988; *Aber et al*., 1989; *Stoddard*, 1994; *Lovett and Goodale*, 2011]. When ecosystem sinks are full, this represents *capacity saturation*, whereas *kinetic saturation* occurs when the rate of N delivery exceeds biological retention of reactive N [*Lovett and Goodale*, 2011]. Several cross-site comparisons have examined the relationship between N deposition and nitrate export from forests [*Mitchell et al*., 1997; *Aber et al*., 2003; *Driscoll et al*., 2003; *Pardo et al*., 2006; *Dise et al*., 2009; *Argerich et al*., 2013]. These studies generally reported higher stream nitrate concentrations at locations where atmospheric N deposition was elevated relative to minimally polluted ecosystems. However, intra-catchment processes that affect the transport and fate of atmospheric nitrate after deposition onto the landscape are less well understood. As mineralization of soil organic N is substantial in some forests, greater nitrate concentrations in streams relative to deposition do occur [*Stoddard*, 1994], making the distinction between microbial and atmospheric nitrate sources in stream water important. Such source differentiation has implications for N saturation theory, particularly in identifying capacity versus kinetic saturation. Source differentiation also provides novel detail about the biological and physical processes affecting N transport and fate within catchments [*Sebestyen et al*., 2008]. For example, by influencing flowpaths and landscape-stream hydrologic connectivity, catchment structure and hydrology may play important—and perhaps underappreciated [*Bain et al*., 2012]—roles in determining the extent of atmospheric source contributions to stream nitrate.

Table 1. Site Locations, Forest Type, Nitrate Isotope Determination Method, and N Deposition and Precipitation Characteristics[a]

Study	Site	Forest Type	Analytical Method for Isotope Determination	Total Wet NO_3^--N Deposition (kg $ha^{-1}yr^{-1}$)	Total Annual Average Precipitation (mm)	% of Precipitation as Snow
Barnes et al. [2008]	CT and MA (USA)	HW/Conif	Denitrifier	1.4	1140	10
Buda and DeWalle [2009]	Central PA (USA)	Mixed HW	Silver nitrate	NA	1043	NA
Burns and Kendall [2002]	Catskills NY (USA)	HW/Conif	Silver nitrate	4.2	1530	20–25
Campbell et al. [2006]	Adirondacks NY (USA)	Mixed HW	Silver nitrate	3.2	1035	47
Goodale et al. [2009]	Upper Susquehanna NY (USA)	HW/Conif	Denitrifier	3.6	932	NA
Mitchell et al. [2006]	Adirondacks NY (USA)	HW/Conif	Silver nitrate	3.2	1010	47
Ohte et al. [2004]	Sleepers River VT (USA)	Mixed HW	Denitrifier	3.5	1323	20–30
Pardo et al. [2004]	Hubbard Brook NH (USA)	Mixed HW	Silver nitrate	3.6	1395	25–33
Pellerin et al. [2012]	Sleepers River VT (USA)	Mixed HW	Denitrifier	3.3	1323	20–30
Piatek et al. [2005]	Adirondacks NY (USA)	HW/Conif	Silver nitrate	3.2	1010	47
Sebestyen et al. [2008]	Sleepers River VT (USA)	Mixed HW	Denitrifier	3.5	1323	20–30
Sebestyen et al. [2014]	Sleepers River VT (USA)	Mixed HW	Denitrifier	3.5	1323	20–30
Spoelstra et al. [2001]	Turkey Lakes (Canada)	Mixed HW	Silver nitrate	NA	1239	35
Tobari et al. [2010]	Gomadansan Exper. For. (Japan)	Japanese cedar/ cypress	Denitrifier	7.0	2650	NA
Tsunogai et al. [2010]	Rishiri Island (Japan)	HW/Conif	Cd/azide reduction to N_2O	4.5	NA	NA
Williard et al. [2001]	Fernow 4 WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14
Williard et al. [2001]	Fernow 10 WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14
Williard et al. [2001]	Otter Run WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14
Williard et al. [2001]	Salamander Run WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14
Williard et al. [2001]	W. Three Spring WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14
Williard et al. [2001]	Karly Spring WV (USA)	Mixed HW	Silver nitrate	4.6	1458	14

[a]NA, data not available.

Previous studies have applied dual isotope (δ^{15}N and δ^{18}O) approaches to assess catchment-scale processing of atmospheric nitrate (Table 1). As significant overlap exists between the ranges of δ^{15}N values for microbial and atmospheric nitrate (the two main nitrate sources in most forests), it has not been as useful in source apportionment [*Kendall et al.*, 2007]. Rather, δ^{15}N-NO_3^- has been used to elucidate the importance of biological N processing (e.g., nitrification, denitrification, and uptake). In contrast, the oxygen isotopic signatures of microbial and atmospheric nitrate are more distinct, making δ^{18}O-NO_3^- a valuable tool for distinguishing between atmospheric and nitrification sources [*Kendall et al.*, 2007; *Burns et al.*, 2009; *Ohte et al.*, 2010]. Atmospheric δ^{18}O-NO_3^- can range from $+45‰$ to $+100‰$, whereas values from nitrification range from $-10‰$ to $+15‰$ [*Kendall et al.*, 2007]. When δ^{18}O-NO_3^- values in streams approach the range of δ^{18}O-NO_3^- in precipitation, this indicates that some deposition inputs are not biologically cycled prior to export from the terrestrial system [*Kendall et al.*, 2007]. The proportion of unprocessed atmospheric nitrate in stream water can be calculated using a two end-member mixing model

$$\%NO_{3atm}^- = \frac{\delta^{18}O-NO_{3str}^- - \delta^{18}O-NO_{3nit}^-}{\delta^{18}O-NO_{3atm}^- - \delta^{18}O-NO_{3nit}^-} \times 100 \quad (1)$$

where the subscripts $_{str}$, $_{nit}$, and $_{atm}$ refer to nitrate in the stream, from the nitrification end-member, and from the atmospheric end-member, respectively. In addition, a newer isotopic technique exploits inherent differences in Δ^{17}O (the ^{17}O isotope excess; $\Delta^{17}O = \delta^{17}O - 0.52(\delta^{18}O)$) of nitrate between atmospheric and terrestrial sources [*Michalski et al.*, 2003]. This technique is increasingly being adopted in terrestrial N cycling studies.

Previous studies of forested catchments in the United States, Asia, and Europe have demonstrated positive relationships between stream nitrate concentrations and atmospheric N deposition [*Mitchell et al.*, 1997; *Aber et al.*, 2003; *Dise et al.*, 2009]. At some sites in the northeastern United States, nitrate concentrations in streams and lakes increased significantly when N deposition rates exceeded 8 kg N ha^{-1} yr^{-1} [*Aber et al.*, 2003], whereas throughfall N in excess of 5 kg N ha^{-1} yr^{-1} resulted in elevated N leaching at 50 sites across China [*Fang et al.*, 2011]. Higher thresholds were observed for European and Japanese forests, where N deposition rates in excess of ~10 kg N ha^{-1} yr^{-1} resulted in elevated nitrate leaching at some sites [*Grennfelt and Hultberg*, 1986; *Mitchell et al.*, 1997]. While the relationships between N deposition and stream nitrate are noteworthy, these studies typically have not differentiated between atmospheric and microbial sources of stream nitrate.

In contrast to mass balance-based approaches, stable isotope-based investigations have not demonstrated the same association between atmospheric nitrate inputs and outputs at the catchment scale. As shown by nitrate isotopic data, most studies report only minor contributions of atmospheric nitrate to stream N export (Table 2) despite wide ranges in deposition (from 4 to 13 kg N ha^{-1} yr^{-1}), stream nitrate yields [*Spoelstra et al.*, 2001; *Williard et al.*, 2001; *Burns and Kendall*, 2002; *Ohte et al.*, 2004; *Pardo et al.*, 2004; *Barnes et al.*, 2008; *Tobari et al.*, 2010] and large proportions of atmospheric N observed in soil water [*Osaka et al.*, 2010; *Templer and McCann*, 2010]. These observations suggest the need for a broader conceptualization of N saturation beyond simply conditions when N supply exceeds biological demand [*Aber et al.*, 1989; *Stoddard*, 1994] and toward a conceptual model that emphasizes the rates of processes such as biological uptake and hydrologic transport [e.g., *Lovett and Goodale*, 2011]. Thus, an examination of the factors driving nitrate export from forested catchments that considers both biological and physical processes is warranted. In this review, we explore major drivers that influence atmospheric nitrate transport in catchments via a review of the literature on nitrate source apportionment, address knowledge gaps, and highlight prospects for future experiments, observations, and interdisciplinary research. We focus primarily on nitrate export dynamics in forests, as most N saturation and isotope apportionment studies address forested ecosystems. Important drivers that regulate atmospheric nitrate export from forests include:

1. *Methodological drivers* including the frequency, seasonality, and scale of sample collection, as well as analytical biases,
2. *Biological drivers* such as terrestrial and in-stream N processing, and the synchrony of wet and dry deposition inputs with biological processing, and
3. *Physical drivers* including the hydrologic regime and landscape characteristics of catchments.

