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Unusual seasonal patterns and inferred processes of nitrogen retention in forested headwaters of the Upper Susquehanna River

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Abstract Atmospheric deposition contributes a large fraction of the annual nitrogen (N) input to the basin of the Susquehanna River, a river that provides two-thirds of the annual N load to the Chesapeake Bay. Yet, there are few measurements of the retention of atmospheric N in the Upper Susquehanna's forested headwaters. We characterized the amount, form (nitrate, ammonium, and dissolved organic nitrogen), isotopic composition (δ^{15}N- and δ^{18}O-nitrate), and seasonality of stream N over 2 years for 7–13 catchments. We expected high rates of N retention and seasonal nitrate patterns typical of other seasonally snow-covered catchments: dormant season maxima and growing season minima. Coarse estimates of N export indicated high rates of inorganic N retention (>95%), yet streams had unexpected seasonal nitrate patterns, with summer peaks (14–96 μmol L^{-1}), October crashes (<1 μmol L^{-1}), and modest rebounds during the dormant season (<1–20 μmol L^{-1}). Stream δ^{18}O-nitrate values indicated microbial nitrification as the primary source of stream nitrate, although snowmelt or other atmospheric source contributed up to 47% of stream nitrate in some March samples. The autumn nitrate crash coincided with leaffall, likely due to in-stream heterotrophic uptake of N. Hypothesized sources of the summer nitrate peaks include: delayed release of nitrate previously flushed to groundwater, weathering of geologic N, and summer increases in net nitrate production. Measurements of shale δ^{15}N and soil-, well-, and streamwater nitrate within one catchment point toward a summer increase in soil net nitrification as the driver of this pattern. Rather than seasonal plant demand, processes governing the seasonal production, retention, and transport of nitrate in soils may drive nitrate seasonality in this and many other systems.

Keywords ^{15}N · ^{18}O · Geologic nitrogen · In-stream uptake · Nitrogen retention · Nitrate seasonality

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Introduction

In the northeastern US, emissions of nitrogen (N) from fossil fuel combustion and agricultural activities have increased atmospheric N deposition to rates approximately 4–10 times those of natural background conditions (Holland et al. 1999; Butler et al. 2003; Galloway et al. 2004; Elliott et al. 2007). Elevated N deposition often leads to increased nitrate (NO_3^-) loss from soils and streams, which contributes to the acidification of soils and surface waters and to eutrophication of coastal ecosystems downstream (e.g., Howarth et al. 2000; Aber et al. 2003; Driscoll et al. 2003a; Galloway et al. 2003). The Susquehanna River supplies two-thirds of the annual N load to the Chesapeake Bay, where excess N drives eutrophication and hypoxia (Hagy et al. 2004; Howarth and Marino 2006). Atmospheric deposition contributes at least 27% of the total annual N input to the Susquehanna River basin, and the majority of this deposition falls on forests (Boyer et al. 2002; Goodale et al. 2002). Forested uplands typically retain a large fraction of deposited N in soils and vegetation (e.g., Nadelhoffer et al. 1999), and stream processes can further retain and remove incoming NO_3^- (e.g., Bernhardt et al. 2003; Mulholland et al. 2008). Therefore, forested headwaters in the Upper Susquehanna River in central New York State likely play an important role in controlling the delivery of N to Chesapeake Bay; yet, we know of no previous measurements of stream N export from forests in this region.

Processes mediating catchment N retention are often inferred from observations of spatial and temporal patterns of stream NO_3^-. Comparisons of NO_3^- across catchments indicate that N retention can respond to rate of N deposition (e.g., Wright et al. 2001; Aber et al. 2003), forest successional status (Vitousek and Reiners 1975; Goodale et al. 2000; Cairns and Lajtha 2005), soil carbon-to-N ratio and net NO_3^- production (Williard et al. 1997; Gundersen et al. 1998; Lovett et al. 2002), and tree species composition, alone or in combination with bedrock base cation status (Lewis and Likens 2000; Lovett et al. 2002; Williard et al. 2005; Christopher et al. 2006).

Seasonal patterns of stream NO_3^- concentration have been used to infer catchment N saturation status and N retention processes. The vast majority of seasonally snow-covered catchments display elevated NO_3^- concentrations during the dormant season, often peaking at snowmelt, followed by low NO_3^- concentrations during the growing season. This pattern has been observed, for example, in western US alpine regions (e.g., Baron and Campbell 1997; Williams et al. 1996; Sickman and Melack 1998), eastern Canada (e.g., Watmough et al. 2004), and northeastern US mountains (e.g., Driscoll et al. 2003b; Murdoch and Stoddard 1993; Likens and Bormann 1995; Goodale et al. 2000), as well as in Scandinavia (de Wit et al. 2008), the United Kingdom (Davies et al. 2005; Curtis et al. 2005), the Czech Republic (Vesely et al. 2002), the Italian Alps (Rogora 2007), and broadly across northern Europe (Wright et al. 2001). This "conventional" seasonal NO_3^- pattern and its amplitude have been used to infer the intensity of biological N demand as a function of the successional status of forest vegetation (Vitousek and Reiners 1975; Likens and Bormann 1995; Goodale et al. 2000; Martin et al. 2000) and degree of N saturation induced by chronic N deposition (e.g., Stoddard 1994; Lovett et al. 2000; Stoddard et al. 2001; Wright et al. 2001). Sites receiving little N deposition and early-successional sites with high N demand are expected to have little NO_3^- loss at any time of year. Early stages of N saturation are expected to show increased NO_3^- concentrations during the dormant season, with late stages displaying persistently elevated NO_3^- concentrations during the growing season as well (Stoddard 1994). These conceptual models assume that the amount and seasonal pattern of stream NO_3^- vary inversely with the demand of terrestrial vegetation and soil microbes, and rarely include roles for seasonally variable hydrologic flowpaths (e.g., Burns et al. 1998; Creed and Band 1998) or in-stream processes (e.g., Mulholland and Hill 1997; Valett et al. 2008).

Here, we characterized seasonal and spatial patterns of stream N loss from small forested catchments in the Upper Susquehanna River basin and identified a suite of processes that may drive these patterns. We expected that stream N losses would follow patterns typical of other seasonally snow-covered catchments, with higher NO_3^- concentrations in the dormant season than during the growing season, and with overall N export generally a function of N deposition (e.g., Dise and Wright 1995; MacDonald et al. 2002; Aber et al. 2003). We quantified the amount, timing,

and form (NO_3^-, NH_4^+, and dissolved organic nitrogen or DON) of stream N loss, and used measurements of the natural abundance of ^{15}N and ^{18}O in NO_3^- to provide broad constraints on the contributions to stream NO_3^- from precipitation, microbial, and geologic sources of N.

Methods

Site description

We identified 13 first- or second-order streams within the Upper Susquehanna River basin at or near its northern boundary in New York State, all within 25 km south of Ithaca, New York. Sampling locations were identified by global positioning system, and catchment boundaries were delineated using ArcGIS ver. 9.2 (ESRI, Redlands, CA). Catchments ranged in size from 26 to 266 ha. Elevations ranged from 317 m at the lowest base to 671 m at the tallest hilltop. Weather records (1971–2000) for Cornell University, Ithaca (42.45°N, 76.45°W, 292 m elevation) indicate an annual mean temperature of 7.8°C, with monthly mean temperatures ranging from −5.2°C in January to 20.4°C in July (Northeast Regional Climate Center 2008). Mean annual precipitation is 932 mm $year^{-1}$, with more precipitation on average in summer (91 mm $month^{-1}$) than winter (56 mm $month^{-1}$). Snowfall averages 1,700 mm $year^{-1}$.

The catchments occur within the Allegheny Plateau, a region characterized by steep-sided and flat-topped hills covered by northern hardwood and mixed oak forests. Many of the forests have regrown on land abandoned from agriculture 60–100 years ago, although steep hillsides often contain primary forest—that is, forest subject to logging but never cleared for agriculture (Smith et al. 1993; Flinn et al. 2005). Dominant tree species in primary forest include sugar maple (*Acer saccharum*), red maple (*A. rubrum*), red oak (*Quercus rubra*), American beech (*Fagus grandifolia*), and eastern hemlock (*Tsuga canadensis*), while post-agricultural stands contain red maple, white pine (*Pinus strobus*), and white ash (*Fraxinus americana*) (Fahey 1998; Flinn and Marks 2007). All 13 catchments are forested and are free from paved roads, human habitation, or agriculture at present (Table 1). Current land cover was obtained at 30 m resolution from the 2001 National Land Cover Database (NLCD; http://www.mrlc.gov/nlcd.php; Homer et al. 2007). Historic land cover was obtained for eight catchments from Flinn et al. (2005), who digitized historic aerial photos to delineate primary forests from forests that developed on abandoned agricultural land.

Catchment soils are largely Inceptisols developed in till deposited by Wisconsinan glaciation. Most soils are Dystrudepts, Fragiaquepts, and Fragiudepts in the Lordstown, Mardin, and Volusia soil series (Neeley 1965), which are acid to strongly acid (pH 4.0–5.0) channery silt loams, often containing 30–70% rock fragments by mass. Both historic cultivation and recent earthworm activity have reduced or eliminated the forest floor in many areas, and surface mineral soils frequently have C:N ratios <16 (Bohlen et al. 2004; Suárez et al. 2006; Flinn and Marks 2007). Bedrock of Devonian shale underlies essentially all western and central New York. Chemung Formation grey shales dominate the catchment geology above about 350 m elevation, with Rock Stream siltstone (Sonyea Formation) at lower elevations. Layers of Ithaca grey shales, Geneseo black shales, and Tully limestone (all Genesee Formation) occur below these formations and within 40 km to the north (Rickard and Fisher 1970; Rogers et al. 1990).

