

## **Report for 2005NY64B: Export of atmospheric nitrogen deposition from forests at the top of the Susquehanna watershed**

### Publications

- There are no reported publications resulting from this project.

### Report Follows

## ***Export of Atmospheric Nitrogen Deposition from Forests at the top of the Susquehanna Watershed.***

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**Abstract:** We proposed that chronic exposure to some of the highest rates of atmospheric  $\text{NO}_3^-$  deposition in the country might have led to elevated  $\text{NO}_3^-$  exports from central NY forests at the top of the Susquehanna Basin, and to decreased uptake of atmospheric  $\text{NO}_3^-$  by plants and microbes in these ecosystems. Monthly sampling of stream N chemistry in 16 small streams over March 2005 to February 2006 and dual isotope analysis ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of select stream  $\text{NO}_3^-$  samples suggests that contrary to expectations, central NY forests retained the vast majority (89-99%) of atmospheric N deposition. Estimated annual stream export of  $\text{NO}_3\text{-N}$  from wholly forested catchments was 0.1 to 0.7 kg N ha<sup>-1</sup> y<sup>-1</sup>, of which direct contributions of atmospheric  $\text{NO}_3^-$  were small (4-20% of annual export) and confined to the snowmelt period. The apparent contribution of atmospheric  $\text{NO}_3^-$  during the March 2005 snowmelt sampling (11 to 59% of stream  $\text{NO}_3^-$ ) appears to be an unusually high delivery for intact forest ecosystems. Despite the low estimated annual  $\text{NO}_3^-$  export, summer  $\text{NO}_3^-$  concentrations were exceptionally high compared to other Northeastern streams. Seasonal patterns of  $\text{NO}_3^-$  concentration (summer peaks, spring and fall minima) were contrary to most other snow-dominated catchments, for reasons that can only be speculated at present, but may provide useful information about controls on N exports from these catchments.

## **Statement of Critical Regional or State Water Quality Problem:**

This work addressed several priority research topics identified by the NY Nonpoint Source Coordinating Committee for FY2005, with particular emphasis on the goal to “Improve understanding of the sources and impact of nutrients including the significance of atmospheric sources and deposition.”

## **Introduction**

The Susquehanna River supplies about three-quarters of the nitrogen (N) delivered annually to Chesapeake Bay. Primary productivity in the Chesapeake Bay is nitrogen limited, and so the added N drives processes of eutrophication and subsequent hypoxia. In turn, these conditions impact seagrass beds and shellfish populations and other indicators of coastal ecosystem health. The majority of the N inputs to the Susquehanna watershed are from agricultural sources, including fertilizer (15%), N-fixing crops (27%), and import of animal feed, yet atmospheric deposition of fixed N (“N deposition”) provides a major contribution (27%) to the watershed’s total N loading (Boyer et al. 2002).

Two-thirds of the Susquehanna basin is in forest land cover, for which atmospheric deposition provides virtually all of the N inputs. In forested catchments, N deposition can lead to acidification of soils and surface waters, nutrient imbalances in vegetation, and decreased biodiversity (Aber et al. 1998, Driscoll et al. 2002). Furthermore, the delivery of exported N downstream can contribute to coastal eutrophication (Howarth et al. 2000). The New York portion of the Susquehanna Basin receives some of the highest rates of N deposition in the country, with total (wet + dry) inorganic N deposition exceeding  $10 \text{ kg N ha}^{-1} \text{ y}^{-1}$  (Butler & Likens 1995, Butler et al. 2003, Sheeder et al. 2002). Recent syntheses of the effects of N deposition on temperate forests indicate that stream  $\text{NO}_3\text{-N}$  exports often increase sharply as N deposition increases above a threshold of approximately  $8 \text{ kg ha}^{-1} \text{ y}^{-1}$  (Aber et al. 2003). However, variability in stream N export increases as well; that is, some, but not all watersheds increase N exports with increasing N inputs. Variability among watersheds receiving comparable rates of N deposition can be quite large, with stream inorganic N exports ranging from 2% to 50% of inorganic N inputs (e.g., Lovett et al. 2000, Goodale et al. 2000). Factors driving variation among watersheds may include differences in tree species composition (Lovett et al. 2000), past land-use history (Goodale et al. 2000), and variation in hydrologic flowpaths across watersheds or through time (Creed & Band 1998). Forests of the Adirondacks and Catskills have the highest N export of forests in the Northeast, yet even basic surveys of N export from forested catchments in the New York portion of the Susquehanna basin had been lacking. Uncertainty over the magnitude and causes of forest export of N derived from atmospheric deposition has been a major source of uncertainty in quantification of nonpoint source N loading for the upper Susquehanna watershed. The North American Nitrogen Center (NANC, [www.eeb.cornell.edu/biogeo/nanc](http://www.eeb.cornell.edu/biogeo/nanc)) has identified improved understanding of the roles of atmospheric N deposition and forest retention of N deposition in the Susquehanna Basin as a major focus for needed research.