While the importance of biological factors (i.e., mineralization and nitrification rates, species composition, stand age) is well recognized, fewer studies have emphasized the methodological and physical drivers of atmospheric nitrate export from catchments. We explore the role of these methodological, biological, and physical drivers in the processing and transport of atmospheric nitrate in forests, and present a new conceptual model of hydrologic and topographic regulation of catchment-scale atmospheric nitrate export.

2. Major Drivers Influencing Atmospheric Nitrate Transport in Catchments

The high retention of atmospheric deposition demonstrated by many previous isotope-based studies (e.g., overall mean of all mean atmospheric nitrate percentages reported in Figure 1 and Table 2 = 10%) suggests that: (1) nitrate isotope data can be used to assess the extent of atmospheric N processing by biota with far less sampling and on much shorter time scales than traditional mass balance approaches [*Church*, 1997], and (2) factors other than biological processing influence atmospheric nitrate export to streams. Physical catchment attributes such as topography and hydrologic status can regulate atmospheric nitrate retention and export by influencing flowpath dynamics and the extent of hydrologic connectivity between landscapes and streams. Additionally, variability in atmospheric nitrate contributions to streams may also arise due to systematic differences in nitrate isotope values resulting from various analytical approaches. While such methodological biases may not reflect actual differences in the amount of atmospheric nitrate exported from catchments, they are an important consideration in isotope-based studies due to their influence on end-member mixing analyses.

2.1. Methodological Factors

Methodological biases are not strictly related to catchment attributes that regulate atmospheric nitrate transport (e.g., biology, hydrology, and topography), but they may strongly influence the interpretation of isotope data and, therefore, source apportionment. Due to the potentially significant influence of methodological biases in interpretations of catchment atmospheric nitrate dynamics, we focus on them first. Methodological biases include factors such as the timing and frequency of sample collection, as well as analytical approaches that may influence apportionments of nitrate sources.

2.1.1. Frequency, Seasonality, and Scale of Sample Collection

Given that atmospheric N delivery to streams varies over time scales as short as individual hydrologic events, the frequency and seasonality of sample collection can strongly influence data interpretation,

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Table 2. Nitrate End-Member $\delta^{15}N$ and $\delta^{18}O$ Values and Estimation Methods, and Fraction of Atmospheric Nitrate in Streams[a]

	Nitrification End-Member		Atmospheric End-Member	$\delta^{15}N\text{-}NO_3^-$ (‰)		$\delta^{18}O\text{-}NO_3^-$ (‰)		
Study	$\delta^{18}O\text{-}NO_3^-$ Value (‰)	Estimation Method	$\delta^{18}O\text{-}NO_3^-$ Estimation Method	Atm	Stream	Atm	Stream	% $NO_{3\ atm}^-$ in Streams
Barnes et al. [2008]	−4	Lowest baseflow NO_3^- value	Average of storm event precipitation	−2	NA (0 to +6)	+71 (+50 to +84)	NA (−4 to +10)	12 (0–25)
Buda and DeWalle [2009]	+5 (0 to +14)	Mean baseflow NO_3^- value	Average of storm event precipitation	0	NA	+44 (+12 to +70)	NA	NA (0–33)
Burns and Kendall [2002]	+15 (+13 to +16)	Incubated soil cores	Average of snowmelt, throughfall, wet deposition	0	+2 (−1 to +4)	+51 (+35 to +70)	+18 (+8 to +30)	8 (1–55)
Campbell et al. [2006]	0 to +3	$\delta^{18}O$ of soil water and O_2	Average of biweekly bulk precipitation	0	+1 (0 to +2)	+80 (+66 to +90)	NA (0 to +14)	<10
Goodale et al. [2009]	−6 to +2	$\delta^{18}O$ of soil water and O_2	Average of weekly bulk precipitation	−1 (−3 to +2)	NA (−2 to +6)	+77 (+71 to +81)	NA (−7 to +34)	NA (4–53)
Mitchell et al. [2006]	NA	NA	Throughfall	NA (−6 to +6)	NA (+1 to +4)	NA (+58 to +77)	NA (−5 to +4)	0
Ohte et al. [2004]	−11 to +21	Groundwater NO_3^- value	Weekly and event wet-only precipitation	NA	NA (+1 to +4)	NA (+78 to +89)	NA (−8 to +18)	9 (0.5–26)
Pardo et al. [2004]	−5 to +15	$\delta^{18}O$ of soil water and O_2	Weekly bulk Precipitation	−2 (−5 to +2)	0 (−3 to +6)	+62 (+46 to +75)	+18 (+12 to +33)	NA (0–45)
Pellerin et al. [2012]	−3	Mean ground-water NO_3^- value from 2004	Average of snowmelt from 2004	NA	NA	+86 (+77 to +96)	+3 (−3 to +10)	7 (0–15)
Piateket al. [2005]	NA	NA	Snowmelt, throughfall, wet deposition	+1 (−6 to +3)	+1 (−6 to +3)	+72 (+58 to +80)	+10 (+6 to +16)	NA
Sebestyenet al. [2008]	−2 to +2	Groundwater NO_3^- value	Weekly and event wet-only precipitation	NA (−4 to +3)	NA (0 to +7)	NA (+76 to +101)	NA (−5 to +43)	13 (0.4–48)
Sebestyen et al. [2014]	−4 to +1	Groundwater or soil water NO_3^- value	Weekly or event wet-only precipitation	NA	+2	NA (+70 to +101)	NA (−1 to +32)	NA (0–33)
Spoelstra et al. [2001]	−1 (−6 to +5)	$\delta^{18}O$ of soil water and O_2	Mass-wt. average of biweekly bulk precipitation	−2 (−4 to +1)	NA (+1 to +6)	+50 (+35 to +59)	NA (+3 to +15)	20 (8–30)
Tobari et al. [2010]	−16	Lowest baseflow NO_3^- value	Average of bulk rainfall	+3 (−7 to +15)	+3 (−3 to +10)	+64 (+43 to +76)	+5 (−16 to +38)	26 (11–45)
Tsunogai et al. [2010]	0	Assumed value for $\Delta^{17}O$ method	Average of daily wet deposition	−1	+2 (−4 to +9)	+87 ($\Delta^{17}O\text{–}NO_3^- = +26$)	+3 (−2 to +18)	7 *(using $\Delta^{17}O$)*
Williard et al. [2001] (Fernow 4)	+10	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+5 (+3 to +9)	3 (0–11)
Williard et al. [2001] (Fernow 10)	+7	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+7 (+2 to +14)	7 (0–21)
Williard et al. [2001] (Otter Run)	+14	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+10 (+2 to +15)	13 (0–23)
Williard et al. [2001] (Salamander Run)	+12	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+10 (+6 to +12)	12 (5–19)
Williard et al. [2001] (W. Three Spring)	+3	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+7 (+3to +11)	7 (0–17)
Williard et al. [2001] (Karly Run)	+8	Incubated soil cores	Average of annual or monthly throughfall	NA	NA	+56 (+50 to +60)	+4 (+1 to +6)	2 (0–7)

[a]Values represent reported mean (range); NA, data not available.

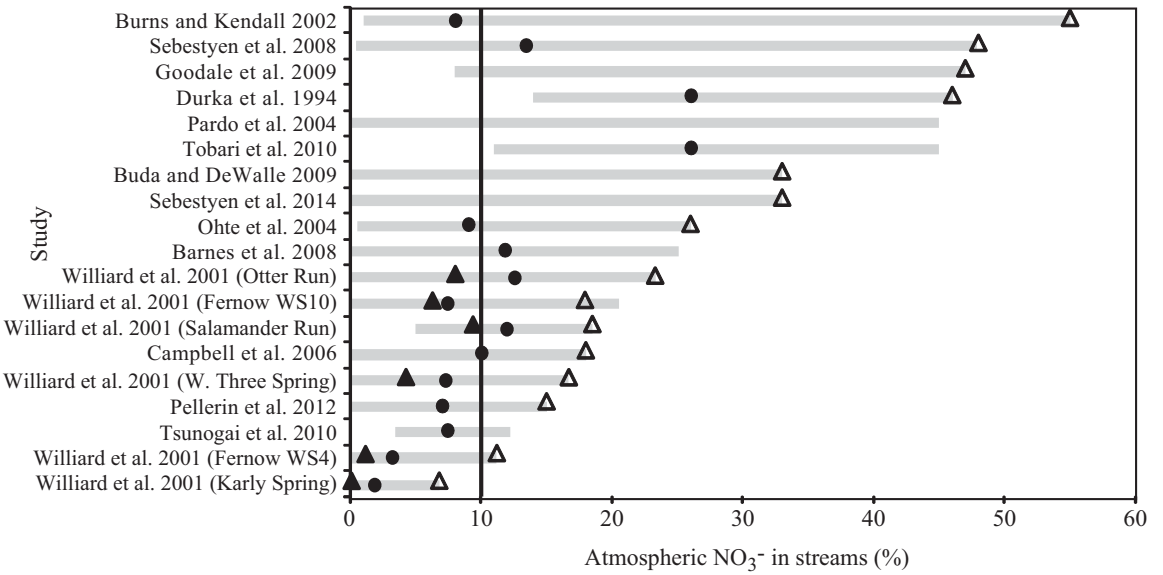

Figure 1. Percent atmospheric nitrate (NO_3^-atm) in streams as reported in various catchment-scale isotope tracer studies. Data were obtained from values reported in publications or were extracted from published figures using g3data software (http://frantz.fi/software/g3data.php) [*Bauer and Reynolds*, 2008; *Snider et al.*, 2010]. Gray bars represent reported ranges of NO_3^-atm in streams for each study. Solid circles represent average % NO_3^-atm during the entire study period; this may represent a combination of baseflow and quickflow (snowmelt and stormflow). Solid triangles represent average % NO_3^-atm reported for baseflow only. Open triangles show the maximum reported % NO_3^-atm in quickflow. For emphasis, the bold line represents 10% NO_3^-atm in streams.