Atmospheric deposition

Nitrogen deposition was measured at Connecticut Hill (42.40°N, 76.65°W, 501 m elevation), a site 15 km southwest of Ithaca. Precipitation chemistry (NH_4^+, NO_3^-) has been monitored since 1978 as part of the U.S. Environmental Protection Agency's Clean Air Status and Trends Network (www.epa.gov/castnet/sites/cth110.html). Dry deposition of nitric acid gas and fine particulates have been measured weekly since 1987 (Butler and Likens 1995) as part of the National Oceanic and Atmospheric Administration's Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN). Recent measurements indicate that deposition of gaseous ammonia may be substantial (JP Sparks, personnel communication). However, spatial and temporal heterogeneity make this flux especially difficult to estimate and so it was not considered further here, but for the caveat that underestimates of N deposition lead to underestimates of N retention.

Table 1 Stream name, abbreviation, sampling point (latitude/longitude), size, and historic and current land cover

No.	Name or nearest landmark	Abbrev.	Lat. (°N), Long. (°W)	Area (ha)	Historic forest cover[a] (%)	Current land cover[b]				
						Decid. forest (%)	Mixed forest (%)	Conif. forest (%)	Wet-land (%)	Open (%)
1	Cornell Natural Area	CNA	42.33, 76.66	89	59	27	44	29	0	0
2	East Carter Creek	ECC	42.34, 76.66	72	30	34	43	12	11	0
3	East Overlook Trail	EOV	42.25, 76.65	52	NA	99	0	0	1	0
4	Michigan Hollow	MIH	42.30, 76.48	266	NA	39	44	15	2	0
5	Pine Creek	Pine	42.27, 76.64	78	NA	75	9	15	0	0
6	Upper Carter Creek	UCC	42.36, 76.66	262	31	42	38	11	6	1
7	West Carter Creek	WCC	42.35, 76.67	210	54	41	38	17	0	4
8	Bald Mtn.	Bald	42.34, 76.35	26	19	49	26	16	9	0
9	Cayutaville Rd.	CYT	42.39, 76.69	128	44	43	39	8	9	0
10	Eastman Hill	EMH	42.34, 76.40	121	64	33	45	19	3	0
11	Honeypot Rd.	HPT	42.32, 76.31	50	28	32	59	5	4	0
12	Swan Rd.	Swan	42.32, 76.71	198	NA	23	53	13	4	7
13	West Overlook Trail	WOV	42.25, 76.65	43	NA	90	10	0	0	0

Decid. = deciduous hardwood forest; conif. = needle-leaved conifer forest, Wetland = forested or herbaceous wetland, Open = old-field/meadow

NA not available

[a] Percent catchment forested in 1900, obtained from Flinn et al. (2005)

[b] Land cover 2001, derived from the National Land Cover database (Homer et al. 2007)

Catchment water sampling and analysis

Stream water was collected monthly from 13 small streams for 1 year, March 2005 to February 2006. Sampling continued at seven of these streams (streams #1–7, Table 1) for a second year, to February 2007. Sampling dates targeted the middle of each month (Fig. 1). At one stream, Pine Creek, longitudinal profiles were collected monthly from August 2006 to March 2007 to discern seasonal changes in solute chemistry at roughly 40 m intervals (10, 41, 86, 118, 165, and 213 m) downstream from the stream's origin at a perennial spring. All stream water samples were collected with pre-rinsed Luer-lok polypropylene syringes, and then filtered in the field through 0.7 μm ashed glass fiber filters (Whatman GF/F) into designated 30–60 mL bottles pre-rinsed three times with filtrate (polyethylene bottles for anions, opaque polyethylene for NH_4^+, and high-density polyethylene for dissolved organic solutes).

Soil and riparian water was collected from December 2006 through November 2007 from a 0.25 ha forested plot directly surrounding the spring origin of Pine Creek. In July 2006, six pairs of zero-tension lysimeters were installed at 10 cm soil depth, and six pairs of tension lysimeters were installed at 50 cm. This mix of lysimeter types follows the instrumentation design used previously at this site (Bohlen et al. 2004). The forest floor was largely absent but for a thin layer of leaf litter, and the mineral soil had little distinct horizonation but for surface enrichment with organic matter. The lysimeter depths represent soil solution within (10 cm) and below (50 cm) the rooting zone; 85–90% of fine root biomass at this site occurs within the top 12 cm (Fisk et al. 2004). The zero-tension lysimeters consisted of

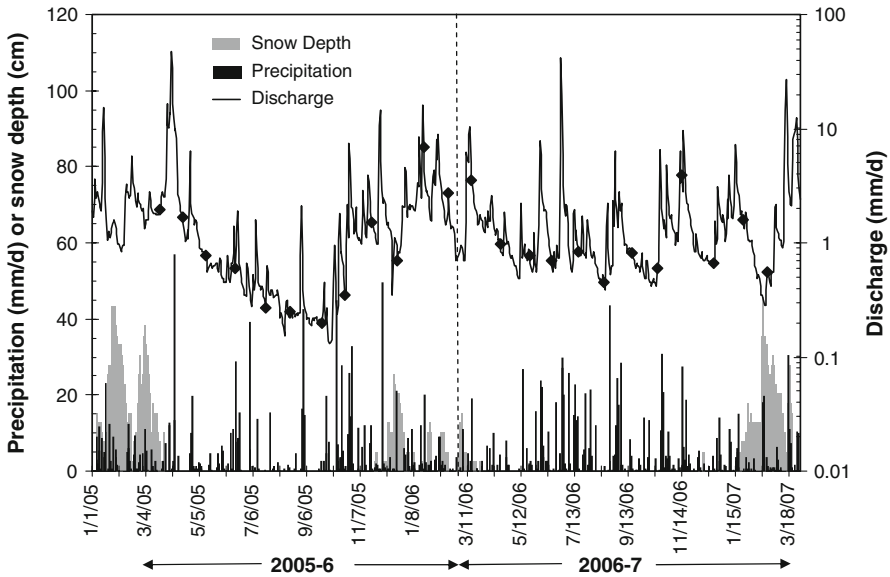

Fig. 1 Daily precipitation (*black bars*) and snowpack depth (*grey bars*) at Ithaca, NY, and discharge (*black line*; log scale) of Six-Mile Creek at Brooktondale, NY. *Diamonds* indicate discharge on stream sampling dates

PVC pipe (25.4 cm diameter × 30.5 long) split in half and capped at one end, and draining to 2 L polyethylene collection bottles placed in soil pits. Zero-tension lysimeter installation occurred via lateral excavation beneath the top 10 cm of undisturbed soil on the upslope side of the pits, which were then backfilled. The deep lysimeters consisted of SoilMoisture 1900 Series ceramic cup lysimeters, installed at 50 cm depth. These samples were collected after sitting for 24 h under 50 kPa of tension applied by a vacuum hand pump. All soil solutions were filtered in the field through ashed, pre-rinsed 0.7 μm glass fiber filters. Riparian wells consisted of 2.5 cm diameter PVC pipe, screened with 125 μm mesh over the last 5 cm. Four wells were installed at 30 cm depth on each side of the stream at roughly 25 m intervals. Most well samples required a settling period of 1–2 days before filtering.

Ammonium was analyzed within 1 day of sample collection by the fluorometric method (Holmes et al. 1999) using a Turner Designs Aquafluor. All other samples were frozen until analysis up to 9 months later. Nitrate, chloride (Cl^-), and sulfate (SO_4^{2-}) were measured using a Dionex ICS-2000 ion chromatograph. Non-purgeable dissolved organic carbon (DOC) was measured, after acidifying and sparging to remove dissolved inorganic carbon, by combustion (680°C) in the presence of a platinum catalyst using a Shimadzu TOC-V_{CPN} analyzer. Total dissolved nitrogen (TDN) was measured simultaneously with DOC by chemiluminescence detection with a Shimadzu TNM-1. Dissolved organic nitrogen was calculated by difference as DON = TDN − (NO_3^- + NH_4^+).

Annual N export (2005–2006) was approximated for all 13 streams by multiplying measured monthly chemistry at each stream by estimates of streamflow (mm $month^{-1}$) derived from area-weighted discharge measurements from six nearby gauged streams (Sapsucker Woods, Cayuga Inlet, Newtown and Fall Creeks, and Six-Mile Creek at both Brooktondale and Bethel Grove). These catchments ranged from 2.0 to 326 km^2, and demonstrated no bias in area-weighted annual discharge (mm $year^{-1}$) with catchment size. Some months displayed slight variations in monthly discharge (mm $month^{-1}$) as a function of catchment size; these relationships were used to estimate monthly streamflow (±1 SD) at the 13 catchments in this study. General temporal patterns in regional daily streamflow are illustrated with discharge measurements from Six-Mile Creek at Brooktondale, south of Ithaca (Fig. 1; USGS #04233286; 42.368°N, 76.395°W, 70 km^2). Catchment N retention was estimated by comparing these rough estimates of N export to measurements of atmospheric N deposition measured at Connecticut Hill, calculated as:

$$\%\,\text{Retention} = (\text{N deposition} - \text{N export})/\text{N deposition} \times 100$$

Coarse sampling frequency and lack of on-site discharge measurements both induce substantial

uncertainties in these estimates of N export and retention. Yet, these estimates provide a first approximation of N export for a region otherwise lacking even broad characterization.