This project obtained information on the quantity and immediate source of N exported from forested catchments at the top of the Susquehanna Basin, a region where human activities have increased rates of N deposition to levels ~8-10 times greater than those occurring during preindustrial conditions. Monthly surveys of stream N concentrations from 16 small forested catchments allowed estimation of landscape variation in N export. In addition, this project used

the power of stable isotopes ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) to estimate the direct contributions of atmospheric deposition of  $\text{NO}_3^-$  to stream  $\text{NO}_3^-$  export from these forests. The isotopic signatures of both nitrogen ( $\delta^{15}\text{N}$ ) and oxygen ( $\delta^{18}\text{O}$ ) differ in nitrate derived from various sources. The  $\delta^{18}\text{O}$  signature of  $\text{NO}_3^-$  is particularly useful for discriminating between atmospheric-derived  $\text{NO}_3^-$  and  $\text{NO}_3^-$  that has been cycled by microbes in soils or sediments (Durka et al. 1994, Kendall 1998, Spoelstra et al. 2001, Williard et al. 2001, Burns & Kendall 2002, Pardo et al. 2004).

The overarching hypothesis tested here is that chronic exposure to highly elevated quantities of atmospheric N deposition has led forests of the Upper Susquehanna region toward N saturation. Hence, we expected that:

(H1) Watershed N exports balance a large fraction of N inputs from deposition, and

(H2) A large fraction of atmospheric  $\text{NO}_3^-$  passes directly through the soil without uptake by plants or microbes.

We tested the first hypothesis by measuring monthly stream N concentrations, estimating stream N exports, and comparing these fluxes to N loading in deposition. This approach focuses on the mass balance between atmospheric inputs and hydrologic losses, allowing some consideration for internal cycling of atmospheric N. We tested the second hypothesis by determining the dual isotopic signature of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) in stream water and comparing it to the signature of  $\text{NO}_3^-$  in wet deposition. This approach focuses on discerning the amount of atmospheric  $\text{NO}_3^-$  that passes directly to the stream without any microbial processing. Specific objectives include:

- 1) Quantify forest N balance for a range of forested catchments in the Upper Susquehanna Basin.
- 2) Identify the direct contributions of atmospheric  $\text{NO}_3^-$  deposition to forest N export through use of the  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  signal of exported  $\text{NO}_3^-$ .

## **Methods**

**Site Description.** Landscape level variation in forest export of atmospheric N deposition was assessed through monthly surveys of stream N concentrations ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and DON) in 16 mostly first-order streams (Table 1). These streams are located within 20 km of Ithaca, NY (42.48 °N, 76.47 °W), and within 25 km of the Connecticut Hill atmospheric deposition monitoring site (CTH110, 42.40 °N, 76.65 °W, 501 m elevation), site CTH110 within EPA's Clean Air Status and Trends Network. All streams have wholly forested catchments free from human habitation or paved roads, although there may be some contributions from agriculture to the upper part of the catchment of stream at the Connecticut Hill deposition station (#16, IES). All streams are within the Susquehanna Basin except for the Connecticut Hill station, which drains north into the Finger Lakes and the St. Lawrence system.

**Climate and Deposition.** Mean (1961-1990) annual temperature at Ithaca, NY is 7.7 °C, with mean monthly temperatures ranging from -5.8 °C in January to 20.3 °C in July. Annual precipitation averages 899 mm/yr, with greater mean monthly precipitation in summer (80-96 mm/month) than winter (46-65 mm/month).

Atmospheric deposition has been monitored continuously at the Connecticut Hill air pollution station since 1978 on a daily or event basis, and the atmospheric concentration of  $\text{HNO}_3$  and fine particulate  $\text{NH}_4^+$  and  $\text{NO}_3^-$  has been measured weekly since 1987 (Butler & Likens 1995). The sum of these forms of atmospheric deposition averaged about 10 kg N ha<sup>-1</sup> y<sup>-1</sup> in the early 1990s,

decreasing to about 8.5 kg N ha<sup>-1</sup> y<sup>-1</sup> in the late 1990s and early 2000s (Butler & Likens 1995, CASTNet online: [www.epa.gov/castnet/sites/cth110.html](http://www.epa.gov/castnet/sites/cth110.html)). Wet deposition of NO<sub>3</sub><sup>-</sup> makes up 3.2 kg N ha<sup>-1</sup> y<sup>-1</sup> of this total (2000-2004; <http://nadp.sws.uiuc.edu/nadpdata/>).

Table 1: Stream abbreviation, name and general location, and GPS location.

Abbreviation	Stream	Lat. (°N), Long. (°W)
1. CYT	Unnamed (Cayutaville Rd., CT Hill State Game Mgt. Area)	42.38742, 76.69048
2. SWN	Unnamed (Swan Rd., CT Hill State Game Mgt. Area)	42.31928, 76.71058
3. UCC	Upper Carter Creek (CT Hill State Game Mgt. Area)	
4. WCC	West fork, Carter Creek (CT Hill State Game Mgt. Area)	42.34632, 76.66477
5. ECC	East fork, Carter Creek (CT Hill State Game Mgt. Area)	42.34421, 76.66002
6. CNA	Unnamed (Cornell Natural Area, Connecticut Hill)	
7. WOV	Unnamed (west fork, Overlook Trail, Rt. 224)	
8. EOY	Unnamed (east fork, Overlook Trail, Rt. 224)	42.25241, 76.64994
9. PYN	Pine Creek (Arnot Forest)	42.27222, 76.63621
10. BAN	Banfield Creek (Arnot Forest)	42.27534, 76.64227
11. MIH	Michigan Hollow (Michigan Hollow Rd., Danby State Forest)	42.29859, 76.48425
12. EMH	Unnamed (Eastman Hill, Coddington Rd.)	42.33775, 76.39951
13. HPT	Unnamed (Honeypot Rd., Shindagan Hollow State Forest)	42.31672, 76.31396
14. BRY	Unnamed (Braley Rd., Shindagan Hollow State Forest)	42.32413, 76.35123
15. BMT	Unnamed (Bald Mountain, Shindagan Hollow State Forest)	42.34045, 76.35107
16. IES	Unnamed (CT Hill Air Monitoring Station / Institute of Ecosystem Studies)	