particularly in catchments with fast hydrologic response times. Some studies have attributed the small amounts of unprocessed atmospheric nitrate in streams to low sampling frequency during snowmelt events or sampling that has occurred after peak nitrate concentrations [*Ohte et al.*, 2004; *Pardo et al.*, 2004; *Piatek et al.*, 2005]. In other cases, nitrate sources to streams vary over longer time scales. Indeed, the largest unprocessed atmospheric nitrate inputs to streams have been measured during hydrologic extremes such as snowmelt and monsoon events that are seasonal [*Sebestyen et al.*, 2008; *Fang et al.*, 2011; *Pellerin et al.*, 2012]. As a result, seasonal sampling biases have also influenced the perceived importance of atmospheric nitrate export to streams.

Sampling scale also influences interpretations of atmospheric nitrate export dynamics. Analysis of a subset of the studies presented in Table 1 demonstrates this point (Figure 2). The data presented in Figures 2a–2c are from forested catchments, undisturbed for at least 40 years prior to the study period, where sample collection occurred on a bimonthly or monthly basis for at least one full year. While the studies shown in Figures 2a and 2b reflect relatively minor inorganic N and nitrate deposition gradients, in both cases declining proportions of atmospheric nitrate in streams with increasing N deposition suggests that chronic elevated atmospheric N inputs can result in greater export of microbial nitrate. Similarly, the proportion of atmospheric nitrate in streams may decrease with increasing average total precipitation among these sites (Figure 2c). However, while regression analyses of the data in Figures 2a–2c indicate negative relationships between the proportions of atmospheric nitrate in streams and atmospheric deposition or precipitation, these relationships are not statistically significant due to variability among studies. In contrast, the deposition-export relationship at a single site and over shorter time periods at Sleepers River Research Watershed, Vermont, USA is statistically significant and shows the opposite pattern (Figure 2d). Proportions of unprocessed atmospheric nitrate in the stream at Sleepers River increased as wet nitrate deposition increased during individual stormflow events ($R^2 = 0.90$; $p < 0.0001$). These examples demonstrate the potential dependence of perceived atmospheric nitrate export dynamics on the spatial and temporal scales at which the nitrate deposition-export relationship is examined.

Sampling biases vary among studies and should be acknowledged. For example, snowmelt events account for a large proportion of annual water and nutrient budgets at some sites [*Sebestyen et al.*, 2008] but are of little to no importance in other catchments [*Barnes et al.*, 2008]. The synchrony of seasonal patterns of

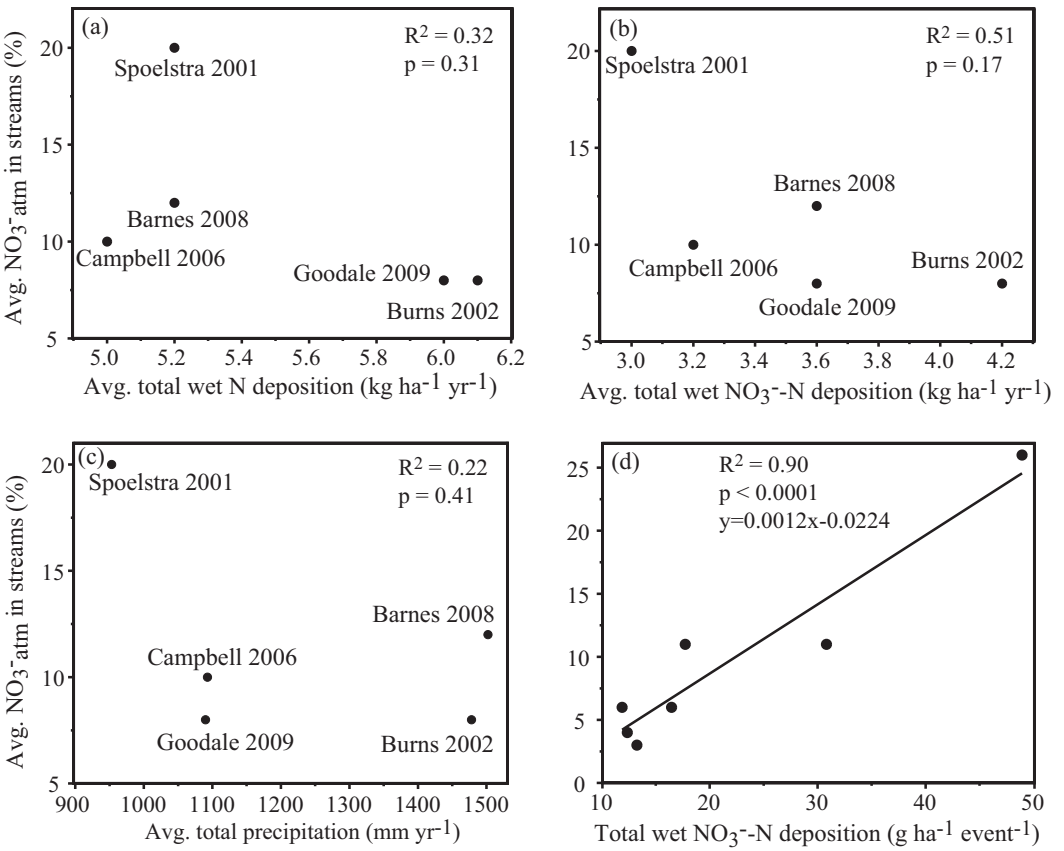

Figure 2. Relationship of average percent atmospheric nitrate in streams to (a) long-term (1984 to the study year) average total wet inorganic N deposition, (b) long-term (1984 to the study year) average total wet NO_3^--N deposition, and (c) annual average total precipitation (for the study years only) at sites across the northeastern USA and eastern Canada. The patterns of the relationships are negative, but none are statistically significant.Average annual precipitation, total N, and total NO_3^--N deposition were calculated from the nearest National Atmospheric Deposition Program site (less than 70 km away for all sites). Average values represent a range of hydrologic conditions, as all studies were conducted for more than one year, with bimonthly or monthly sampling. (d) The relationship between average percent atmospheric nitrate in streams and total wet NO_3^--N deposition during individual storm events measured at the Sleepers River Research Watershed. While relationships between average atmospheric nitrate in streams with long-term average N deposition and precipitation are not significant (Figures 2a–2c), on an event basis increasing atmospheric nitrate inputs are significantly correlated with increasing percent of atmospheric nitrate in streams at some sites (Figure 2d).

atmospheric deposition and biological uptake also influences nitrate transport to streams. Seasonal differences in peak nitrate export among United States, European, and Asian catchments exemplify the reasons why the timing and frequency of sampling must be considered [*Mitchell et al*., 1997]. The paucity of nitrate isotopic data from summer and autumn stormflow may particularly bias our assessment of unprocessed atmospheric nitrate contributions to streams. To date, few publications have documented substantial inputs of unprocessed atmospheric nitrate to streams outside of snowmelt [*Williard et al*., 2001; *Buda and DeWalle*, 2009; *Sebestyen et al*., 2014; *Wexler et al*., 2014].

2.1.2. Analytical Biases

Dual isotope techniques to evaluate unprocessed atmospheric nitrate export and N processing in catchments have evolved during the past decade. Natural abundance isotopic studies relied primarily on $\delta^{18}O$-NO_3^- to differentiate atmospheric and microbial sources in natural waters. However, sample preparation using silver nitrate with sealed glass tube combustion during analysis can result in abnormally high nitrification and low atmospheric $\delta^{18}O$ end-member values due to contamination [*Revesz and Böhlke*, 2002]. Additionally, high concentrations of dissolved organic matter can bias results of the silver nitrate method [*Chang et al*., 1999; *Casciotti et al*., 2002]. More recently, the bacterial denitrifier method has become a preferred and accepted approach for dual nitrate isotopic analysis; this method is not subject to the same biases as the combustion-based methods [*Sigman et al*., 2001; *Casciotti et al*., 2002]. *Xue et al*. [2010] compared $\delta^{18}O$-NO_3^- values in surface waters analyzed using both techniques, and concluded that the silver nitrate- and

denitrifier-derived results were highly correlated and generally statistically comparable. However, no precipitation samples were analyzed by *Xue et al*. [2010] and the range of δ^{18}O-NO_3^- values in their study was $-19‰$ to $+31‰$. It is unclear whether analysis of precipitation nitrate samples would show the same degree of correlation between analytical methods. Because of these potential differences, the analytical methods used by the studies considered in this meta-analysis are listed in Table 1.