Isotopic separation of nitrate sources

Stream NO_3^- was partitioned between precipitation and microbial sources for 2005–2006 through use of δ^{18}O-NO_3^- values (e.g., Durka et al. 1994; Kendall 1998). That is, the percent of stream water NO_3^- derived directly from precipitation was calculated as:

$$\left(\delta^{18}\text{O - NO}^-_{3\,\text{stream}} - \delta^{18}\text{O - NO}^-_{3\,\text{microbial}}\right) \Big/ \left(\delta^{18}\text{O - NO}^-_{3\,\text{precip.}} - \delta^{18}\text{O - NO}^-_{3\,\text{microbial}}\right) \times 100$$

All isotopic values are expressed in per mil units (‰) relative to customary standards of atmospheric N_2 for δ^{15}N and Vienna Standard Mean Ocean Water (V-SMOW) for δ^{18}O. Nitrate in precipitation typically has δ^{18}O values of +50‰ or higher (Kendall et al. 2007; Table 2). Nitrate produced by nitrifying bacteria has much lower δ^{18}O values, −10 to +10‰, calculated by assuming that O_2 in air (δ^{18}O = 23.5‰) supplies one-third of the oxygen atoms in NO_3^- and that soil water supplies the other two-thirds (Kendall 1998; Kendall et al. 2007). Values of δ^{18}O-NO_3^- allow better distinction between atmospheric and microbial sources than do δ^{15}N-NO_3^- values, since δ^{15}N-NO_3^- values typically fall in overlapping ranges for precipitation and for forest soils (−5 to +20‰; Kendall 1998; Kendall et al. 2007; Table 2). The δ^{18}O-NO_3^--based approach for NO_3^- source separation provides a lower bound on the contribution to stream NO_3^- derived ultimately from N deposition. That is, the only form of N deposition this approach considers is precipitation NO_3^-; it ignores precipitation NH_4^+ and many forms of dry deposition. Also, NO_3^- from precipitation that is taken up, quickly cycled by microbes, and then lost in stream water reflects microbial δ^{18}O-NO_3^- values but has a recent atmospheric source.

The isotopic composition of NO_3^- (δ^{15}N and δ^{18}O) in precipitation at Connecticut Hill was measured for 107 precipitation events for the year 2000 as part of a larger study of δ^{15}N- and δ^{18}O-NO_3^- in deposition (Elliott et al. 2007; Kendall et al. 2007; Burns et al. 2009). Briefly, reanalysis in 2003 confirmed little alteration of sample NO_3^- concentration since 2000 (slope = 1.008, R^2 = 0.9995) during storage at 4°C, with minimal fractionation likely to have occurred (Elliott et al. 2007). Archived samples from individual events were analyzed for δ^{15}N and δ^{18}O at the U.S. Geological Survey, Menlo Park, CA, in 2003 using the microbial denitrifier method (Sigman et al. 2001; Casciotti et al. 2002). Here, we report seasonal average precipitation δ^{15}N- and δ^{18}O-NO_3^- values for comparison with other isotopic endmembers.

Stream water samples selected for dual isotope analysis were shipped frozen to the Woods Hole Oceanographic Institution for analysis using the microbial denitrifier method. Analytical cost prevented analysis of all stream samples. To maximize characterization of spatial and temporal patterns of δ^{15}N and δ^{18}O, two streams—Pine Creek and West Carter Creek—were analyzed for all months during 2005–2006 with sufficient NO_3^- to allow isotopic analysis (>2 μmol L^{-1}), and eight streams were analyzed for 2 months. March and July 2005 were chosen for the cross-stream comparisons to represent snowmelt and summer conditions, respectively.

The δ^{18}O of water was measured for Pine and West Carter Creeks for 7 months spanning July 2005 to February 2006, allowing calculation of δ^{18}O-NO_3^- values expected from microbial nitrification. These analyses were conducted at the Cornell Stable Isotope Lab, using a GFL 1086 water equilibrator unit interfaced to a Finnigan MAT Delta Plus IRMS. Stream δ^{18}O-H_2O ranged from −11.5‰ (February 2006) to −9.4‰ (October 2005). Using these values of δ^{18}O-H_2O and an assumed δ^{18}O of 23.5‰ for atmospheric O_2, δ^{18}O-NO_3^- derived from nitrification should be +0.2 to +1.6‰. These values are similar those calculated for other forested sites (Table 2), yet are higher than the minimum stream δ^{18}O-NO_3^- values observed here (−6.7‰), an occurrence observed elsewhere as well (e.g., Barnes et al. 2008). Stream NO_3^- sources were partitioned using δ^{18}O-NO_3^- values of +77‰ for precipitation and −3‰ for nitrification, with sensitivity of this partitioning assessed using the range of δ^{18}O-NO_3^- values estimated for this site for precipitation (+70 to 81‰) and for microbially produced NO_3^- (−6 to +2‰) (Table 2).

Table 2 Values of $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ (‰) in precipitation, soils, and streams, relative to V-SMOW (^{18}O) or air-N_2 (^{15}N)

Site	Method[a]	$\delta^{18}O$-nitrate (‰)				$\delta^{15}N$-nitrate (‰)			References
		Precipitation	Nitrified, calculated[b]	Soil water or extract	Stream	Precipitation	Soil water or extract	Stream	
Turkey Lakes, Ontario	Exch. Col.	+50 (+35 to +59)	−1 (−2 to +0.5)	+5 to +20[c]	+3 to +15	−2 (−4 to +1)	+1 to +6[c]	+1 to +6	Spoelstra et al. (2001)
Harp Lake, Ontario	Exch. Col.	+42 (+30 to +54)	~0	+5 to +24[c]	NA	−5 to −2	−2 to +5[c]	0 to +5	Schiff et al. (2002)
Pennsylvania–West Virginia	Exch. Col.	+57 (+17 to +76)	−0.8	+8[d] (0 to +14)	+2 to +22	NA	NA	NA	Williard et al. (2001)
Biscuit Brook, NY	Exch. Col.	+51 (+35 to +70)	−0.7 to +2.4	+13 to +16[d]	+17 (+10 to +30)	−0.2	+2 to +16[d]	+2 (−1 to +4)	Burns and Kendall (2002)
Huntington Forest, NY	Exch. Col.	+41 to +73	NA	+7 to +17[c]	+10 (+6 to +16)	−6 to +4	+7 to +17[c]	+1 (−6 to +3)	Piatek et al. (2005)
Huntington Forest, NY	Exch. Col.	+54 to +82 (+26 to +90)	−0.2 to +2.5	0 to +19[c]	0 to +14	−3 to +3	−1 to +3[c]	+1 (0 to +2)	Campbell et al. (2006)
Camels Hump, VT	Exch. Col.	+47 (+26 to +57)	−0.5	+14 (+9 to +22)[c]	+13 (+12 to +16)	−1 (5 to +2)	−10 to +10[c]	+2 to +3	Hales et al. (2007)
Hubbard Brook, New Hampshire	Exch. Col.	+62 (+44 to +77)	NA	NA	+18 (+12 to +33)	−2 (−5 to +2)	NA	0 (−3 to +6)	Pardo et al. (2004)
Sleeper's River, Vermont	Denitrifier	+90	−4 to −2	−7 to +70[c]	−8 to +18	NA	NA	NA	Ohte et al. (2004)
Sleeper's River, Vermont	Denitrifier	+76 to +101	NA	−11 to +71	−5 to +43	−4 to +3	−12 to +7	0 to +7	Sebestyen et al. (2008)
Northern Connecticut	Denitrifier	+71 (+50 to +84)	−3 to +8	NA	−4 to +10	−2 ± 3	NA	0 to +6	Barnes et al. (2008)
Upper Susquehanna, NY	Denitrifier	+77 (+71 to +81)	0 to +2	NA	+1 (−7 to +34)	−1 (−3 to +2)	NA	−2 to +6	This study

Values indicate mean (range) in the literature for forested catchments in the northeastern US and southeastern Canada

NA not available

[a] Method for extracting NO_3^- from solution for dual isotope analysis. Exch. Col. = anion exchange column, elution, and conversion to silver nitrate (Chang et al. 1999; Silva et al. 2000); Denitrifier = microbial conversion to N_2O (Sigman et al. 2001; Casciotti et al. 2002)

[b] Calculated assuming that one oxygen atom in NO_3^- is from air (O_2) at 23.5‰, and two are from water

[c] Measured in soil water or [d] in extracts of incubated soils

Geologic nitrogen

Unusually high concentrations of NO_3^- during summer low flows led to several hypotheses on the source of this N. We analyzed a small number of rock samples to broadly characterize the potential for geologic contributions. Six samples of Chemung Formation grey shale, the dominant bedrock for these catchments (Rickard and Fisher 1970), were collected from in or near the stream channel of Pine Creek at points spanning the stream length and passing through a small gorge. Stream chemistry can reflect till composed of both locally weathered material and material transported by glacial processes from more northern sources (e.g., Bailey and Hornbeck 1992; Hornbeck et al. 1997; Bailey et al. 2003). Other shale formations occur at the surface to the north and at depth beneath the Chemung shale in these catchments (Rickard and Fisher 1970; Rogers et al. 1990), and so another six rock samples from various adjacent strata (Ithaca shale, Geneseo black shale, Tully limestone) were collected from Taughannock Gorge and Portland Point outcrop, 10–15 km north of Ithaca.