The isotopic composition of atmospheric N deposition to this site is being measured through a NYSERDA-funded project led by Elizabeth Boyer (Univ. California Berkeley) and Carol Kendall (USGS, Menlo Park, CA), with work still in progress as of June 2006.

**Vegetation and Soil.** Forests are composed of mixed hardwood species including red oak (*Quercus rubra*), sugar and red maple (*Acer saccharum* and *A. rubrum*), white ash (*Fraxinus americana*), basswood (*Tilia americana*), American beech (*Fagus grandifolia*), and black birch (*Betula lenta*) with occasional inclusion of some conifers, including eastern hemlock (*Tsuga canadensis*) and white pine (*Pinus strobus*) or planted red pine (*P. resinosa*). Most forests are second-growth, re-grown after harvest or cultivation ~60-100 years ago. Two of the catchments (BAN – Banfield Creek, and BRY – Braley Rd.) included recent partial harvest. Soils are mostly inceptisols (Dystrochrepts and Fragiochrepts) developed in glacial till composed largely of locally transported Devonian shales.

**Field Methods.** Stream samples were collected monthly from March 2005 to February 2006 from 15 small streams, with a 16<sup>th</sup> stream from the Connecticut Hill atmospheric deposition site added in June 2005. Sampling dates targeted the middle of each month, although sampling was usually delayed when coinciding with high-flow events. Water samples were filtered with Luerlok, 60 mL polypropylene syringes in the field through Whatman 0.7 μm pre-combusted glass fiber filters into six sample bottles designated for NO<sub>3</sub><sup>-</sup> (30 mL), NH<sub>4</sub><sup>+</sup> (2 × 30 mL opaque polyethylene bottles), DOC and DON (60 mL high-density polyethylene bottles), and dual-isotope NO<sub>3</sub><sup>-</sup> analysis (60 mL) analyses, as well as an archive sample (60 mL).

**Analytical Methods.** Ammonium was analyzed within 24 hours of return from the field using the sensitive fluorometric method (Holmes et al. 1999) with a Turner Designs Aquafluor. The rest of the samples were frozen until analyses up to 9 months later. Nitrate, chloride, and sulfate

were measured on thawed samples using a Dionex ion chromatograph. After acidifying and sparging to remove dissolved CO<sub>2</sub>, dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured using high-temperature oxidation with a platinum catalyst using a Shimadzu TOC-V analyzer. Dissolved organic nitrogen was calculated by difference as DON = TDN – (NO<sub>3</sub><sup>-</sup>-N + NH<sub>4</sub><sup>+</sup>-N).

Samples for simultaneous analysis of δ<sup>15</sup>N and δ<sup>18</sup>O of NO<sub>3</sub><sup>-</sup> were shipped frozen to the Casciotti lab at the Woods Hole Oceanographic Institution for separation and analysis using the microbial denitrifier method (Sigman et al. 2001, Casciotti et al. 2002). Analytical cost precluded dual isotope analysis of all streams by month combinations. To maximize characterization of spatial and temporal patterns of δ<sup>15</sup>N and δ<sup>18</sup>O of NO<sub>3</sub><sup>-</sup>, we selected two months (March, July) to be analyzed for 9 of the 16 streams, and two streams to be analyzed for most months. March and July 2005 were chosen for the cross-stream comparisons to represent snowmelt and growing-season conditions, respectively. Dual isotope analyses were conducted for most months for two streams – Pine Creek, Arnot Forest (PYN) and West Fork Carter Creek, Connecticut Hill State Game Management Area (WCC) – for all months except for those autumn samples where NO<sub>3</sub><sup>-</sup> concentrations were too low (<14 μg N/L) to conduct the analyses (Oct. for WCC and Oct., Nov., and Dec. for PYN).

Estimates of N Flux and Retention. Stream N export was estimated for the 15 streams with a year’s worth of monthly stream chemistry by combining these chemistry measurements with measurements of monthly discharge at Fall Creek near Ithaca. With a catchment of 326 km<sup>2</sup>, Fall Creek is many times larger than the streams sampled here, but is the smallest stream nearby with a USGS gauge. Nitrogen retention was estimated by comparing these estimates of N export to measurements of atmospheric N deposition to the region, obtained for the Connecticut Hill air pollution site for 2001-2004 (<http://nadp.sws.uiuc.edu/nadpdata/>).