To differentiate atmospheric and microbial N sources, δ^{18}O-NO_3^- has frequently been used as their ranges are relatively distinct. However, δ^{18}O-NO_3^- data from an increasing number of studies has widened the overall ranges of both microbial and atmospheric isotopic signatures, making δ^{18}O-based source apportionment more challenging. Uncertainties in source apportionment can be exacerbated when theoretical end-member isotopic values are accepted to be true rather than directly measured, as often occurs with respect to designation of the nitrification end-member value [*Michalski et al*., 2004]. Nitrification end-member values have been variously estimated using baseflow, soil water, or groundwater δ^{18}O-NO_3^- values, or from an "expected" isotope value [*Kendall et al*., 2007] based on assumed or measured δ^{18}O values of soil water and O_2 and the assumed ratio of oxygen atoms contributed from each during nitrification (Table 2), where

$$\delta^{18}\mathrm{O}-\mathrm{NO}_3^- = \frac{1}{3}\left(\delta^{18}\mathrm{O}-\mathrm{O}_2\right) + \frac{2}{3}\left(\delta^{18}\mathrm{O}-\mathrm{H}_2\mathrm{O}\right) \quad (2)$$

Such differences in the method of estimation can lead to substantial uncertainties in the nitrification end-member value (Figure 3). Direct measurement of nitrate isotopic composition for both precipitation and nitrification end-members provides a higher degree of certainty that apportionment values represent reasonable estimates of nitrate sources.

Adding to this uncertainty is the potential influence of abiotic oxygen exchange between nitrite and soil water during nitrification. Depending on the degree to which it occurs in forest soils, abiotic oxygen exchange may alter the δ^{18}O-NO_3^- value of the nitrification end-member [*Snider et al*., 2010], potentially erroneously inflating estimates of microbial source contributions to stream nitrate. However, it is unclear to what extent abiotic oxygen exchange occurs in natural settings, as this process has so far only been evaluated in laboratory settings and nitrite is typically not detectable in most natural waters. The absence of nitrite in most water implies that nitrite residence times are short [*Isobe et al*., 2012] and that nitrite uptake is a rate-limiting step in nitrification reactions; thus little or no isotopic fractionation and exchange should occur during nitrification. In addition, *Snider et al*. [2010] observed decreasing fractions of abiotic oxygen exchange with increasing net nitrification in laboratory incubation experiments. Spatial variability in net nitrification rates (both within and among catchments) may, therefore, also influence the degree to which this abiotic process affects microbial end-member δ^{18}O-NO_3^- values.

Source apportionment is further complicated by mass-dependent fractionation of δ^{18}O-NO_3^-, particularly during biological processes such as denitrification or coupled nitrification and denitrification. Such fractionating processes enrich the δ^{18}O of residual nitrate pools, thereby complicating data interpretation [*Kendall et al*., 2007]. As the fractionation due to biological transformation is often difficult to quantify and is not constant through time [*Koba et al*., 1997, 2012], the isotopic fractionation inherent in such biological processes must be considered in interpretations of dual nitrate isotope data. More recently, Δ^{17}O-NO_3^-—a mass-independent tracer of atmospheric nitrate—has been increasingly adopted in addition to δ^{18}O analysis. Atmospheric nitrate has positive Δ^{17}O values ($+20‰$ to $+30‰$), whereas microbial nitrate has a Δ^{17}O value of $0‰$ [*Michalski et al*., 2003]. Positive Δ^{17}O-NO_3^- values, therefore, indicate that some proportion of atmospheric nitrate is present in a sample. As Δ^{17}O is not subject to mass-dependent fractionation, the Δ^{17}O signature of the residual nitrate pool remains unchanged during fractionating processes such as assimilation and denitrification. This makes Δ^{17}O a conservative tracer of unprocessed atmospheric nitrate contributions to streams. One major advantage of combining δ^{18}O and Δ^{17}O analyses is the potential for a wealth of process-based information such an approach provides [*Michalski et al*., 2004]. For example, *Riha et al*. [2014] estimated approximately 10% greater contributions of unprocessed atmospheric nitrate in urban and suburban runoff using a δ^{18}O-based mixing model versus Δ^{17}O-based estimates. The overestimation based on δ^{18}O-NO_3^- values was attributed to enrichment of biological nitrate end-member values during mass-dependent fractionating processes such as denitrification and biological uptake. Whereas differences in atmospheric and stream δ^{18}O-NO_3^- values can be used to infer the extent and types of biological processing, Δ^{17}O-NO_3^- values provide information about direct contributions of unprocessed atmospheric nitrate to streams. The distinction between δ^{18}O and Δ^{17}O-based

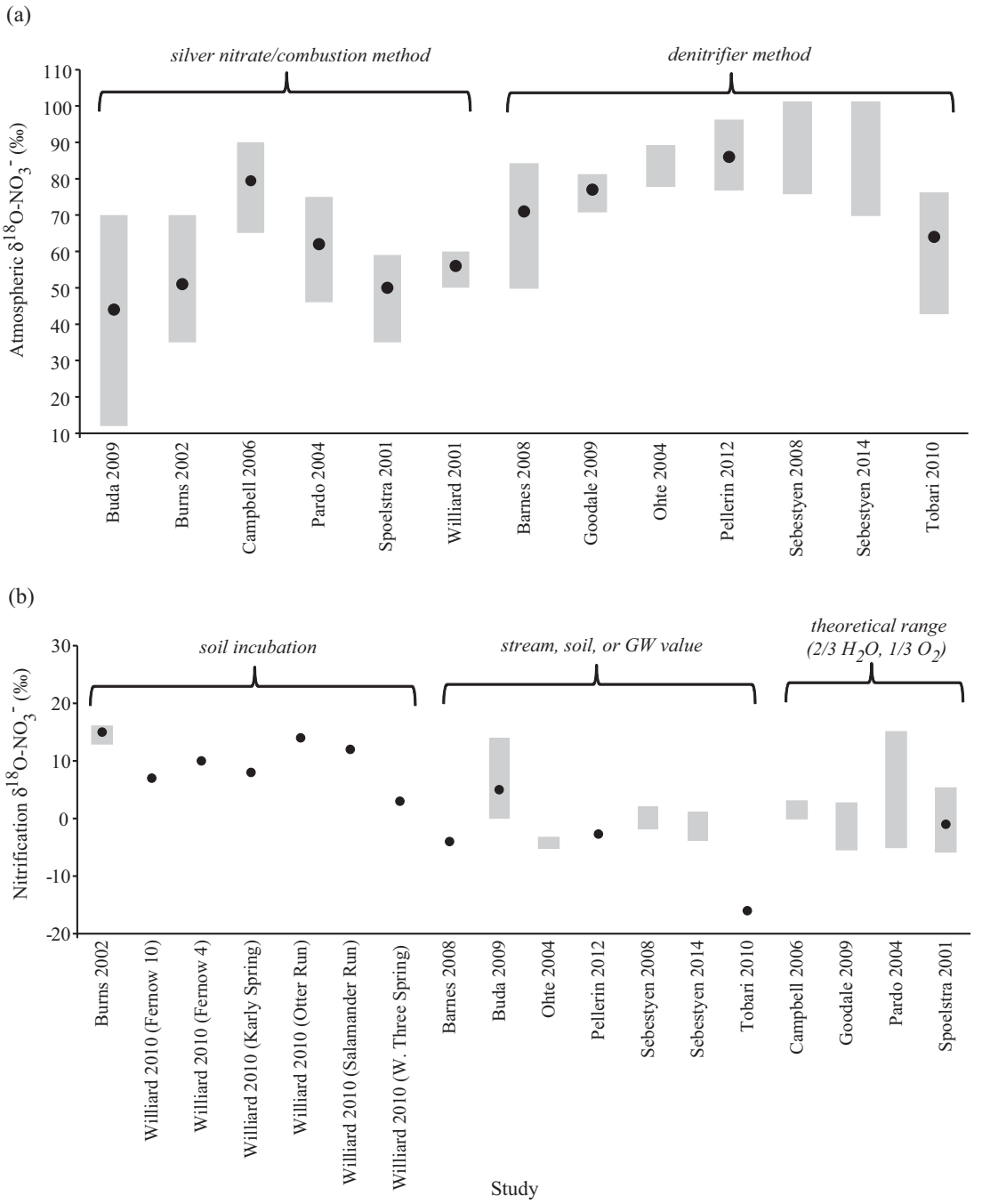

Figure 3. Estimated $\delta^{18}O\text{-}NO_3^-$ means (black dots) and ranges (shaded areas) for (a) atmospheric and (b) nitrification end-members using various analytical techniques. Studies using the silver nitrate/combustion method generally report lower atmospheric nitrate $\delta^{18}O$ values than studies using the denitrifier method. Soil incubation approaches to estimating the nitrification end-member $\delta^{18}O\text{-}NO_3^-$ value generally report higher values than studies that estimate the nitrification end-member value using a stream, soil, or groundwater $\delta^{18}O\text{-}NO_3^-$ value or that calculate a theoretical end-member value based on the assumption of two oxygen atoms contributed to the nitrate molecule from soil water and one oxygen contributed from O_2. The wide ranges of potential nitrification and atmospheric nitrate end-member values presented in some studies lead to considerable uncertainty in the calculated proportion of atmospheric nitrate in streams.

interpretations is subtle, yet important to consider as each provides unique information about ecosystem processes. In addition, the $\Delta^{17}O\text{-}NO_3^-$ approach circumvents a key source of uncertainty in the estimation of microbial nitrification end-member values arising from differences in analytical approaches (i.e., silver nitrate/combustion versus bacterial denitrifier methods), as the absence of mass-independent ^{17}O isotope enrichment in microbial nitrate sets this end-member $\Delta^{17}O$ value to zero.