Rock samples were prepared according to Holloway and Dahlgren (1999). Exposed surfaces were removed with a rock hammer to reveal unweathered material, which was immersed in a 5% peroxide bath for 24 h to remove surface organic contaminants. Samples were crushed to a fine powder and split. Half were ashed in a muffle furnace at 500°C for 8 h to remove organic matter. Both ashed and unashed samples were analyzed for $\delta^{15}N$ at the Cornell Stable Isotope Laboratory using a Carlo Erba NC2500 elemental analyzer interfaced to an IRMS, by combustion at 1,000°C in the presence of chromium and copper oxide.

Results

Weather and streamflow

The first year (March 2005 to February 2006) received near-average annual precipitation, but included a summer drought and an unusually wet autumn. Summer 2005 was the driest and third hottest on record since 1879 (Northeast Regional Climate Center 2007). The drought was relieved by remnants of Hurricanes Katrina and Rita at the ends of August and September, followed by a series of October storms (Fig. 1). The second year (March 2006 to February 2007) was 10% wetter than average, with a dry spring and wet summer. Winter conditions also varied across years. The winter of 2004–2005 was cold, leading to development of a large snow pack that persisted until sampling started in late March. By contrast, the following winter of 2005–2006 was much warmer than normal, with an unstable snow pack throughout early 2006. The winter of 2006–2007 had a warm December, with a cold late winter that formed a snow pack that lasted until mid-March 2007. The catchments' higher elevation (317–671 m) tended toward slightly larger snow packs and later melt than observed at the weather station in Ithaca (292 m; Fig. 1). Most sampling dates represented non-event conditions (Fig. 1), although five of 24 sampling dates occurred within 2 days of precipitation $\geq$1 cm (Figs. 1, 2).

Atmospheric deposition

The sum of wet and dry atmospheric deposition at Connecticut Hill averaged ($\pm$1 SD) 8.3 ± 0.5 kg N ha^{-1} $year^{-1}$ over 2000–2006, with no significant trend over this period. Wet deposition of NO_3^- contributed 3.0 ± 0.4 kg N ha^{-1} $year^{-1}$ (36%) of this total, with volume-weighted mean concentrations of 20.7 μmol L^{-1} for NO_3^- and 15.3 μmol L^{-1} for NH_4^+.

Precipitation $\delta^{18}O\text{-}NO_3^-$ averaged 77.3‰ (Table 2), and varied from 70.7‰ in summer to 81.0‰ in winter. Precipitation $\delta^{15}N\text{-}NO_3^-$ values ranged from +1.6‰ in winter to −2.7‰ in summer, with an annual mean of −0.9‰.

Stream and soil water chemistry

Stream NO_3^- concentrations varied little across all 13 streams but varied markedly across seasons (Fig. 2). Nitrate concentrations demonstrated an unexpected seasonal pattern of highest concentrations during the growing season, an October NO_3^- crash, and a modest rebound during the rest of the dormant season (November–March). This pattern was amplified in the drought year of 2005–2006 and was qualitatively similar if less pronounced in 2006–2007 (Fig. 2). Chloride averaged 20 μmol L^{-1} in most streams, with increases during the 2005 drought

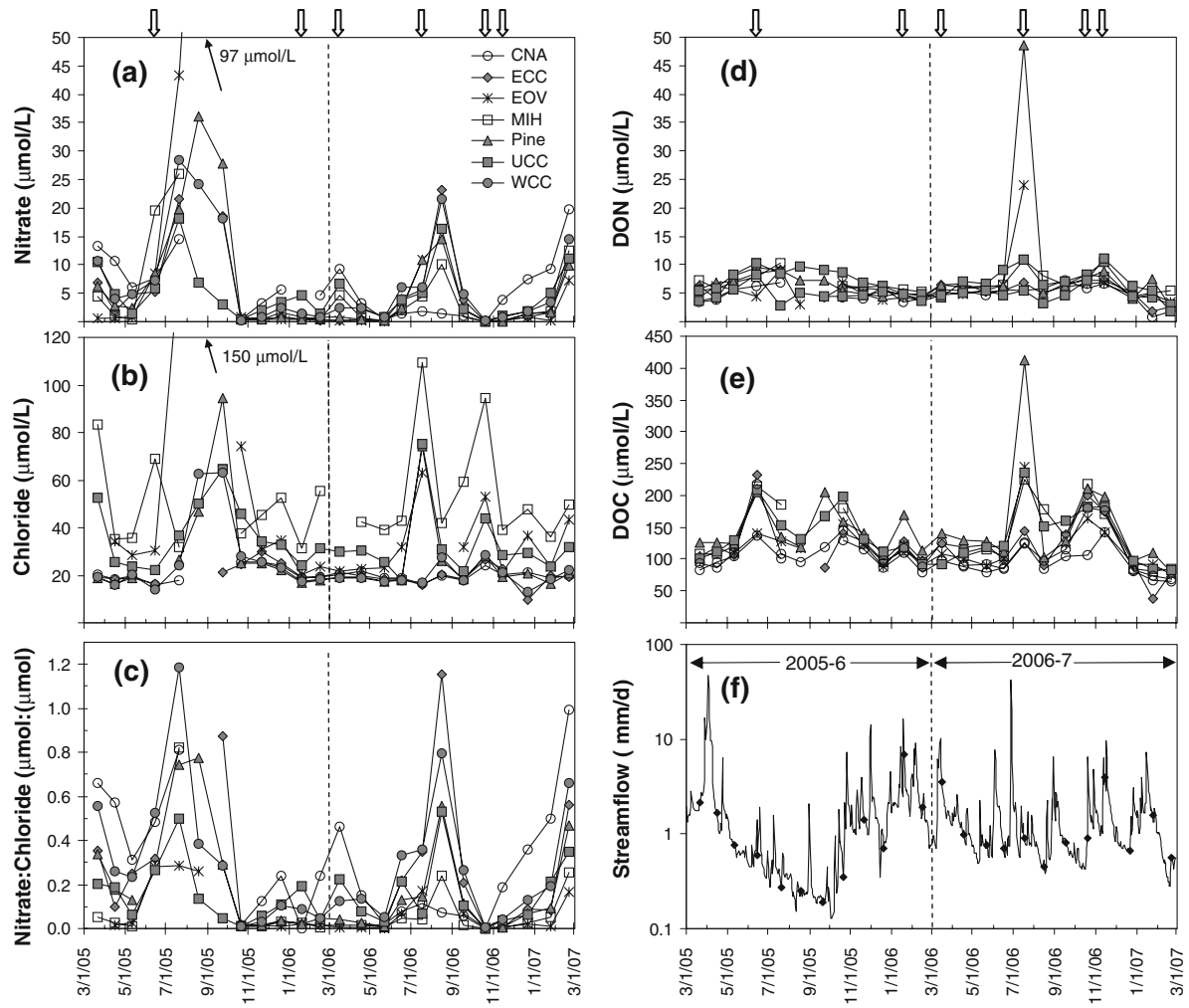

Fig. 2 Seasonal (mm/dd/yy) patterns of **a** nitrate, **b** chloride, **c** nitrate:chloride ratio, **d** DON, **e** DOC for seven streams and **f** streamflow at Six-Mile Creek over 2005–2006 and 2006–2007. *Arrows* indicate samples collected within 2 days of precipitation events ≥1 cm

presumed due to evaporative concentration. Although it is under some biological control, Cl^- sometimes acts as a conservative solute (i.e., sources and sinks small relative to inputs and outputs, Lovett et al. 2005). Considering NO_3^- patterns relative to Cl^-, NO_3^-:Cl^- ratios peaked at similar levels in both 2005 and 2006, indicating consistent enrichment in NO_3^- relative to Cl^- during summer.

When averaged across the streams that were sampled for 2 years, NO_3^- concentration correlated inversely with discharge measured at Six-Mile Creek on the date of sampling (Fig. 3). That is, high NO_3^- concentrations occurred on dates with low discharge, and dates with high flows generally had lower NO_3^- concentrations. Exceptions to this pattern occurred in October of both years and during snowmelt periods: NO_3^- concentrations during both Octobers were much lower than predicted by the NO_3^-/streamflow regression and NO_3^- concentrations in snowmelt periods were somewhat higher (Fig. 3).

Ammonium concentrations were consistently low, averaging 0.1 ± 0.1 µmol L^{-1} (mean ± 1 SD), with a maximum of 0.8 µmol L^{-1} (not shown). DON averaged 5.8 ± 1.7 µmol N L^{-1} with little variation across streams or seasons, although July 2006 provided an exception. Spikes of DON and DOC occurred in several streams on that date, perhaps a response to a 14 mm rainfall 2 days earlier (Figs. 1, 2).