Isotopic Separation of Nitrate Sources. The contribution of atmospheric NO<sub>3</sub><sup>-</sup> to stream NO<sub>3</sub><sup>-</sup> export was estimated through use of δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values, assuming that the observed stream δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> values were a proportional mix of atmospheric and microbial-derived NO<sub>3</sub><sup>-</sup>. Atmospheric values of δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> in the Northeast US and Southeast Canada typically fall ~50-60‰. By contrast, microbially cycled nitrate is expected to have δ<sup>18</sup>O values around -5 to 2‰, based on the assumption that one of the three oxygen atoms in NO<sub>3</sub><sup>-</sup> are derived from atmospheric O<sub>2</sub> (δ<sup>18</sup>O = 23.5‰) and two are from soil water (δ<sup>18</sup>O = -25 to +4; Kendall 1998). The percentage of stream water derived directly from atmospheric NO<sub>3</sub><sup>-</sup> was calculated as:

$$(\delta^{18}\text{O-NO}_3^- \text{Stream} - \delta^{18}\text{O-NO}_3^- \text{Microbial}) / (\delta^{18}\text{O-NO}_3^- \text{Precip.} - \delta^{18}\text{O-NO}_3^- \text{Microbial}) \times 100$$

Table 2: Isotopic ratios (‰) of δ <sup>15</sup> N-NO <sub>3</sub> <sup>-</sup> and δ <sup>18</sup> O-NO <sub>3</sub> <sup>-</sup> in precipitation and microbial nitrification in soils. Values indicate mean (range) in the literature for the Northeast US and southeast Canada.					
Site	δ <sup>18</sup> O Precip.	δ <sup>18</sup> O Microbial	δ <sup>15</sup> N Precip.	δ <sup>15</sup> N Microbial	Reference
Turkey Lakes, ON	50 (35-59)	-2 to +0.5*	-2 (-4 to +0.8)	0 to +6	Spoelstra et al. 2001
Mid-Appalachia, PA-WV	57 (17-76)	3 to 10 (-0.8*)	Not meas.	Not meas.	Williard et al. 2001
Biscuit Brook, NY	51 (35-70)	13 to 16 (-0.7 to +2.4*)	-0.1	+1.5 to +16	Burns & Kendall 2002
Huntington Forest, NY	54-82	1.2 to 11 (-0.2 to +2.5*)	-3 to +3	-1 to +2	Campbell et al., In press
Sleeper’s River, VT	90	-2 to -4	Not reported	Not reported	Ohte et al. 2004
Hubbard Brook, NH	62 (44-77)	-5 to +15*	-2 (-5 to +2)	Not meas.	Pardo et al. 2004

\*Calculated assuming that 1/3 of the O in NO<sub>3</sub><sup>-</sup> derived from air (O<sub>2</sub>), and 2/3 derived from soil water.

This approach assumes that atmospheric deposition and microbial nitrification are the only processes that provide  $\text{NO}_3^-$  to these streams. Because direct measurements of  $\delta^{18}\text{O}-\text{NO}_3^-$  are not yet available at the local Connecticut Hill atmospheric deposition station, we used mean (60‰) and range (40-80‰) values from the literature (Table 2) to constrain the possible contribution of atmospheric  $\text{NO}_3^-$  to stream  $\text{NO}_3^-$  export. Microbial  $\text{NO}_3^-$  was assigned a mean (-3‰) and range (-5 to 0‰) based on both literature values (Table 2) and the minimum  $\delta^{18}\text{O}-\text{NO}_3^-$  values observed here.

## Results and Discussion

### Climate and Streamflow.

The year spanning March 2005 to February 2006 received near-average precipitation at Ithaca, NY (962 mm), but included an exceptional summer drought and wet autumn. Summer 2005 was the driest and third hottest in the period of record since 1879: June through August temperatures were 2.8 °C warmer than average, and only 46 mm of rain fell within the two-month period of July 1 to August 29, 26% of average for this period. The drought was relieved by remnants of Hurricanes Katrina and Rita at the ends of August and September, respectively, followed by a series of fall storms that combined for an October total rainfall (185 mm) 223% of average. The winter of 2004-5 was slightly (0.6 °C) colder than average, leading to development of a large snowpack that held until late March. By contrast, the winter of 2005-6 was 2.7 °C warmer than

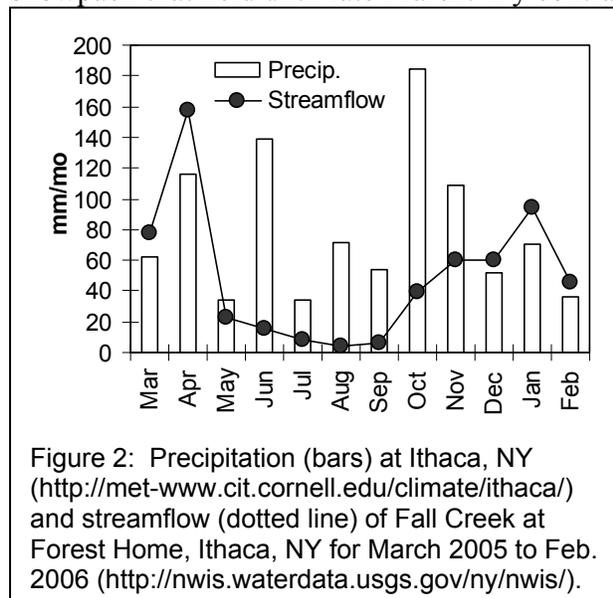


Figure 2: Precipitation (bars) at Ithaca, NY (<http://met-www.cit.cornell.edu/climate/ithaca/>) and streamflow (dotted line) of Fall Creek at Forest Home, Ithaca, NY for March 2005 to Feb. 2006 (<http://nwis.waterdata.usgs.gov/ny/nwis/>).