As the $\Delta^{17}O\text{-}NO_3^-$ approach is relatively new and not implemented in many isotope laboratories, few studies have applied it to questions in catchment biogeochemistry. Based on $\Delta^{17}O\text{-}NO_3^-$ measurements in precipitation and discharge water (spring, lake, and stream water), *Tsunogai et al*. [2010] estimated that ~9% of deposited atmospheric nitrate was exported without biological processing. *Costa et al*. [2011] used $\Delta^{17}O\text{-}NO_3^-$ measurements in a northern hardwood forest to determine that on average, 9% of soil solution nitrate originated from atmospheric deposition. In a semiarid mixed conifer/sage scrub ecosystem, *Michalski et al*. [2004] reported large proportions of unprocessed atmospheric nitrate (20–40%) during stormflow, and smaller proportions (3–8%) in baseflow. They also quantified the difference in estimated atmospheric nitrate contributions to streams using both $\delta^{18}O$ and $\Delta^{17}O$ analyses. In that study, $\delta^{18}O$-based estimates ranged from 40% less to 10% more than estimated contributions based on $\Delta^{17}O$ analysis. The disparity between $\delta^{18}O$ and $\Delta^{17}O$-based estimates of atmospheric nitrate export demonstrates the importance of careful interpretation of $\delta^{18}O$ and $\Delta^{17}O$ data to ensure that conclusions about the influence of biological versus depositional processes are accurate.

2.2. Biological Drivers

2.2.1. Terrestrial N Processing

Most studies of atmospheric nitrate deposition to forested catchments have focused on the influence of biology, particularly uptake and cycling of atmospheric N by vegetation and microbes. Important insights have been gained from such work, including species-level responses to N deposition [*Templer and Dawson*, 2004; *Templer et al*., 2005; *McNeil et al*., 2007; *Clark and Tilman*, 2008], functional responses of microbial communities to atmospheric N inputs [*Tietema*, 1998; *Corre and Lamersdorf*, 2004; *Frey et al*., 2004], and a better appreciation of the spatially heterogeneous response of these biological drivers to atmospheric N deposition [*Lovett et al*., 2002; *McNeil et al*., 2007; *Costa et al*., 2011].

Forest characteristics, such as stand age and species composition, play important roles in N transport from terrestrial to aquatic systems [*Vitousek and Reiners*, 1975; *Lovett et al*., 2002, 2004]. However, among the few studies comparing N dynamics in catchments with differing forest type (e.g., coniferous versus deciduous), most have focused on nitrate concentrations rather than nitrate isotopes in throughfall, soil waters, or stream water. Catchment studies that rely on concentration measurements do not differentiate nitrate sources, processing of atmospheric N inputs, or effects of forest type on processing of atmospheric N inputs. In a comparison of N leaching in 21 deciduous and 37 coniferous forests across Europe, *Van der Salm et al*. [2007] found no effect of forest type on the relationship between N deposition and soil N leaching. Conversely, microbial nitrate production rates were nine times greater in a hardwood forest than a conifer forest at the Fernow Experimental Forest (West Virginia, USA), where the N deposition was ~12 kg ha^{-1} [*Kelly et al*., 2011]. However, neither study distinguished between atmospheric and within-catchment nitrate sources. The study of *Durka et al*. [1994] was one of the few to employ a dual nitrate isotope approach to examine unprocessed atmospheric nitrate export from coniferous forests. Lower proportions of atmospheric nitrate were observed in streams draining healthy Norway spruce plantations than in stands that were already in a deposition-induced state of decline [*Durka et al*., 1994]. Nonetheless, comparison to hardwood forests was not possible because their study did not include deciduous species.

In some cases, forest age may exert a strong influence on ecosystem retention of atmospheric inputs and the proportion of unprocessed atmospheric nitrate in streams. *Tobari et al*. [2010] observed greater proportions of unprocessed atmospheric nitrate in streams draining stands of Japanese cedar (*Cryptomeria japonica*) and cypress (*Chamaecyparis obtusa*) older than 25 years. Low total N uptake in younger stands led to higher nitrate concentrations and fractions of atmospheric nitrate deposition exported to streams, while proportions of atmospheric nitrate in streams were lower in younger stands due to greater contributions from nitrification [*Tobari et al*., 2010].

The nutrient demands of microbes and vegetation, as well as abiotic incorporation into soil organic matter, influence how atmospheric N inputs are cycled. Uptake and conversion of dissolved N from inorganic to organic forms by vegetation and microbes explains the high rates of nitrate retention in some forests [*Aber et al*., 1998], while other studies have demonstrated that the plasticity of microbial carbon (C) to N ratios (C:N) can exert significant control on ecosystem N dynamics [*Perakis et al*., 2005; *Taylor and Townsend*, 2010]. *Perakis et al*. [2005] calculated that the decrease in microbial biomass C:N from 8.4 to 4.8 following experimental N additions to a coastal old-growth forest in Chile would yield a 40% increase in soil organic

matter N storage. Other studies have also reported high rates of nitrate assimilation and sequestration in microbial biomass [*Davidson*, 1992; *Stark and Hart*, 1997], highlighting the importance of the overall N availability in catchments to nitrate retention in general, and retention of atmospheric N inputs in particular [*Ågren and Bosatta*, 1988].

Denitrification also influences catchment N retention and nitrate export to streams, and has been measured along subsurface flowpaths, as well as within streams and hyporheic zones [*Böhlke and Denver*, 1995; *Seitzinger et al*., 2006; *Inamdar et al*., 2009; *Osaka et al*., 2010; *Zarnetske et al*., 2011]. Denitrification is sensitive to the balance between hydrologic conditions and redox state, and can be minimal even when the supply of nitrate is ample [*Cirmo and McDonnell*, 1997; *Hedin et al*., 1998; *Vidon et al*., 2010]. *Hill et al*. [2000] reported greater denitrification in riparian subsurface sediments where nitrate-rich groundwater flowed through isolated pockets of organic matter, whereas low denitrification rates have been attributed to shorter water residence times and lower organic matter contents in coarser sediments [*Vidon and Hill*, 2004]. Thus, while vegetation and soil microbial communities consume nitrate, the relative importance of these biological controls can vary depending on catchment hydrologic factors.

The degree of biological processing varies with distance and depth along soil water and groundwater flowpaths [*Gold et al*., 2001; *Inamdar et al*., 2009]. Unprocessed atmospheric nitrate has been found in both shallow groundwater [*Nolan et al*., 2002; *Osaka et al*., 2010] and in the deeper groundwater of arid systems [*Michalski et al*., 2004; *Dejwakh et al*., 2012]. *Durka et al*. [1994] found unprocessed atmospheric nitrate in spring waters, indicating the presence of unprocessed atmospheric nitrate along groundwater flowpaths. *Osaka et al*. [2010] reported decreasing nitrate concentrations and increasing δ^{15}N-NO_3^- with depth in a headwater catchment, indicating greater denitrification along deeper flowpaths. Interestingly, δ^{15}N values of stream nitrate fell between those of the shallow and deep groundwater nitrate, suggesting mixing from two different flowpaths and the effect of denitrification on nitrate concentrations and isotope values in streams [*Koba et al*., 1997; *Osaka et al*., 2010].

2.2.2. In-Stream N Processing

In-stream uptake and processing strongly influences the amount of nitrate exported to the catchment outlet, and potentially the fraction of unprocessed atmospheric nitrate observed in the stream. *Sebestyen et al*. [2014] concluded that decreased in-stream nitrification coupled with greater heterotrophic nitrate uptake during autumn leaf fall contributed to declining nitrate concentrations in streams of a deciduous forest in Vermont. *Campbell et al*. [2002] reported stable proportions of atmospheric and microbial nitrate in stream water during summer snowmelt in an alpine forest, despite a reduction in stream nitrate concentrations. The decline in stream nitrate concentrations was partially attributed to in-stream uptake. However, differential elution of snowpack solutes and temporal variability in soil nitrate flushing also reduced stream nitrate concentration while maintaining the relatively constant proportions of nitrate sources in the stream.

The importance of in-stream uptake and processing on catchment-scale nitrate export is not limited to event or seasonal time scales but has been observed on decadal time scales [*Bernhardt et al*., 2005] and for several years following catastrophic disturbance [*Bernhardt et al*., 2003]. Longitudinal variability of in-stream processes (such as denitrification), coupled with spatially variable nitrate inputs from groundwater, can also affect the magnitude and sources of nitrate export observed at the catchment outlet [*Burns*, 1998]. Indeed, *Burns* [1998] showed that differential in-stream nitrate processing among catchments receiving similar atmospheric N deposition inputs could contribute to differences in stream nitrate concentrations. Thus, the complexity of interactions among terrestrial and aquatic N biogeochemical cycles influences catchment nitrate export in general and the proportion of unprocessed atmospheric nitrate in streams specifically.