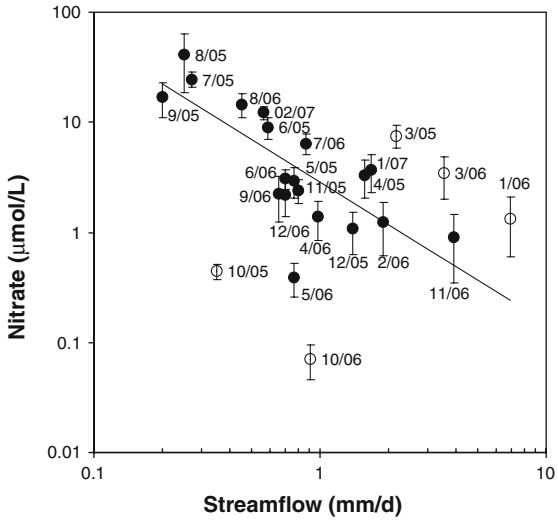

Fig. 3 Mean (±1 SE) NO_3^- concentration (µmol L^{-1}) of seven forested streams in the Upper Susquehanna basin versus streamflow on sampling dates (mm/yy) at Six-Mile Creek (Fig. 1). Regression line was fit to *solid symbols* (Log NO_3^- = 0.46–1.28 log flow; $R^2 = 0.58$, $P < 0.001$). *Open symbols* indicate October and snowmelt exceptions discussed in text

Stream DOC averaged 119 ± 14 µmol C L^{-1} across streams and sampling dates. The ratio of DOC:DON (mol:mol) averaged 21.8 ± 5.3, and did not show seasonal or stream-to-stream differences. Neither DOC nor DON concentration correlated with daily discharge at Six-Mile Creek (not shown; $R^2 < 0.02$, $P > 0.5$ for both).

The roughly estimated N exports from these Upper Susquehanna catchments were small, averaging 0.4 kg ha^{-1} $year^{-1}$ for NO_3^--N, <0.05 kg ha^{-1} $year^{-1}$ for NH_4^+-N, and 0.5 kg ha^{-1} $year^{-1}$ for DON and across all 13 streams (Table 3). Corresponding estimates of N retention averaged 90% of inorganic N deposition (8.3 kg N ha^{-1} $year^{-1}$) when including DON losses, and 96% when excluding them. Differences among sites in annual N export were small (Table 3) relative to uncertainties in these flux calculations (discussed below).

In Pine Creek, longitudinal sampling during 2006–2007 demonstrated few changes in solute concentrations with distance downstream from the stream's source at a perennial spring (Fig. 4). October was an exception: NO_3^- concentration declined exponentially from 5 µmol L^{-1} at 10 m from the spring to <0.1 µmol L^{-1} within 120 m downstream (NO_3^- = $8.91e^{-0.0433 \times \text{distance}}$; NO_3^- in µmol L^{-1} and distance in m; $R^2 = 0.96$). This pattern translates to a net removal distance of 23 m, similar to N uptake lengths (S_W, Newbold et al. 1983) estimated for similarly sized streams using additions of ^{15}N-NO_3 (Thomas et al. 2001; Mulholland et al. 2008; Valett et al. 2008). DON and DOC concentrations increased steadily over the top 120 m during October, and DOC:DON ratios increased from 20 to over 60 (Fig. 4). October Cl^- concentrations increased from 20 to 34 µmol L^{-1}, whereas SO_4^{2-} concentrations remained steady.

Table 3 Estimated annual stream export (kg ha^{-1} $year^{-1}$) and N retention for 2005–2006

	Stream	Stream export (kg ha^{-1} $year^{-1}$)			N retention (%)	
		NO_3^--N	DON	DOC	DIN (%)	TDN (%)
1	Cornell Natural Area	0.6	0.3	6.9	92	88
2	East Carter Creek	0.2	0.4	8.2	98	92
3	East Overlook Trail	0.3	0.4	7.9	97	92
4	Michigan Hollow	0.2	0.5	8.2	98	92
5	Pine Creek	0.3	0.5	9.8	97	91
6	Upper Carter Creek	0.4	0.5	8.8	95	89
7	West Carter Creek	0.4	0.4	7.6	95	91
8	Bald Mtn.	0.4	0.6	10.3	94	87
9	Cayutaville Rd.	0.5	0.6	9.0	94	89
10	Eastman Hill	0.6	0.4	6.6	93	88
11	Honeypot Rd.	0.4	0.6	9.2	96	88
12	Swan Rd.	0.3	0.5	9.3	97	90
13	West Overlook Trail	0.1	0.5	8.0	98	93
AVE		0.4	0.5	8.4	96	90
SD		0.2	0.1	1.1	2	2

All NH_4^+-N fluxes estimated at <0.05 kg ha^{-1} $year^{-1}$

Soil water near the origin of Pine Creek showed large summer NO_3^- peaks during 2007 (Fig. 5a). In the shallow (10 cm) lysimeters, NO_3^- concentrations were <4 µmol L^{-1} during winter and spring 2007, then rose at the end of May to reach 20–40 µmol L^{-1} during summer and early fall, and decreased throughout late fall to <4 µmol L^{-1} by the end of November. Soil water at 50 cm displayed a similar seasonal pattern and slightly higher NO_3^- concentrations as at 10 cm. The tension lysimeters at 50 cm presumably sampled pore water as well as free-draining soil water collected by the zero-tension lysimeters at 10 cm.

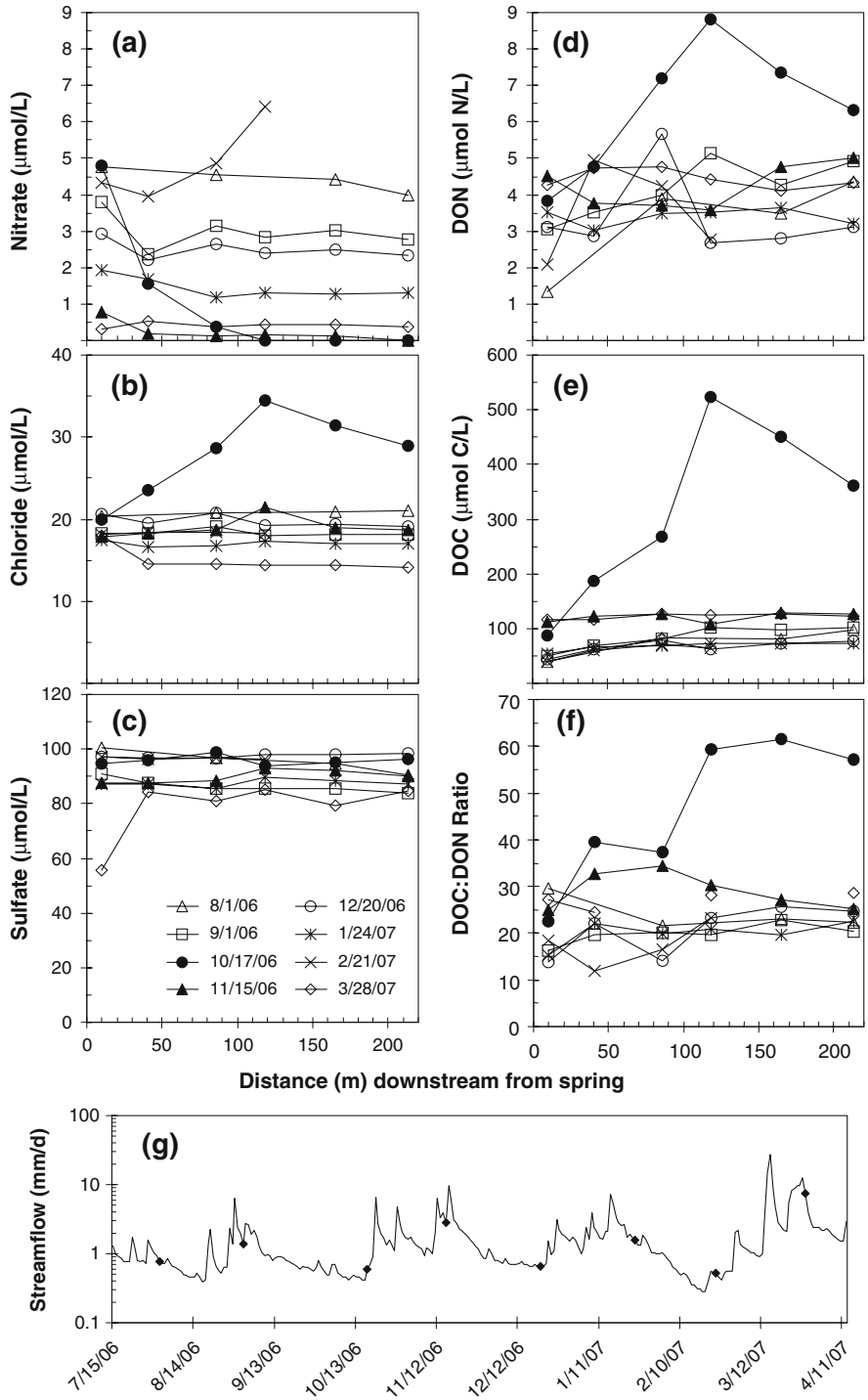

Fig. 4 Longitudinal profile of **a** nitrate, **b** chloride, **c** sulfate, **d** DON, **e** DOC, and **f** DOC:DON ratio in monthly samples from Pine Creek, downstream from a perennial spring source, and (**g**) streamflow at Six-Mile Creek on sampling dates, August 2006–March 2007. All concentrations are μmol L^{-1} or mol:mol

Streamside wells displayed little NO_3^- seasonality. Stream NO_3^- below the spring was highest in late winter and late summer, though this summer 2007 NO_3^- rise was far smaller than in soil water (Fig. 5b) or in stream water collected from the base of the catchment during 2005–2006 (Fig. 2a).

