Biogeochemistry **62:** 87–117, 2003.

Biogeochemistry of unpolluted forested watersheds in the Oregon Cascades: temporal patterns of precipitation and stream nitrogen fluxes

KRISTIN L. VANDERBILT[1,4,*], KATE LAJTHA[2] and FREDERICK J. SWANSON[3]

*[1]Department of Forest Science, Oregon State University, Corvallis, OR 97331, USA; [2]Department of Botany and Plant Pathology, Oregon State University, Corvallis, OR 97331, USA; [3]Pacific Northwest Research Station, USDA Forest Service, Corvallis, OR 97331, USA; [4]Current address: Department of Biology, University of New Mexico, Albuquerque, NM 87131, USA; *Author for correspondence (e-mail: vanderbi@sevilleta.unm.edu; phone: (505) 277-1909; fax: (505) 277-5355)*

Received 20 November 2001; accepted in revised form 20 January 2002

Key words: DON, H.J. Andrews Experimental Forest, Hydrology, Nitrogen, Streams, Watershed

Abstract. We analyzed long-term organic and inorganic nitrogen inputs and outputs in precipitation and streamwater in six watersheds at the H.J. Andrews Experimental Forest in the central Cascade Mountains of Oregon. Total bulk N deposition, averaging 1.6 to 2.0 kg N ha^{-1} yr^{-1}, is low compared to other sites in the United States and little influenced by anthropogenic N sources. Streamwater N export is also low, averaging <1 kg ha^{-1} yr^{-1}. DON is the predominant form of N exported from all watersheds, followed by PON, NH_4-N, and NO_3-N. Total annual stream discharge was a positive predictor of annual DON output in all six watersheds, suggesting that DON export is related to regional precipitation. In contrast, annual discharge was a positive predictor of annual NO_3-N output in one watershed, annual NH_4-N output in three watersheds, and annual PON output in three watersheds. Of the four forms of N, only DON had consistent seasonal concentration patterns in all watersheds. Peak streamwater DON concentrations occurred in November-December after the onset of fall rains but before the peak in the hydrograph, probably due to flushing of products of decomposition that had built up during the dry summer. Multiple biotic controls on the more labile nitrate and ammonium concentrations in streams may obscure temporal DIN flux patterns from the terrestrial environment. Results from this study underscore the value of using several watersheds from a single climatic zone to make inferences about controls on stream N chemistry; analysis of a single watershed may preclude identification of geographically extensive mechanisms controlling N dynamics.

Introduction

In recent decades, as atmospheric nitrogen (N) deposition has risen substantially over historical levels in many locations (Fenn et al. 1998; Holland et al. 1999), stream chemistry data have been analyzed to evaluate how elevated N deposition and other ecosystem properties affect N cycling through forests and streams. Investigators have used streamwater N records from a range of forested watersheds with different size, N deposition, vegetation, and soil characteristics to infer which of these factors affect N output (Dise and Wright 1995; Lepisto et al. 1995). Others

have examined long-term records from a few watersheds to learn how changes in N deposition or climate influence N output (Murdoch and Stoddard 1992; Mitchell et al. 1996; Swank and Vose 1997). These studies offer insights into N cycling in watersheds where the N cycle has been altered by anthropogenic additions of N. However, understanding the causes of natural variability of stream N solute chemistry in unpolluted sites is essential for providing baseline information against which data from elevated N deposition sites can be compared (Hedin et al. 1995). Few long-term records exist, however, for sites that are free from anthropogenic N inputs.

Unlike many areas in the United States, the H.J. Andrews Experimental Forest, OR, (HJA) is almost completely unaffected by N inputs from anthropogenic sources. The Andrews Forest has six watersheds where N fluxes and hydrology have been monitored for as much as thirty-two years. This is one of the longest records of N fluxes in forested watersheds receiving low N inputs in the United States. In addition, while most stream chemistry records include only dissolved inorganic N (DIN), the Andrews record also includes dissolved organic N (DON) and particulate organic N (PON). Processes influencing N export in this N-limited ecosystem can be investigated using this rich record of the natural variability of N inputs and outputs.