2.2.3. Phase of N Deposition and Synchrony With Biological Processing

While the amount of atmospheric nitrate in wet deposition has often been implicated in the development of forest N saturation, the phase (wet versus dry) and timing of atmospheric nitrate inputs may influence the degree of biological cycling within catchments. In a study of dry nitrate deposition in Ohio, Pennsylvania, and New York, *Elliott et al*. [2009] reported positive correlations between stationary source nitrogen oxide (NO_x) emissions (e.g., electricity generation) and particulate nitrate concentrations during all seasons except summer. Preferential formation of particulate nitrate at lower temperatures, combined with

increased stationary source NO_x emission rates during colder months [*Elliott et al*., 2009], may cause higher rates of dry nitrate deposition across the northeastern United States during the dormant season. The ways in which this potentially significant source of N—dry deposition constitutes up to 40% of the total N deposition in some areas [*Elliott et al*., 2009]—interacts with hydrologic and climatic drivers may profoundly affect the degree to which atmospheric nitrate is biologically cycled or transported directly to streams.

Vegetation canopies are highly effective scavengers of dry N deposition, with nitric acid (HNO_3) vapor comprising nearly 50% of annual average atmospheric nitrate flux to canopies in the southeastern United States [*Lindberg et al*., 1986]. Dry deposition is a particularly important N source in western United States forests, where it dominates total N deposition and is scavenged (i.e., deposited onto leaf surfaces) with great efficiency by conifer-dominated stands [*Bytnerowicz and Fenn*, 1996; *Fenn et al*., 2003]. Such interactions between vegetation canopies and dry deposition often yield throughfall N inputs in excess of those observed in bulk deposition [*De Schrijver et al*., 2007], potentially altering the temporal dynamics of N deposition and stream nitrate export. Several studies have reported similar isotopic compositions of nitrate in rain and throughfall [*Kendall et al*., 1995; *Burns and Kendall*, 2002; *Osaka et al*., 2010].

Synchrony between atmospheric N deposition and biological uptake influences nitrate isotopic values in stream water. In the United States, dormant season hydrologic events associated with snowmelt runoff often contribute large proportions of unprocessed atmospheric nitrate to streams [*Spoelstra et al*., 2001; *Sebestyen et al*., 2008; *Goodale et al*., 2009]. Catchment-scale studies in monsoonal climates such as Japan also report increased proportions of unprocessed atmospheric nitrate in streams during winter, but overall nitrate export is greatest during the growing season, when production and consumption of microbial nitrate is also greatest [*Mitchell et al*., 1997; *Ohte et al*., 2010; *Fang et al*., 2011; *Nakamura et al*., 2011; *Ohte*, 2012; *Kohzu et al*., 2013; *Shi et al*., 2014]. As the growing season coincides with the rainy season in Japan, greater nitrate export observed during this season likely reflects the combined influence of increased microbial nitrate production and high water drainage [*Mitchell et al*., 1997; *Mitchell*, 2001]. In a study of forested catchments near Tokyo, *Tabayashi and Koba* [2011] reported higher stream nitrate concentrations and δ^{18}O-NO_3^- values in areas receiving elevated N deposition inputs. However, maximum δ^{18}O-NO_3^- values only reached $+6‰$, showing that nitrification sources dominated stream nitrate even in catchments with high stream nitrate concentrations. These studies point to increased stream nitrate concentrations during periods of greater microbial nitrate production (as regulated by factors such as soil temperature, moisture, and C and N availability [*Stark and Firestone*, 1995; *Stark*, 1996; *Taylor and Townsend*, 2010]), high atmospheric deposition rates, and peak precipitation inputs. Further investigations comparing δ^{15}N and δ^{18}O of nitrate in Asian, North American, and European catchments can elucidate the roles that synchrony among N deposition, biology, and hydrology play in determining the proportion of atmospheric nitrate observed in forest streams. For example, the coincidence of hydrologic events (e.g., monsoons) and peak seasonal uptake and denitrification activity in some catchments may result in greater atmospheric N processing prior to export. Conversely, short transit times of atmospheric deposition through forests during the rainy season or asynchrony between biological activity and hydrologic events (e.g., snowmelt) may preclude extensive biological processing and yield greater proportions of unprocessed atmospheric nitrate in streams.

Other studies have reported no seasonal trends in atmospheric nitrate export. *Pardo et al*. [2004] observed similar proportions of atmospheric nitrate in streams during both the winter and non-winter months in a mixed hardwood catchment in the northeastern United States. The authors attributed this pattern to short hydrologic residence times on steep hillslopes and significant storage capacity in well-mixed subsurface reservoirs that dampened seasonal differences in stream water nitrate isotopic signatures. *Cirmo and McDonnell* [1997] speculated that increased litter decomposition at the end of the growing season would create a significant dissolved inorganic N pool in soil waters, though such concentration increases were not observed during and after autumn leaf fall in a Vermont forest [*Sebestyen et al*., 2014]. Subsequent hydrologic flushing from that nitrification source during the dormant season may result in elevated stream nitrate concentrations [*Ohte*, 2012] but not necessarily increased proportions of unprocessed atmospheric nitrate. However, *Sebestyen et al*. [2014] reported a significant decline in stream nitrate concentrations during the end of the growing season, with assimilatory nitrate uptake and decreased rates of in-stream nitrification responsible for the retention of up to 72% of nitrate entering the stream.

2.3. Physical Drivers

A variety of physical factors influence unprocessed atmospheric nitrate contributions to streams in N-polluted forests. The hydrologic regime of a catchment and its landscape characteristics are particularly important drivers of nitrate transport dynamics.

2.3.1. Hydrologic Regime

Given the commonality across many studies of low proportions of unprocessed atmospheric nitrate in streams during baseflow (Figure 1 and Table 2), it is important to consider the influence of catchment hydrologic regime on biological processing of deposition inputs. If processing is more rapid than transport, then only minor contributions of unprocessed atmospheric nitrate to streams can result [*Hales et al*., 2007; *Osaka et al*., 2010]. *Helliwell et al*. [2007] suggested that greater soil water residence times in catchments with shallower slopes increase soil N pools and enhance nitrification, whereas rapid hydrologic routing likely outweighs N retention in steep catchments. Hydrologic residence times in old (4.1 million years) Hawaiian soils increased as saturated hydraulic conductivities decreased and soil thickness increased [*Lohse and Matson*, 2005]. Low hydraulic conductivities impeded nitrate leaching and thick soils were associated with increased biological uptake and inorganic N retention [*Lohse and Matson*, 2005]. In contrast, short hydrologic residence times in a younger (300 year old) Hawaiian soil led to rapid and large losses of added nitrate following precipitation events when limited contact time between soils and drainage waters prevented plant and microbial retention of added N [*Lohse and Matson*, 2005]. While their study did not apportion nitrate sources, their results demonstrate the potential for hydrologic residence times to influence the degree of nitrate retention and loss from catchments.

Water and nitrate can be quickly routed to streams along preferential flowpaths during rain and snowmelt events in some forests [*McGlynn et al*., 1999; *Sebestyen et al*., 2008] with the potential for elevated unprocessed atmospheric nitrate export. In other forests, water and nitrate contributed during storm events and snowmelt may rapidly move into groundwater, with delayed export to the stream [*Schiff et al*., 2002; *Pardo et al*., 2004], although this speculation has not been validated through measurement of nitrate isotopes along deeper subsurface flowpaths. *Burns and Kendall* [2002] reported small proportions of unprocessed atmospheric nitrate ($<$9%) in baseflow from streams draining two forested catchments in the Catskill Mountains (USA), but the occurrence of a storm event with a 10 year recurrence interval during the study resulted in large contributions of unprocessed atmospheric nitrate (55%) to stormflow. These results provide further evidence that variations in hydrologic flowpaths influence the connectivity of catchment areas to the stream and exert control on the export of unprocessed atmospheric nitrate. Similarly, elevated proportions of atmospheric nitrate in streams during stormflow relative to baseflow have been demonstrated in a number of isotope-based studies (Figure 1).