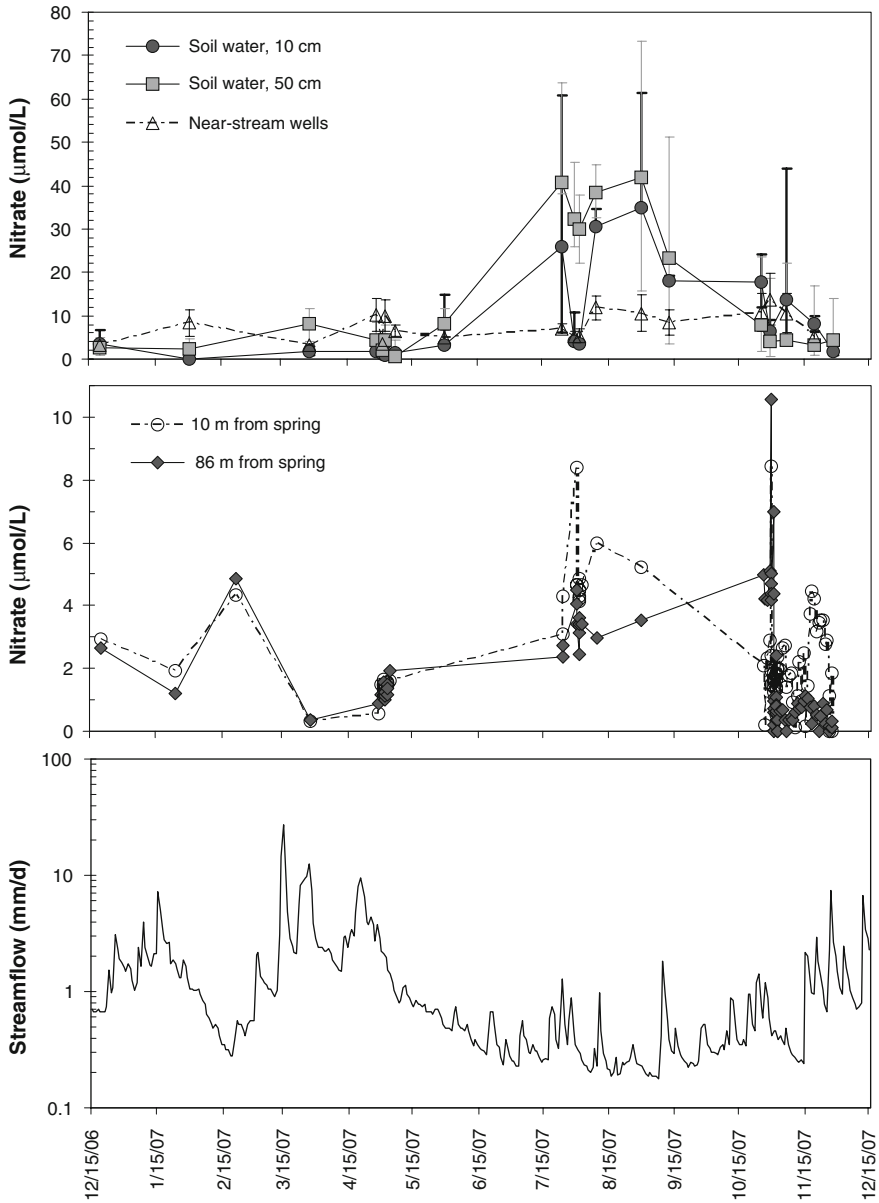

Fig. 5 Nitrate concentration during 2007 near the source of Pine Creek in **a** soil water (10 and 50 cm) and in streamside wells and **b** at two distances from the spring source, along with (**c**) streamflow at Six-Mile Creek on sampling dates. Soil and well water samples are median, 25th and 75th percentile. Note scale difference between *panels*

Isotopic separation of nitrate sources

Stream NO_3^- sources were partitioned using δ^{18}O-NO_3^- values to discern between precipitation NO_3^- (+77‰) and microbially produced or cycled NO_3^- (−3‰) (Table 2; Fig. 6a). In March 2005, stream δ^{18}O-NO_3^- values ranged from +4.8‰ (Eastman Hollow) to +34.2‰ (West Carter Creek) across nine streams, indicating that 10–47% of stream NO_3^- on this date derived directly from melting snow or other precipitation source. This range stretched to 4–53% if calculated using the range of atmospheric (+70 to +81‰) and microbial (−6 to +2‰) δ^{18}O-NO_3^- values for this area. During the rest of the year (April 2005–February 2006), stream δ^{18}O-NO_3^- values ranged from −6.7 to +3.4‰, indicating that <8% of stream NO_3^- came directly from atmospheric sources (Fig. 6a).

Stream δ^{15}N-NO_3^- values ranged from −1.9 to +5.9‰, with relatively depleted values in spring and enriched values in late summer (Fig. 6b). Compared across all samples, stream δ^{15}N-NO_3^-

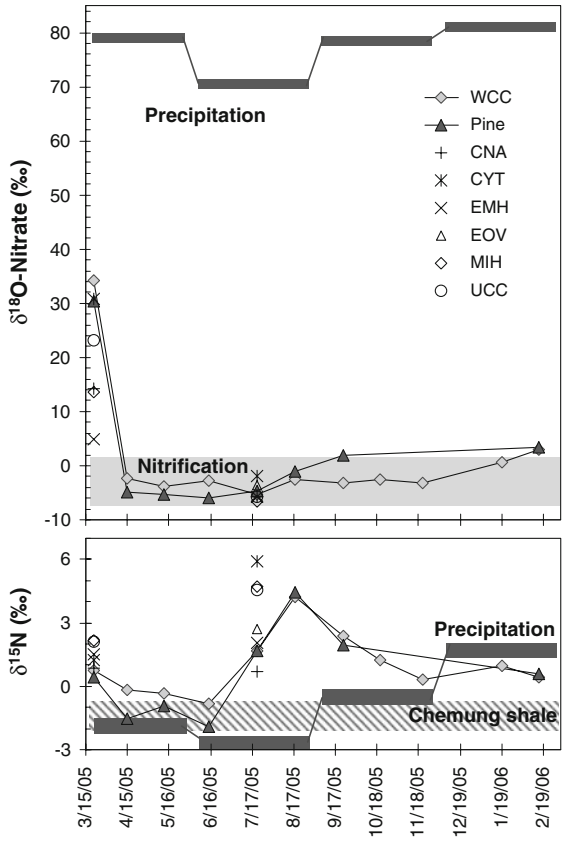

Fig. 6 The **a** $\delta^{18}O$ and **b** $\delta^{15}N$ values of stream NO_3^- from West Carter Creek (*diamonds*), Pine Creek (*triangles*) for all months during 2005–2006 with sufficient NO_3^- to allow analysis, and for seven other streams for March and July only. *Shaded bars* indicate isotopic range for precipitation (Connecticut Hill), theoretical $\delta^{18}O$-NO_3^- values for nitrifiers, and $\delta^{15}N$ values for Chemung shale

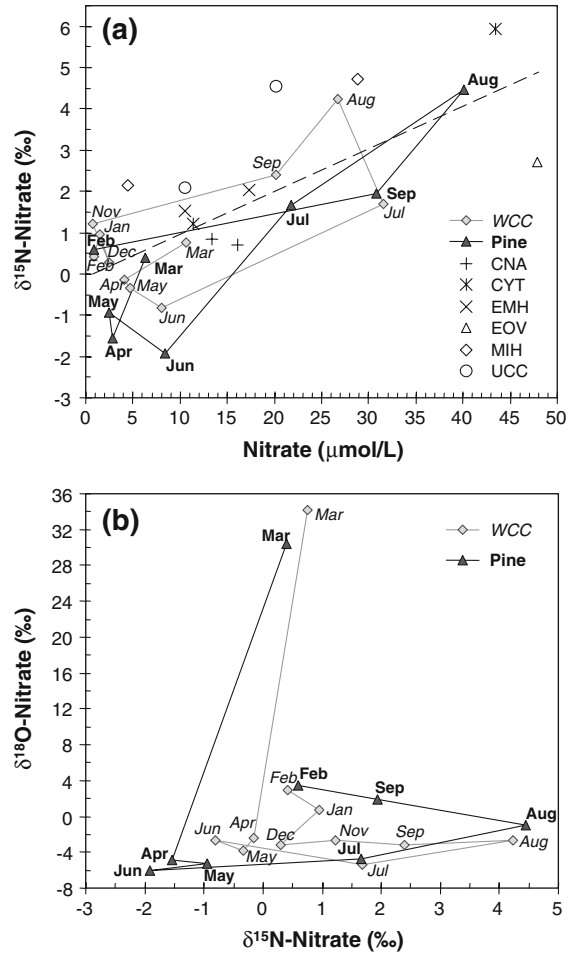

Fig. 7 **a** Nitrate concentration and $\delta^{15}N$-NO_3^- values of all stream samples with $\delta^{15}N$ measurements (2005–2006), and **b** $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^- values for Pine and West Carter Creeks. *Symbols* as in Fig. 6, with sample month indicated for Pine and West Carter Creeks. *Dotted line* in **a** indicates regression across all samples, $\delta^{15}N$ (‰) $= -0.1 + 0.1$ NO_3^- (μmol L^{-1}); ($R^2 = 0.55$, $P < 0.0001$)

values increased with NO_3^- concentration (Fig. 7a; $R^2 = 0.47$, $P < 0.001$).