Terrestrial and aquatic processes affect DIN concentrations in streamwater. Watershed geomorphology (Creed and Band 1998), soil characteristics (Gundersen et al. 1998; Seely et al. 1998), land-use or fire history (Pardo et al. 1995; Johnson et al. 1997), vegetation type or successional stage (Vitousek and Reiners 1975; Wigington et al. 1998), and atmospheric loading (Stoddard 1994) may all affect the quantity of DIN entering a stream from the terrestrial ecosystem. N uptake by vegetation or soil microfauna may also influence seasonal patterns of stream DIN export (Likens and Bormann 1995; Vitousek 1977; Foster et al. 1989). In-stream processes, such as denitrification, cycling of N through biota, organic matter storage and particulate matter transport, can also modify stream DIN concentrations (Meyer et al. 1998; Burns 1998). Hydrologic processes, in particular, are frequently correlated with streamwater DIN concentrations. Several studies document seasonal NO_3-N concentration-discharge relationships (Bond 1979; Foster et al. 1989; Hill 1986; Newbold et al. 1995) and spikes in NO_3-N concentration associated with high discharge events (Hill 1993; Newbold et al. 1995).

Much less is known about processes influencing DON concentrations and fluxes in streamwater. Stream discharge was positively correlated with DON concentrations in five of nine watersheds studies in New England (Campbell et al. 2000) and five out of ten streams in the Lake Tahoe Basin (Coats and Goldman 2001). Peaks in DON concentrations were observed during storm events in an Appalachian stream (Buffam et al. 2001). McHale et al. (2000) found that DON concentrations were positively related to stream discharge in both dormant and growing seasons, and concluded that biotic controls seem to have a greater impact on NO_3-N concentrations than on DON concentrations. Due to differences in sorption behavior in soils and microbial lability between organic and inorganic forms of N, controls on DON in streams may differ substantially from controls on DIN.

Long-term datasets from HJA are used in this study to seek consistent relationships between DON and DIN export and watershed hydrology across years and across watersheds. Our objectives were to 1) characterize long-term patterns of N dynamics in precipitation and streamwater at the HJA, 2) analyze relationships between annual output of N solutes and annual stream discharge, 3) analyze relationships between seasonal streamwater N solute concentrations and precipitation and stream discharge, and 4) compare our results with those from other forested watersheds.

Methods

General site description

The H.J. Andrews Experimental Forest is located in the west-central Cascade Mountains of Oregon (Figure 1). This rugged, 6400-ha area is characterized by dense coniferous forests and steep slopes. Elevation ranges from 412 m to 1630 m. The Pacific Ocean lies 160 km to the west and strongly influences the climate of HJA. At 430 m elevation, mean January and July temperatures are 2 and 18 °C, respectively, and annual precipitation averages 250 cm. About 80% of annual precipitation falls in the October-March period during storms of relatively long duration (12–72 hours) and low intensity. Precipitation is typically dominated by rain below 350 m and snow above 1100 m. At elevations above 750 m, snowpack may persist for several months. Rain and snow events both occur between 400 and 1200 m elevation (Harr 1981).

Watershed characteristics

Stream chemistry data from six watersheds at HJA were used in this study (Table 1). Vegetation within all watersheds is dominated by Douglas-fir (*Pseudotsuga mensiezii*). Age classes differ between watersheds due to fires and silvicultural treatments. Less common tree species include *Tsuga heterophylla*, *Thuja plicata*, and, at high elevation, *Abies amabilis*. Understory shrub species include *Rhododendron macrophyllum*, *Acer circinatum*, and *Castanopsis chrysophylla*. WS6 and WS7 have had high cover of N-fixing *Ceanothus velutinus* during the last 20 years, although it has been overtopped by Douglas-fir and is presently dying out.

Soils of WS6, WS7, and WS8 are frigid Andic Dystrudepts, with fine-loamy or loamy-skeletal texture (Lammers, pers. comm). Soil depth in these three watersheds typically ranges from one to three meters to bedrock (Dyrness and Hawk 1972). Soils in WS2 are fine-loamy or loamy skeletal Typic Haplumbrepts, and fine-loamy Typic Dystrochrepts. WS10 soils are Typic Dystrochrepts with fine-loamy to loamy-skeletal texture, Umbric Dystrochrepts, and Typic Hamplumbrepts. Soils in WS9 are Typic Haplumbrepts with fine-loamy texture, Typic Dystrochrepts with coarse-loamy texture, and Ultic Hapludalfs of fine-silty texture. Soil depth to saprolite is