At several sites, the relationship between baseflow discharge rate and δ^{18}O-NO_3^- values is generally positive (Figure 4a), whereas the same catchments show a variety of patterns in δ^{18}O-NO_3^- values with increasing discharge during snowmelt/stormflow conditions (Figure 4b). For example, *Sebestyen et al*. [2008] and *Pellerin et al*. [2012] attributed high nitrate concentrations and δ^{18}O-NO_3^- values during relatively low peak flows to melting of snow in the stream channel and saturation overland flow (SOF) in near-stream areas during two snowmelt events at Sleepers River. Such direct routing of high-concentration meltwater resulted in high proportions of unprocessed atmospheric nitrate (up to 48%) during early snowmelt, with decreasing proportions of unprocessed atmospheric nitrate in the stream thereafter [*Sebestyen et al*., 2008]. In contrast to the atmospheric nitrate-streamflow dynamics observed at Sleepers River, other studies have shown increasing stream nitrate concentrations and δ^{18}O values with increasing discharge during hydrologic events [*Williard et al*., 2001; *Piatek et al*., 2005], although the relationships are not always statistically significant (Figure 4b). Such patterns have been attributed to flushing of accumulated soil N with increasing stormflow [*Creed et al*., 1996; *Williard et al*., 2001; *Piatek et al*., 2005]. Although *Piatek et al*. [2005] and *Williard et al*. [2001] observed higher δ^{18}O-NO_3^- values during snowmelt/stormflows, the reported δ^{18}O-NO_3^- values in these studies fall within the theoretical source range of microbial nitrate ($-5‰$ to $+16‰$; [*Kendall et al*., 2007]). Thus, while higher stream δ^{18}O-NO_3^- values during hydrologic events may indicate flushing of atmospheric nitrate to streams, most nitrate mobilized by increasing discharge was contributed by nitrification. This is also the case during baseflow for all catchments shown in Figure 4a. It is noteworthy that stream δ^{18}O-NO_3^- values appear to increase with increasing baseflow at all sites in Figure 4a, however, δ^{18}O-NO_3^-

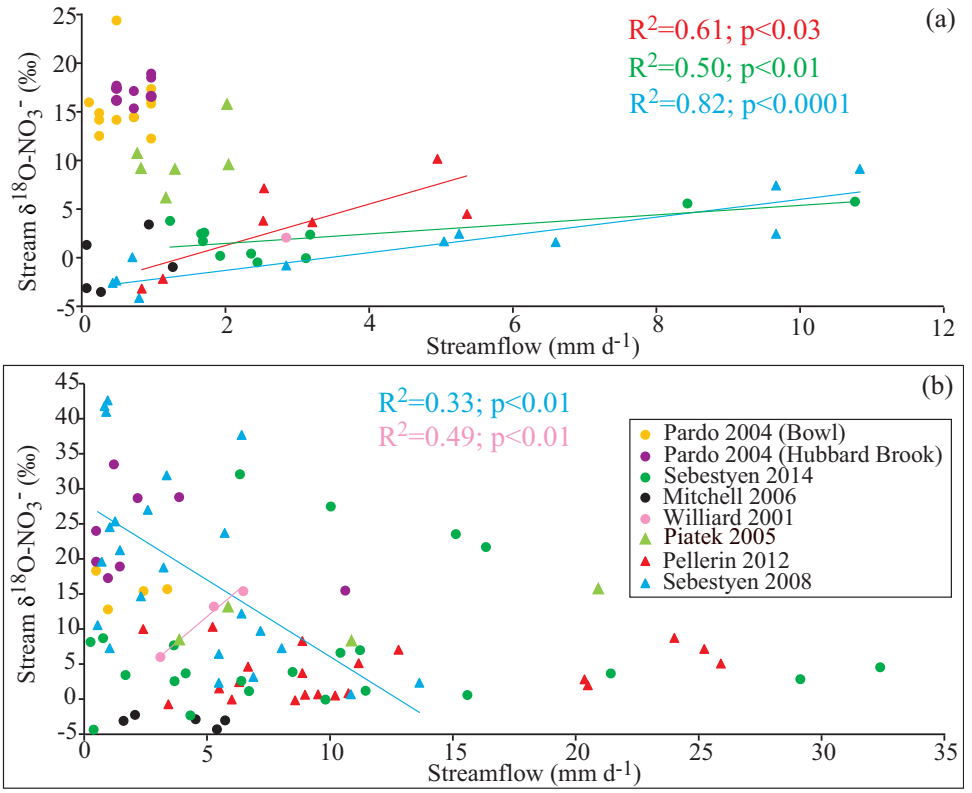

Figure 4. Streamflow versus stream $\delta^{18}O\text{-}NO_3^-$ values during (a) base flow and (b) stormflow/snowmelt events at multiple sites. Circles represent rainfall events and triangles represent snowmelt events. Data were obtained either from published tables or were extracted from published figures using g3data software (http://frantz.fi/software/g3data.php) [*Bauer and Reynolds*, 2008; *Snider et al*., 2010]. Direct comparison of patterns across studies should be done with caution, as differences in the analytical method used for $\delta^{18}O\text{-}NO_3^-$ determination (i.e., silver nitrate/combustion method versus denitrifier method) may confound direct comparisons. Linear fit lines, R^2 values, and p values are shown only for studies with statistically significant relationships.

values predominantly in the nitrification source range indicate that proportions of unprocessed atmospheric nitrate in streams are small under baseflow.

Our understanding of hydrologic controls on catchment N export has been highly influenced by coupled hydroecological models [*Creed et al*., 1996; *Creed and Band*, 1998] that have advanced our understanding of nitrate transport during hydrologic events (i.e., snowmelt and rainfall) when stream nitrate responses are most dynamic. Runoff processes include some combination of overland flow and subsurface stormflow [*Dunne and Black*, 1970, 1971; *Hibbert and Troendle*, 1988], and the hydrologic and biogeochemical processes that control atmospheric nitrate export are rarely discernible from measurements at the catchment outlet alone. As such, the catchment sciences community still faces the challenge of elucidating similarities and differences among rainfall-runoff processes and N deposition-runoff dynamics. This represents a striking example of the double paradox in catchment hydrology [*Kirchner*, 2003], wherein stream flow and chemistry rapidly respond to precipitation inputs, but water from that precipitation event is not a large component of stormflow. However, precipitation nitrate may constitute a large proportion of stream nitrate during such stormflows. Making progress on this front is particularly important for better constraining mechanisms responsible for the low proportions of unprocessed atmospheric nitrate in streams during baseflow and dynamic variation during stormflow.

2.3.2. Landscape Characteristics

While catchment hydrology and topography are important drivers of overall forest nitrate export, the factors that affect unprocessed atmospheric nitrate delivery to streams are more nuanced. The hydrologic regime of a catchment is often closely related to landscape characteristics, including geology, pedology, and topography [*Dunne and Black*, 1970; *Jencso et al*., 2009]. Topography may be a first-order control on