Geologic nitrogen

All rock samples contained detectable quantities of N (Table 4), ranging from 0.03% in Tully limestone and 0.04% in Chemung grey shales to 0.15% in Geneseo black shale. In the Geneseo black shale, N was distributed evenly between organic and inorganic forms. The other rock types contained little organic N; the N in these rocks was presumed to be NH_4^+ incorporated into clay minerals during diagenesis. These values of % N for central New York shales are similar to those reported from cores of these formations in western New York (Sageman et al. 2003), and are within the broad range reported for sedimentary rocks elsewhere (Holloway and Dahlgren 2002). Shale $\delta^{15}N$ values averaged −0.1‰ across all rock types and ranged from −2.6 to +2.3‰ (Table 4). The Chemung Formation shale that dominated the study catchments had $\delta^{15}N$ values that ranged from −2.6 to +0.5‰. These rock $\delta^{15}N$ values largely overlap $\delta^{15}N$ values observed for stream NO_3^-, except during late summer, when stream NO_3^- (+0.7 to +5.9‰) was more enriched in ^{15}N relative to the sampled rocks (Fig. 6b).

Table 4 Mean (SD) concentration of nitrogen (%) and δ^{15}N values (‰) in sedimentary rock formations in central New York

	n	N (%)		δ^{15}N (‰)	
		Total	Ashed	Total	Ashed
Chemung grey shale	6	0.04 (0.01)	0.03 (0.01)	−0.4 (1.1)	−0.3 (1.1)
Ithaca grey shale	1	0.08	0.06	−0.5	0.4
Geneseo black shale	3	0.15 (0.01)	0.07 (<0.01)	0.6 (0.4)	0.5 (1.6)
Tully limestone	2	0.03 (0.02)	BD	−2.8 (0.6)	BD

BD below detection limits of 0.01% N

Discussion

Retention of atmospheric N appeared strong within these Upper Susquehanna headwater catchments, even with large uncertainties in the estimated N exports. Despite strong N retention, these streams displayed an unexpected seasonal NO_3^- pattern, with highest NO_3^- concentrations during summer. Temperate forest catchments with high rates of N retention are expected to have seasonal NO_3^- patterns marked by low concentrations during the growing season and higher concentrations during the dormant season, a pattern attributed to biological demand for N during the growing season (e.g., Likens and Bormann 1995; Stoddard 1994; Church 1997). Old-growth forests (Vitousek and Reiners 1975) or sites in late stages of N saturation (e.g., Stoddard 1994; Stoddard et al. 2001; Wright et al. 2001) may lack a summer NO_3^- dip due to diminished or saturated biological N demand; summer NO_3^- peaks lack an explanation within this simple framework. Below, we outline potential processes driving N retention and the unusual seasonal NO_3^- patterns observed in the central New York catchments and in comparable systems—the summer peaks, autumn crashes, and NO_3^- losses at snowmelt.

Annual N loss and retention

Monthly stream sampling and lack of on-site discharge measurements allowed only coarse estimates of annual stream N export for the 13 Upper Susquehanna catchments (Table 3).

Uncertainties in monthly streamflow produced uncertainties in annual total N exports estimated at $\pm <$ 0.3 kg N ha^{-1} year^{-1}, calculated by increasing then decreasing all monthly discharge estimates by standard deviations derived from the area-discharge relationships determined from six nearby gauged streams. Lack of explicit event sampling likely led to underestimates of annual N flux. In western New York, storm events accounted for 13, 39, and 34% of the annual flux of NO_3^-, DON, and NH_4^+ (Inamdar et al. 2006). Comparisons of various methods for computing annual NO_3^- flux from nine Pennsylvania and West Virginia streams determined that coarse flux estimates derived from monthly chemistry and monthly discharge yielded values to within 0.7 to 40% of annual fluxes estimated from more than 250 chemistry samples distributed across flow conditions (Swistock et al. 1997). The flux estimates presented here (Table 3) provide a first approximation, only. However, even if these estimates captured just one-third of true NO_3^- export, inorganic N retention in this part of the Upper Susquehanna basin would average 87% of inputs. Some retention may be due to accumulation of N into re-growing biomass and re-accumulating soil (e.g., Goodale and Aber 2001; Flinn and Marks 2007), although even catchments dominated by primary forest (Table 1) had high rates of apparent N retention (Table 3).

The stream NO_3^- exports estimated here are lower than those estimated from comparably quantified estimates from elsewhere in New York for the Adirondack (2–3 kg N ha^{-1} year^{-1}; Ito et al. 2005) and Catskill Mountains ($\sim$3 kg N ha^{-1} year^{-1}; Lovett et al. 2000), regions which have slightly higher rates of N deposition (9–12 kg ha^{-1} year^{-1}) compared to the 8.3 kg ha^{-1} year^{-1} received in central New York. Past work in temperate forests using similar approaches to estimate N inputs and outputs indicates an N deposition threshold of around 8–10 kg N ha^{-1} year^{-1}, below which there is near complete N retention and above which NO_3^- export increases sharply, with much site-to-site variation (Dise and Wright 1995; MacDonald et al. 2002; Aber

et al. 2003). The central New York streams occur at this deposition threshold and appear to have high rates of N retention, consistent with these regional input/output responses. However, seasonal NO_3^- patterns differ greatly from those of other seasonally snow-covered catchments.

Summer nitrate peaks

The summer peaks in stream NO_3^- were unexpected, and might have been driven by several mechanisms, including: (1) concentration through summer evapotranspiration; (2) summer release of NO_3^--rich water flushed to groundwater during snowmelt or other high-flow period; (3) weathering of geologic N; and (4) summer increases in soil net nitrification.

High rates of evapotranspiration in summer may concentrate solutes, especially during droughts. Mulholland and Hill (1997) suggest that the concentrating effects of evapotranspiration may partly drive summer NO_3^- peaks in Walker Branch, Tennessee. In central New York, especially high anion concentrations occurred during the drought summer of 2005 (Fig. 2). Nonetheless, stream NO_3^-:Cl^- ratios showed NO_3^- enrichment relative to Cl^- during summer in both 2005 and 2006, suggesting that processes beyond evaporative concentration enhanced stream NO_3^- concentrations relative to Cl^- during summer months.

The negative concentration/discharge relationship observed here across seasons (Fig. 3) implied either temporal covariation between N retention processes and catchment moisture status (e.g., nitrification and denitrification) or a broad seasonal dilution of a relatively constant source of NO_3^--rich water. Burns et al. (1998) proposed a mechanism for producing NO_3^--rich groundwater for the Catskill Mountains, NY: movement of large amounts of NO_3^- to groundwater at snowmelt that then seeps out during the rest of the year. This process decouples the supply of NO_3^- to groundwater at snowmelt from plant demand during the growing season, and requires that soil capacity to retain N be bypassed or overwhelmed during snowmelt. This process also yields a negative concentration-discharge relationship under summer baseflow conditions (Burns et al. 1998). It is difficult to estimate the importance of this process for the central New York streams from existing observations. There is little indication of consistently elevated NO_3^- in the spring source at Pine Creek (Figs. 4, 5a); regular measurements from springs in other catchments might further test this mechanism for these systems.

Weathering of N from sedimentary rock provides another possible means of supplying high NO_3^- to groundwater. In California, Holloway et al. (1998) observed high NO_3^- concentrations in streams with catchments composed of N-rich lithologies: one catchment dominated by an N-rich phyllite (0.10–0.18% N) had an annual NO_3^- export of 20 kg N ha^{-1} $year^{-1}$, with >90% of geologic origin. Geologic N clearly provided a much smaller NO_3^- source to the central New York catchments. Furthermore, $\delta^{15}N$ values indicate a stream NO_3^- source during summer other than simple weathering of geologic N. That is, $\delta^{15}N$ for the Chemung Formation shale that dominates the New York catchments ranged between −2.6 and +0.5‰, whereas stream $\delta^{15}N$-NO_3^- values ranged from +0.7 to +5.9‰ in late summer (Fig. 6b). A great many processes can affect the natural abundance of ^{15}N, however. Weathering studies might provide further information on the importance of geologic N to central New York streams.

A seasonal increase in soil net nitrification could also supply NO_3^--rich water in summer. Net nitrification rates in temperate forests often peak during the growing season (e.g., Nadelhoffer et al. 1983; Bohlen et al. 2001), presumably driven by the strong effect of temperature on nitrification (Stark 1996). Furthermore, seasonal drying should increase soil aeration, favoring nitrification over NO_3^- reduction. At the plot scale, net nitrification in soils with low C:N ratios can produce growing-season NO_3^- peaks in soil solution, such as those observed at Pine Creek (Fig. 4), as well as at Turkey Lakes, Ontario (Foster et al. 1989), and near Tokyo, Japan (Ohrui and Mitchell 1997). At the catchment scale, Tague and Band (2004) used the RHESSys model to conclude that summer NO_3^- peaks in a forested stream near Baltimore, Maryland, result from the source of stream water from riparian wetlands shifting from denitrification during the dormant season to net NO_3^- production as these soils dry out during the growing season. Ohrui and Mitchell (1997, 1999) and Ohte et al. (2001) invoke both rapid summer nitrification and flowpath-related mechanisms for the summer NO_3^- peaks they observed in Japanese catchments.