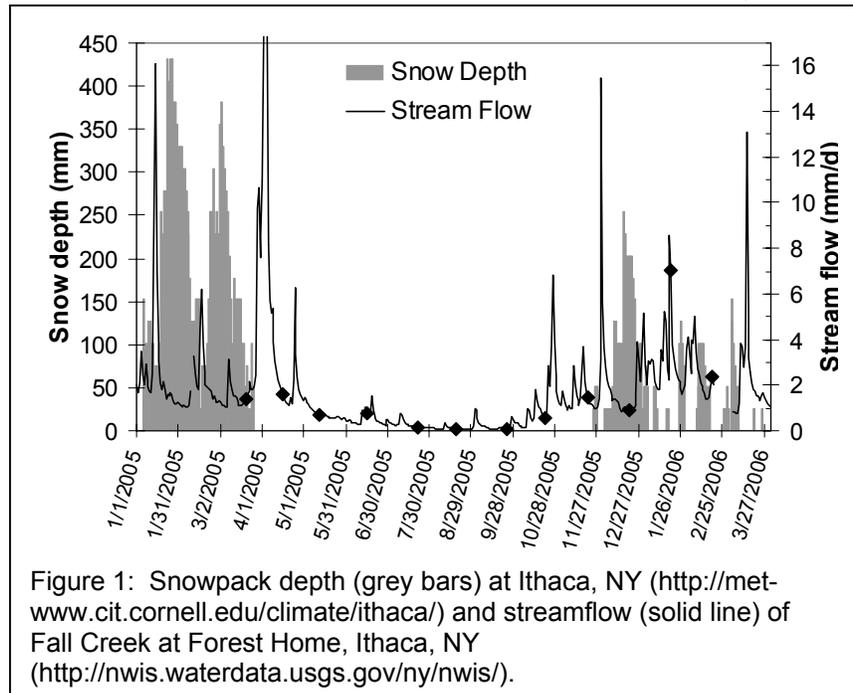


Figure 1: Snowpack depth (grey bars) at Ithaca, NY (<http://met-www.cit.cornell.edu/climate/ithaca/>) and streamflow (solid line) of Fall Creek at Forest Home, Ithaca, NY (<http://nwis.waterdata.usgs.gov/ny/nwis/>).

normal, including a mean January temperature above freezing (0.1 °C) and consequent unstable snowpack throughout January and February 2006 (Figure 1). Streamflow peaked in response to events of both precipitation and snowmelt. Flows were very low during July, August, and September 2005 in response to the drought (Figures 1, 2). Lack of surface flow precluded sample collection at 4, 10, and 7 of the 16 streams during these months, respectively.

Stream Chemistry. Nitrate concentrations in all streams demonstrated an unexpected seasonal pattern of peak concentrations in summer (July – Sept.) and lowest

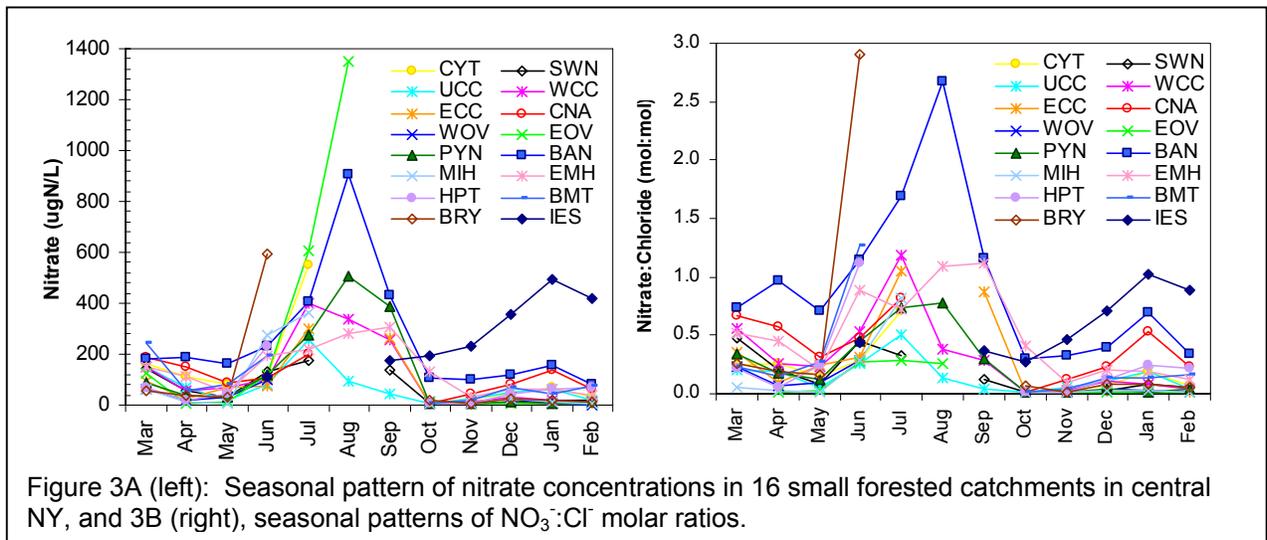


Figure 3A (left): Seasonal pattern of nitrate concentrations in 16 small forested catchments in central NY, and 3B (right), seasonal patterns of  $\text{NO}_3^-:\text{Cl}^-$  molar ratios.