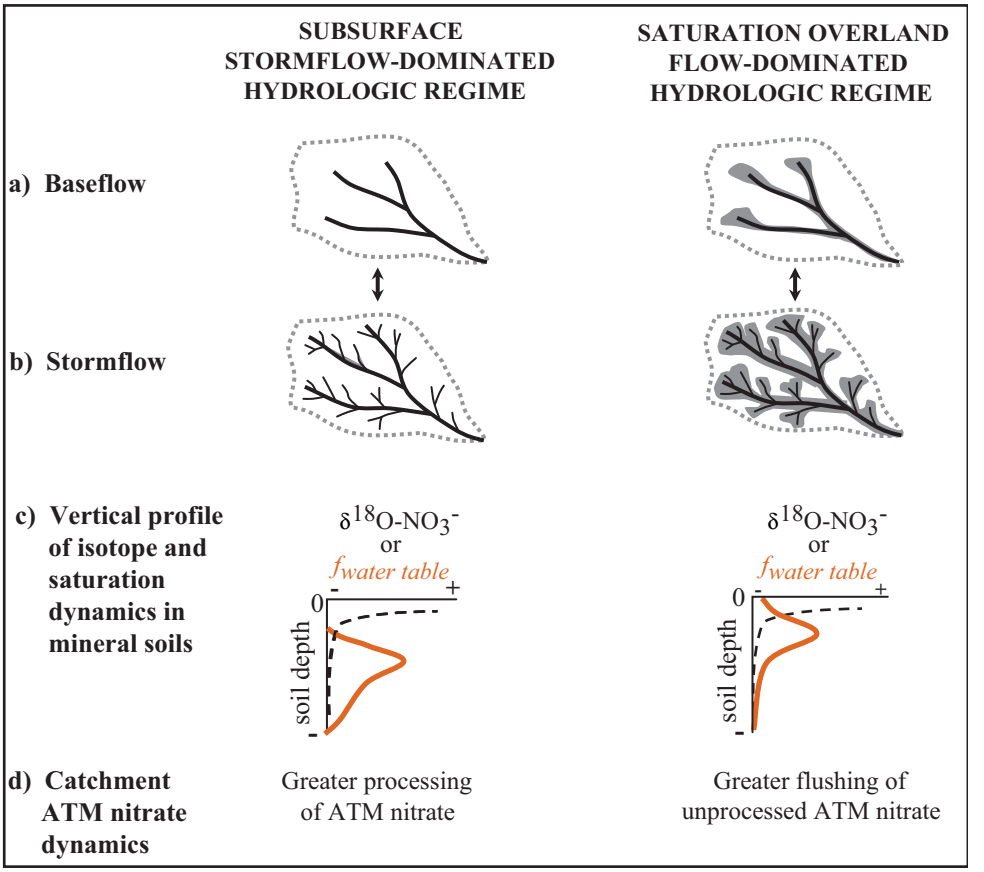

Figure 5. Conceptual model of hydrological and topographic regulation of catchment-scale atmospheric nitrate export. (a) During base flow, subsurface stormflow (SSF)-dominated systems maintain little hydrologic connectivity between hillslope surficial soils and streams, whereas saturation overland flow (SOF)-dominated systems maintain more extensive hydrologic connectivity between catchment areas and streams. (b) Under stormflow conditions, channel networks and hydrologic connectivity of surficial soils to streams expand from topographic lows and near-stream areas in SSF-dominated catchments; larger areas of hydrologic connectivity to surficial soils and source areas develop during storms in SOF-dominated systems. (c) $\delta^{18}O\text{-}NO_3^-$ reflects the proportion of unprocessed atmospheric nitrate in soils; under baseflow conditions, $\delta^{18}O\text{-}NO_3^-$ decreases with soil depth in both SSF- and SOF-dominated systems (dashed line). However, the degree of atmospheric nitrate flushing from upper soil layers to streams during storms depends on the dominant hydrologic regime of the catchment and the depth of the water table (solid orange line which represents the frequency distribution of and zone over which the water table fluctuates within a soil profile). In SSF-dominated systems, the water table does not intersect the land surface and also may not intersect surficial soils (i.e., frequency goes to zero), keeping atmospheric nitrate in upper soil layers hydrologically disconnected from the stream. In SOF-dominated systems, the water table may periodically intersect the land surface during stormflow events, resulting in SOF and flushing of atmospheric nitrate in upper soil layers to the stream. The vertical $\delta^{18}O\text{-}NO_3^-$ profile is therefore particularly dynamic in SOF-dominated systems. As the water table intersects surficial soils, $\delta^{18}O\text{-}NO_3^-$ values temporarily decrease as microbial nitrate from deeper soil layers is transported upward and atmospheric nitrate is flushed to the stream. Subsequent atmospheric deposition inputs gradually increase the $\delta^{18}O\text{-}NO_3^-$ values of upper soil layers again. These saturation and isotope dynamics are expected to be particularly relevant in flatter near-stream areas.

source areas of water that affect streamflow variation, meaning that landform acts as the primary determinant of streamflow characteristics [*Dunne and Black*, 1970; *Jencso et al*., 2009]. Topographic characteristics such as slope steepness and aspect, upslope accumulated area (UAA), bedrock and soil type, and soil thickness influence water and N storage and movement [*Creed et al*., 1996; *Creed and Band*, 1998; *Lohse and Matson*, 2005; *Jencso et al*., 2009; *Speiran*, 2010]. Topographic influences on the hydrologic storage capacity of various reservoirs (e.g., in bedrock, riparian areas, and on hillslopes) may also affect the degree of atmospheric nitrate processing by controlling water transit times and biological uptake and cycling [*Inamdar et al*., 2009]. As biological processing resets the $\delta^{18}O$ of atmospheric nitrate from a range of $+45$ to $+100‰$ to the range of -10 to $+15‰$, the residence times of water in various catchment reservoirs can influence the isotopic values of stream nitrate [*Pardo et al*., 2004; *Hales et al*., 2007; *Osaka et al*., 2010]. For example, landscape and soil characteristics that promote rapid water movement facilitate greater unprocessed atmospheric nitrate delivery to streams in some catchments [*Durka et al*., 1994]. Similarly, water and nitrate

rapidly flow over exposed rock surfaces, which has resulted in greater unprocessed atmospheric nitrate export in some cases [*Curtis et al*., 2011]. Conversely, nitrate may be stored in groundwater for longer periods than in shallow soils, potentially influencing the timing of nitrate export to streams while allowing more time for microbial processing of atmospheric inputs [*Burns et al*., 1998; *Schiff et al*., 2002; *Pardo et al*., 2004].

Interactions between catchment topography and hydrologic regime are highly dynamic through space and time, as variations in seasonal and event-scale precipitation cause expansion or contraction of source areas of stream water [*Dunne and Black*, 1970, 1971]. The concepts of variable source areas and spatiotemporal heterogeneities of hillslope-riparian-stream connectivity have important implications for delivery of unprocessed atmospheric nitrate to streams. For example, areas of topographic concavity (e.g., convergent hillslope hollows) may have more persistent connectivity to streams and greater influence on the isotopic composition of stream nitrate than areas of topographic convexity (e.g., tops of slopes). Topographic lows in near-stream areas (e.g., wetlands) often have low nitrate concentrations during baseflow and high denitrification rates due to greater soil water content and C-rich sediments [*Groffman and Tiedje*, 1989; *Gold et al*., 2001; *Ogawa et al*., 2006; *Inamdar et al*., 2009]. Conversely, *Durka et al*. [1994] reported greater proportions of unprocessed atmospheric nitrate in streams draining forests with waterlogged soils, demonstrating direct routing of unprocessed atmospheric nitrate to streams via saturation-excess overland flow. Still other studies have reported considerable differences in total nitrate export but only minor differences in the proportion of unprocessed atmospheric nitrate in streams draining catchments with widely differing topographies [*Schiff et al*., 2002].

3. Knowledge Gaps and Next Steps With Respect to Future Experiments, Observations, and Interdisciplinary Research

A better conceptual, functional, and observational understanding of the factors regulating atmospheric nitrate transfer to streams is needed. While studies on the importance of biological factors are prevalent in the N saturation literature, less research has focused on catchment hydrology and landscape topography as related to N processing and transport. A fundamental challenge of catchment-scale biogeochemistry is the integration of hydrologic processes and landscape form and function into conceptual and computational models. In light of this need, we present a conceptual model of hydrologic and topographic regulation of catchment-scale atmospheric nitrate export (Figure 5). Additionally, in order to establish a more comprehensive view of "catchment processes," below we suggest some potential areas of future research.

3.1. High Resolution Temporal and Spatial Sampling of Nitrate Isotopes

Hydrologic connectivity and N transport between terrestrial and aquatic systems can be highly transient in space and time, creating "hotspots" and "hot moments" within catchments [*Vidon et al*., 2010]. Frequent, spatially intensive sampling for isotopic analysis of N sources and sinks across a range of hydrologic conditions is critical to advancing our understanding of the influence of hydrologic and topographic factors on atmospheric N transport. Given a variety of analytical advantages, the bacterial denitrifier method for nitrate isotope analysis makes such high resolution sampling and analysis viable.

3.2. The Importance of Catchment Processes and Dynamics

Heterogeneities of flowpaths through landscapes result in some areas serving as nutrient sources and some as sinks [*Fortescue*, 1980; *Sebestyen et al*., 2008; *Inamdar et al*., 2009]. Investigating the relative magnitude of N transport along various flowpaths and the biological processes taking place along them would better constrain the importance of biological versus physical drivers in unprocessed atmospheric nitrate delivery to streams. Additional research on the ways that these biological and physical dynamics differ under baseflow and event conditions would provide critical details about the processes by which catchment hydrology and topography affect unprocessed atmospheric nitrate export.

3.3. Models to Conceptualize and Parameterize Distinctions Among Nitrate and Water Sources

Catchment-scale hydrologic models are powerful tools for hypothesis testing and evaluating the sensitivity of ecosystem responses to changes in hydrologic parameters. In order to better understand how hydrology, topography, and biogeochemistry interact across a range of spatial and temporal scales to influence the transport and fate of atmospheric N, new and more integrated models are needed. In addition, existing

spatially explicit hydroecological process models such as the Regional Hydro-Ecologic Simulation System (RHESSys) [*Band et al*., 1993; *Tague and Band*, 2004] are also useful for examining catchment-scale N dynamics. Although most existing biogeochemical models do not explicitly simulate isotope dynamics within ecosystem compartments, coupling mass-balance models with software packages such as the Non-Equilibrium Stable Isotope Simulator (NESIS) [*Rastetter et al*., 2005] may facilitate such calculations. Future biogeochemical models could also emphasize the incorporation of parameters that capture the spatiotemporal influence of landscape topography and vegetation on both water and N dynamics, as well as the incorporation of biogeochemical and hydrologic isotope parameters.

4. Implications

Identifying the factors that most influence atmospheric nitrate processing in and transport through forests has important implications for the study and management of these resources. The concept of N saturation as a condition where ecosystem N supply exceeds biological demand may be too simplistic [*Lovett and Goodale*, 2011], given the overwhelming nitrification source of most nitrate in stream waters (Figure 1 and Table 2). Indeed, observations that demonstrate the greatest percentage of unprocessed atmospheric nitrate in streams during periods of hydrologic extremes (e.g., snowmelt and storm events) show a direct role of catchment hydrology and, perhaps less directly, topography in atmospheric nitrate export to streams. Coupled isotopic analyses of water and nitrate can also inform the parameterization of hydrologic models, as the pathways and processing of the two may not always be the same [*Sebestyen et al*., 2008, 2014; *Buda and DeWalle*, 2009; *Osaka et al*., 2010].

With respect to land management, understanding how catchment hydrology affects stream nitrate sources: (1) unequivocally proves that atmospheric pollutants directly affect forests and streams, (2) may inform practices to maximize the potential for N retention through biological uptake or denitrification within landscapes, and (3) offers valuable information to regulators and management agencies when evaluating critical loads, nutrient criteria, and emission regulations. In addition, the importance of seasonal variability in hydrologic regime (e.g., snowmelt and monsoon events) on both total N export, as well as the delivery of unprocessed atmospheric nitrate to streams, can help focus management efforts to mitigate the effects of episodic acidification during those times when N export is likely to be greatest.

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