In Pine Creek, the large summer peaks in soil water NO_3^- seem to suggest a source of NO_3^- from

nitrification. The large decrease in NO_3^- concentration between the lysimeters and the stream (Fig. 5) indicates either hydrologic decoupling between the stream and nearby soils, or a net removal of NO_3^- in deeper soils or the near-stream zone by deep roots, denitrification, or other biotic or abiotic processes. Summer NO_3^- peaks in streams could occur should only a fraction of this NO_3^- reach the stream. Denitrification can reduce NO_3^- concentrations, and should yield elevated $\delta^{15}N$ values and $\delta^{18}O$ values in the residual NO_3^-, unless the process goes to local completion and removes all NO_3^- (Böttcher et al. 1990; Kendall 1998; Kendall et al. 2007; Burns et al. 2009). The positive correlation between $\delta^{15}N$-NO_3^- and NO_3^- concentration across streams and months (Fig. 7a) would seem to point against denitrification as an important process in these catchments. However, a large increase in net NO_3^- production in surface soils, coupled with partial removal of NO_3^- at depth through denitrification could produce seasonally elevated stream NO_3^- concentrations especially enriched in ^{15}N. That is, high nitrification rates in summer could fuel increases in both NO_3^- leaching and denitrification.

Nitrate crash at leaffall and in-stream uptake

In-stream processes appear to retain NO_3^- during autumn leaffall. In October of both 2005 and 2006, NO_3^- concentrations in all streams dropped sharply from summer peaks to trace levels (Fig. 2), concentrations far less than predicted from the NO_3^-/discharge regression (Fig. 3). The difference between predicted and observed NO_3^- concentrations amounted to approximately 0.4–0.5 g N ha^{-1} day^{-1} on those dates (Fig. 3). In Pine Creek, October was the only month in which stream NO_3^- decreased with distance downstream from the stream's spring source (Fig. 4a). The exponential decrease of stream NO_3^- corresponded with increases in Cl^-, DOC, DON, and DOC:DON ratio (Fig. 4). Both Cl^- (Lovett et al. 2005) and labile DOC (McDowell and Fisher 1976) leach rapidly from fresh leaf litter. We believe that the sharp decrease in October stream NO_3^- concentration likely occurred through immobilization of N by heterotrophic microbes, due to input of labile dissolved and particulate C from fallen leaves. This NO_3^- uptake is likely restricted to the period of labile C input from fresh leaffall, often just a few days (McDowell and Fisher 1976). Higher resolution sampling (e.g., Sebestyen et al. 2009) might reveal the duration of in-stream N uptake in autumn.

At Walker Branch, Tennessee, autumn peaks in stream DOC and minima in NO_3^- were attributed to inputs of leaves and corresponding heterotrophic uptake of N (Mulholland and Hill 1997; Mulholland 2004). Later measurements of stream metabolism supported these inferences (Roberts and Mulholland 2007). In Tennessee and North Carolina, rates of gross ^{15}N-NO_3^- uptake were higher following leaffall than during spring and summer (Valett et al. 2008). Early fall minima in NO_3^- concentrations occur in Catskill, NY, streams (Murdoch and Stoddard 1993), and Sobczak et al. (2003) demonstrated that DOC from litter leachate could induce heterotrophic uptake of $\sim$40 µmol L^{-1} NO_3^- in model Catskill systems, with no denitrification. Similarly, experimental additions of acetate to a stream at Hubbard Brook, New Hampshire, increased heterotrophic uptake of NO_3^-, but not denitrification (Bernhardt and Likens 2002). Autumn minima in stream NO_3^- have been reported recently for Hubbard Brook (Dittman et al. 2007) and for Sleepers River, Vermont (Sebestyen et al. 2009). Beyond the work cited here, we are aware of few others who have discussed an autumn crash in stream NO_3^-, perhaps because it is easily masked by low NO_3^- concentrations in the preceding growing season in the "conventional" seasonal NO_3^- pattern. Low NO_3^- concentrations in early fall become prominent when contrasted against elevated summer NO_3^- concentrations, as observed here.

Nitrate loss during the dormant season

Previous studies have observed increases in stream $\delta^{18}O$-NO_3^- values during snowmelt indicating modest contributions (up to $\sim$35%) to stream NO_3^- directly from melting snow or other precipitation source (e.g., Spoelstra et al. 2001; Burns and Kendall 2002; Pardo et al. 2004; Piatek et al. 2005; Campbell et al. 2006; Hales et al. 2007). The central New York catchments studied here show similar results, but with especially elevated stream $\delta^{18}O$-NO_3^- values (>30‰) in three streams (Pine, West Carter, and Cayutaville Creeks) in March 2005, indicating about 42–47% contribution from melting snow or other atmospheric source to NO_3^- in these samples

(Fig. 6a). Other winter samples from January and February 2006 showed higher stream NO_3^- concentrations than predicted from the NO_3^-/discharge regression (Fig. 3), but these samples lacked elevated δ^{18}O-NO_3^- values (Fig. 6a). These winter observations indicate that this NO_3 is derived from microbial processing, presumably from nitrification in surface soils under that year's patchy snow pack or from deeper and older sources of NO_3^- (e.g., Piatek et al. 2005).

High-frequency measurements at Sleepers River, Vermont, demonstrate that δ^{18}O-NO_3^- values can vary substantially throughout the course of snowmelt. Sampling during snowmelt in 2003 and 2004 at intervals of minutes to hours revealed highest δ^{18}O-NO_3^- values (+18 to +43‰) at the start of snowmelt, dropping within a day or so to modestly elevated levels ($\sim$+5‰) sustained throughout the rest of snowmelt, then dropping to about −3‰ by the time the snow pack had melted completely (Ohte et al. 2004; Sebestyen et al. 2008). These observations were interpreted as a first phase of melt from snow directly covering the stream channel, contributing nearly half of stream NO_3^- in some samples, but persisting only a few days (Ohte et al. 2004; Sebestyen et al. 2008). High-resolution δ^{18}O-NO_3^- measurements would help discern the duration of direct snowmelt inputs in these central New York streams.

Common drivers of unusual nitrate seasonality

The unusual seasonal NO_3^- patterns observed in central New York have been observed previously in a few other sites. These sites include Walker Branch, Tennessee (Mulholland 2004) and Coweeta Forest, NC (Swank and Vose 1997), both with modest (<4 μmol L^{-1}) peak NO_3^- concentrations during summer and high rates of N retention; the Pond Branch catchment in Baltimore, Maryland, with summer NO_3^- peaks near 15 μmol L^{-1} (Band et al. 2001; Tague and Band 2004); and catchments across a range of N deposition rates in Japan (Ohrui and Mitchell 1997, 1999; Ohte et al. 2001). Do the unusual seasonal NO_3^- patterns in these catchments have common explanations?

Mulholland and Hill (1997) and Mulholland (2004) observed that catchments with summer NO_3^- peaks occur in warmer regions than catchments with more conventional winter NO_3^- peaks, and they suggest that above-freezing winter temperatures and lack of snow cover may allow year-round activity and N demand by soil microbes. However, catchments in places like the United Kingdom display "conventional" NO_3^- seasonality despite winter temperatures typically above freezing (Davies et al. 2005; Curtis et al. 2005), and the central New York catchments studied here displayed "summer peak" seasonality despite significant snow cover in winter. Together, these observations suggest that some factor other than winter snow cover drives the unusual NO_3^- seasonality.

The different NO_3^- seasonality patterns also broadly covary with soil type. Areas with "conventional" NO_3^- seasonality, such as northern Europe and mountains of the western and eastern US, largely coincide with regions of podzolic soils (Spodosols), typified by thick forest floors and surface mineral horizons leached of organic matter. By contrast, sites with "summer peak" NO_3^- seasonality typically have soil types with more complete decomposition, limited forest floor development, and surface mineral horizons enriched with organic matter (Inceptisols, Alfisols, or Ultisols). At the plot scale, past work in the Pine Creek catchment on invasive earthworms demonstrated that lysimeter NO_3^- displays "summer peak" seasonality in plots in which worms had eliminated the forest floor, whereas nearby plots with forest floor intact have elevated NO_3^- concentrations throughout the year (Bohlen et al. 2004). Further understanding of soil controls on N retention may be gained from tracer and N budget studies in the forest floor and surface mineral soils, with special focus on both seasonal and cross-site variation.

Conclusions

Most seasonally snow-covered catchments display seasonal stream NO_3^- patterns with summer minima and dormant season maxima, a pattern commonly attributed to summer demand for N by plants and soil microbes. Seasonally snow-covered headwater catchments in the Upper Susquehanna River basin had high rates of roughly estimated N retention but displayed unusual seasonal NO_3^- patterns consisting of summer peaks, an autumn crash, and modest rebound during the dormant season. Explanations for the summer NO_3^- peaks include seasonal variation in

the production and transport of NO_3^- in soil. The fall NO_3^- crash appears likely due to in-stream heterotrophic uptake of N driven by labile C inputs at leaffall. Dormant-season NO_3^- losses derive from NO_3^- from microbial nitrification, except for pulses of NO_3^- directly from melting snow. Rather than simply responding to seasonal variation in plant demand, seasonal NO_3^- patterns in these streams appear driven by seasonal variation in a range of processes, with key roles for soil nitrification and in-stream N uptake at leaffall.

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