concentrations in spring (April, May) and autumn (Oct., Nov.) (Figure 3). Ammonium concentrations were consistently low, and will not be discussed further: median concentrations were  $1 \mu\text{g/L}$  with a maximum of  $11 \mu\text{g/L}$  in one sample. The seasonal pattern of  $\text{NO}_3^-$  contrasts with the expected dormant season and spring snowmelt  $\text{NO}_3^-$  peaks and growing-season minima typical of most snow-dominated catchments (e.g., Stoddard 1994, Likens & Bormann 1995, Campbell et al. 2000, Goodale et al. 2000, Lovett et al. 2000). A similar pattern of summer maxima and spring and fall minima has been observed in southern streams, where the pattern was attributed to expected peaks in in-stream biotic demand for N at a site in Tennessee (Mulholland 2005) or to lags induced by deep geological flowpaths at a site in North Carolina (Swank & Vose 1997). The  $\text{NO}_3^-$  concentrations we observed exceeded those in Tennessee by a factor of 3 to 28 (e.g., summer maxima of 150 to  $1400 \mu\text{g/L}$  v.  $\sim 50 \mu\text{g/L}$ ). Some of these summer peaks are among the highest concentrations reported among comparable forested catchments in the Northeastern U.S. (cf. Aber et al. 2003).

We speculate that the cause for the unexpected seasonal pattern we observed may be due to a combination of climatic, hydrological, and biological factors. Seasonal patterns of the ratio of  $\text{NO}_3^-$  to  $\text{Cl}^-$  (Figure 3B) suggest that evaporative concentration during the summer drought (July – Sept.) may have partly driven the high late-summer  $\text{NO}_3^-$  concentrations observed in several streams (EOV, CYT, WCC, PYN). However,  $\text{NO}_3^-$  to  $\text{Cl}^-$  ratios more clearly illustrate strong seasonal patterns in  $\text{NO}_3^-$  concentration beyond those that can be explained by evaporative concentration alone. These seasonal patterns are characterized by modest increases at snowmelt, spring dips, summer maxima, and dips at leaf-fall (Figure 3B). The dips in May and October may be due to biological uptake of N for autotrophic (May) or heterotrophic (Oct.) demand. Hydrological factors may also play a role if, for example, deep flowpaths during the summer drought essentially decouple groundwater nutrient supply from surface biological demand (e.g., Burns et al. 1998, Schiff et al. 2002). Land use practices from agriculture (IES) or forest harvests (BRY and BAN) may explain the relatively high nitrate concentrations in these three streams (Figure 3A).

Stream N Export. Estimated  $\text{NO}_3^-$  export fluxes were consistently low, with a median value of  $0.3 \text{ kg N ha}^{-1} \text{ y}^{-1}$  (Table 3). Although stream  $\text{NO}_3^-$  concentrations were surprisingly high during summer, streamflow was so low during the June to September period (6% of the annual flow) that these high  $\text{NO}_3^-$  concentrations contributed little toward elevating annual  $\text{NO}_3^-$  fluxes. Over

Table 3: Annual stream DON and NO<sub>3</sub>-N export estimated by multiplying monthly flow from a gauged stream (Fall Creek, mm/mo) by measured monthly stream chemistry at the streams in this survey. Percent retention estimated by comparing stream export of NO<sub>3</sub>-N with atmospheric deposition of inorganic N measured at Connecticut Hill (8.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>). The amount of annual stream NO<sub>3</sub><sup>-</sup> flux derived directly from atmospheric deposition of NO<sub>3</sub><sup>-</sup> (uncycled) was estimated assuming an atmospheric δ<sup>18</sup>O value of 60‰ (range 40-80‰) and a microbial value of -3‰ (range -5 to 0‰) (e.g., figure 3), weighted by the monthly flux of NO<sub>3</sub><sup>-</sup>. These fluxes of atmospheric NO<sub>3</sub><sup>-</sup> were then compared with total stream NO<sub>3</sub><sup>-</sup> export and atmospheric NO<sub>3</sub><sup>-</sup> deposition (3.2 kg N ha<sup>-1</sup> y<sup>-1</sup>).

Stream	Stream N Export (kg ha <sup>-1</sup> y <sup>-1</sup> )		DIN Export / Deposition %	Stream NO <sub>3</sub> -N Derived Directly from Atmospheric Deposition		
	DON	NO <sub>3</sub> -N		kg ha <sup>-1</sup> y <sup>-1</sup>	% of Stream NO <sub>3</sub> <sup>-</sup>	% of NO <sub>3</sub> <sup>-</sup> Dep.
1. CYT	0.7	0.5	6%	0.07 (0.05-0.12)	15% (10-24%)	2% (2-4%)
2. SWN	0.6	0.3	3%			
3. UCC	0.7	0.4	5%	0.05 (0.03-0.09)	14% (9-23%)	2% (1-3%)
4. WCC	0.6	0.4	4%	0.07 (0.05-0.11)	20% (14-32%)	2% (2-4%)
5. ECC	0.6	0.2	2%			
6. CNA	0.5	0.7	8%	0.05 (0.03-0.10)	8% (4-14%)	2% (1-3%)
7. WOV	0.6	0.1	1%			
8. EOY	0.4	0.2	2%			
9. PYN	0.7	0.2	3%	0.04 (0.03-0.06)	16% (11-25%)	1% (1-2%)
10. BAN	0.4	1.0	11%	0.06 (0.03-0.12)	6% (3-12%)	2% (1-4%)
11. MIH	0.6	0.2	2%	0.01 (0.01-0.02)	8% (5-14%)	0% (0-1%)
12. EMH	0.6	0.6	7%	0.02 (0.01-0.05)	4% (1-8%)	1% (0-1%)
13. HPT	0.6	0.3	4%			
14. BRY	0.5	0.2	3%			
15. BMT	0.5	0.5	5%			
16. IES	0.1*	1.1*				
Median	0.6	0.3	4%	0.05 (0.03-0.09)	11% (7-18%)	2% (1-3%)

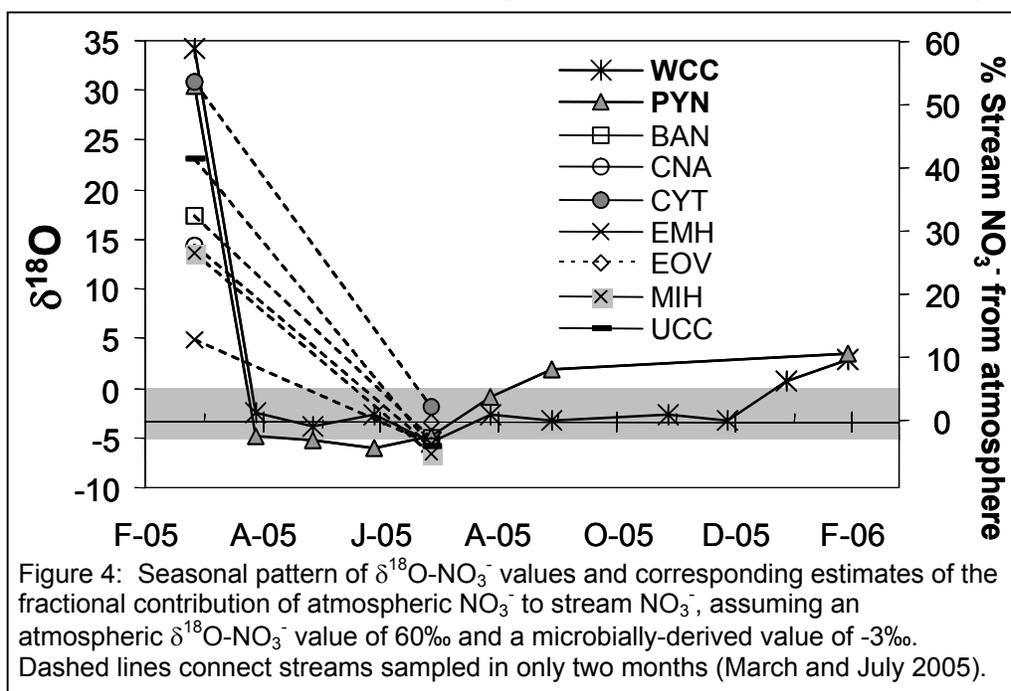
\* Period June 2005 – Feb. 2006, only.

half of the estimated annual NO<sub>3</sub><sup>-</sup> export in most streams occurred during March and April, driven by modestly elevated snowmelt NO<sub>3</sub><sup>-</sup> concentrations (Figure 3) or high April streamflow (Figure 2). Differences among streams in NO<sub>3</sub><sup>-</sup>-N export were small, ranging from estimated lows of 0.1-0.2 kg ha<sup>-1</sup> y<sup>-1</sup> and highs of 0.6-0.7 kg ha<sup>-1</sup> y<sup>-1</sup>. The one stream with a NO<sub>3</sub><sup>-</sup>-N export greater than 1.0 kg ha<sup>-1</sup> y<sup>-1</sup> (during June – February alone) was the small stream at the Connecticut Hill atmospheric deposition station (IES), which was also the one stream with likely contributions of non-forest land cover in the upper part of the catchment. These NO<sub>3</sub><sup>-</sup>-N export values are lower than median export fluxes observed elsewhere in New York in the Adirondack (2-3 kg ha<sup>-1</sup> y<sup>-1</sup>; Ito et al. 2005) and Catskill Mountains (ca. 3.4 kg ha<sup>-1</sup> y<sup>-1</sup>; estimated from Lovett et al. 2000), but are roughly similar to median NO<sub>3</sub><sup>-</sup>-N export rates observed in the White Mountains, New Hampshire (Campbell et al. 2000, Goodale et al. 2000). Both New York mountain ranges have slightly higher rates of atmospheric N deposition (9-12 kg ha<sup>-1</sup> y<sup>-1</sup>) compared to the ~8.5 kg ha<sup>-1</sup> y<sup>-1</sup> received in both central NY and the White Mountains. Past work has suggested an N deposition threshold of around 8-10 kg N ha<sup>-1</sup> y<sup>-1</sup> below which there is near complete N retention, and above which N export increases sharply (Aber et al. 2003). The streams sampled in this study hover right around this threshold and demonstrate near complete N retention, averaging about 96% (range 89-99%; Table 3).

Sources of Stream Nitrate. Values of  $\delta^{18}\text{O}\text{-NO}_3^-$  were used to partition streamwater  $\text{NO}_3^-$  into contributions from atmospheric deposition and from microbially produced (or microbially recycled)  $\text{NO}_3^-$  (Table 3, Figure 4). Although we lacked field-measured  $\delta^{18}\text{O}\text{-NO}_3^-$  end-members for atmospheric deposition and microbial  $\text{NO}_3^-$ , consideration of a wide range of values from the literature (Table 2) provided relatively tight constraints on the contribution of direct atmospheric deposition to stream  $\text{NO}_3^-$  export (Table 3). Very little ( $\leq 4\%$ ) atmospheric  $\text{NO}_3^-$  deposition passed through the forest ecosystem directly, and the preponderance of the  $\text{NO}_3^-$  exported in streamwater (80-96%) derived from microbial nitrification (Table 3). This result is consistent with most previous  $\delta^{18}\text{O}\text{-NO}_3^-$  measurements in forested catchments which have found that atmospheric deposition typically contributes less than 10% of the  $\text{NO}_3^-$  in streams during baseflow conditions, with somewhat greater contributions (up to 20-30%) during snowmelt or other high-flow events (Spoelstra et al. 2001, Williard et al. 2001, Burns & Kendall 2002, Pardo et al. 2004). As an exception to this pattern, precipitation contributed 39% (range: 16-100%) of the  $\text{NO}_3^-$  in springs in a declining forest stand in Germany exposed to high rates of atmospheric deposition (Durka et al. 1994).

The small amount of atmospheric  $\text{NO}_3^-$  deposition that did pass through these central NY forests occurred entirely at snowmelt, particularly in March 2005, when  $\delta^{18}\text{O}\text{-NO}_3^-$  values indicated that 12% (EMH) to perhaps 59% (WCC) of stream  $\text{NO}_3^-$  in the March samples derived directly from atmospheric deposition (Figure 4). Values of  $\delta^{18}\text{O}\text{-NO}_3^-$  during the early snowmelt in January and February 2006 suggested much smaller direct contributions from atmospheric deposition in 2006 than in 2005. Because each stream had only one sample per month, it is unclear whether the relatively high fractions of atmospheric  $\text{NO}_3^-$  contributed in March 2005 were a result of the large snowpack development that year or to melt conditions particular to that sampling date. Values of  $\delta^{18}\text{O}\text{-NO}_3^-$  can vary substantially throughout the course of snowmelt. High-frequency (daily to 3-6 hours) sampling during snowmelt in 2003 at Sleepers River, Vermont, revealed high  $\delta^{18}\text{O}\text{-NO}_3^-$  values (18‰) at the start of snowmelt, with a substantial drop in within a day or so down to modestly elevated levels ( $\sim 5\%$ ) sustained throughout the rest of snowmelt, eventually

dropping to about  $-3\%$  by the time the snowpack had melted completely (Ohte et al. 2004). Ohte et al. (2004) suggest that the first phase of snowmelt includes melt water from snow directly covering the channel, a process that might have



occurred during the March 2005 sampling at the central NY streams measured here, as snow did cover many channels on that date. Interestingly, several of the March 2005  $\delta^{18}\text{O}-\text{NO}_3^-$  values observed here (up to 34‰, Figure 4) exceeded the maximum value recorded at Sleepers River sampled over the full course of snowmelt (maximum of 18.3‰; Ohte et al. 2004), and suggest some of the highest direct contributions of atmospheric  $\text{NO}_3^-$  ever reported in North America, although forthcoming measurements of  $\delta^{18}\text{O}-\text{NO}_3^-$  in atmospheric deposition for the Connecticut Hill deposition station will help confirm that result.

### **Student Training, Publications, and Facilitated Grants**

This project provided funding for two undergraduate assistants, including one full-time assistant in summer 2005 (Robin Schmidt, Bard College), and one part-time assistant during the academic year (Kimberly Falbo, Natural Resources major, Cornell University). Both students learned methods of stream water collection and analysis, and were exposed to other areas of research in forest ecosystem ecology in central NY forests.

In addition, co-investigator Steve Thomas led a Cornell graduate student workshop on stream  $^{15}\text{N}$  tracers which involved an experiment in fall 2004 on nitrate and DOC interactions in one of the streams sampled here (WCC). Continued sampling of the chemistry of that stream through this WRI project has provided significant context for the original experiment. Results from that experiment are in preparation for submission for publication (Thomas et al., in prep.), and have been presented at three meetings: the 2005 North American Benthological Society annual meeting, the 2005 Gordon Conference on Catchment Biogeochemistry, and the 2006 BIOGEOMON Conference.

The results described here in detail are now in preparation for a separate submission for publication expected in fall 2006, anticipated for *JGR-Biogeochemistry*, *Hydrological Processes*, or similar journal.

Finally, the preliminary stream chemistry enabled by this WRI grant made possible the submission of a successful research proposal to the competitive “Mesogrants” program within Cornell’s Agricultural Ecology Program (AEP) to assess contributions of atmospheric N to the Upper Susquehanna River. The new project provides \$60,000 to Goodale and Thomas over two years to follow the movement of an added  $^{15}\text{N}-\text{NO}_3^-$  tracer through the upper part of one of the catchments described here, Pine Creek in Arnot Forest (PYN). We anticipate that the new project will both complement the WRI project, and will serve as a pilot experiment for an anticipated submission to NSF in July 2007 or January 2008.

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