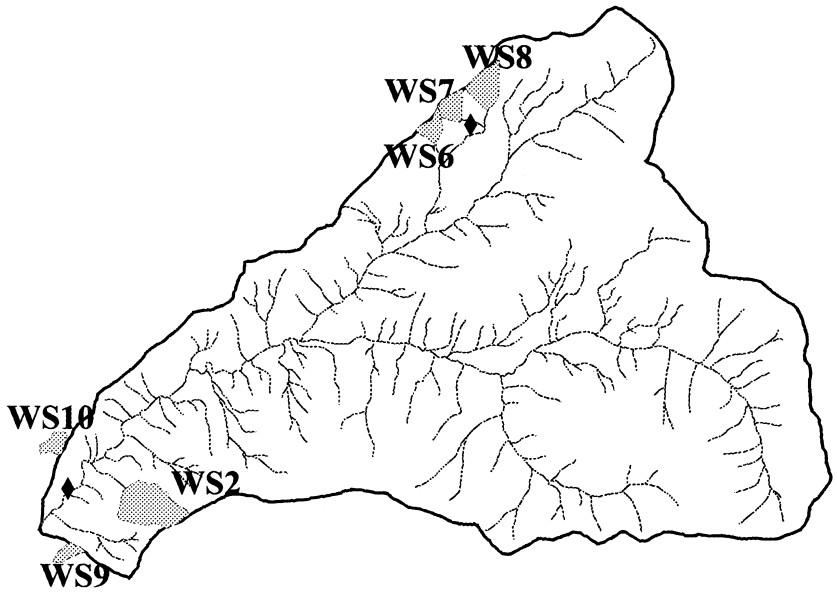

Figure 1. Six gauged watersheds are located in the H.J. Andrews Experimental Forest, Oregon in the Cascade Mountains of Oregon. Triangles are locations of precipitation collectors.

probably less than 3 m in WS9 (Fredriksen 1975), between one and two meters in WS2 (Rothacher et al. 1967), and as much as six meters in WS10 (Fredriksen 1975). Soils in all the watersheds have similar hydraulic characteristics (Perkins 1997). Hydraulic conductivity and subsurface flow are high (Harr 1977).

Precipitation and streamwater sampling

Precipitation samplers were located in clearings at 922 m elevation in WS7 and at 430 m elevation near WS9. Precipitation was collected at three-week intervals from 10/1/1968 until 5/24/1988 and at one-week intervals thereafter. From 1968 until 1988, both precipitation collectors consisted of stainless steel funnels to catch bulk precipitation that was fed through plastic tubing to an acid-washed polyethylene carboy within an insulated box. In 1988, the high elevation funnel collector was replaced with an Aerochem Metrics precipitation collector that collects both wet and dry precipitation; only the wet precipitation data are analyzed.

Streamwater was sampled just above the weir at the outlet of each watershed. Sampling location has not changed since the inception of the study. Samples were collected by flow-proportional water sampler (Fredriksen 1969). Until June 1988, individual samples were composited in an acid-washed polyethylene carboy, stored in the dark, and collected at three-week intervals. Since June 1988, carboys were collected once a week, refrigerated, and combined at three-week intervals for chemical analysis. To test whether water chemistry changed during the three-week storage period, two grab samples were collected during each sampling period in 1981–

Table 1. Characteristics of the six gauged watersheds at HJA.

Watershed	Area (ha)	Elevation (m)	Aspect	% Basal Area Logged (Year of Harvest)	Type of Harvest	Douglas-fir age in 2000	Period of Stream Chemistry Record (water years)
WS2	60	530–1070	NW	0	Uncut	470 years	1982–2001
WS9	8.5	425–700	SW	0	Uncut	470 years	1969–2001
WS10	10.2	430–670	SW	100 (1975)	Clear-cut	25 years	1969–2001
WS6	13.0	863–1013	S	100 (1974)	Clear-cut	25 years	1972–1987
WS7	15.4	908–1097	SSE	60 (1974) 40 (1984)	Shelterwood Cut	25 years	1972–1987
WS8	21.4	955–1190	SSE	0	Uncut	170 years	1972–2001

1982, and one was left in the gauge house for three weeks and the other was immediately analyzed. Martin and Harr (1988) reported that concentrations of NO_3-N and NH_4-N did not change significantly ($p > 0.05$) during the three-week storage period. In 1989, a quality control procedure was implemented. Once or twice a year, one grab sample was collected and analyzed immediately, while another was collected at the same time and left in the gauge house and collected with the next sample collection. Paired t-test analysis ($n = 12$) indicated that NO_3-N, NH_4-N, filtered total Kjeldahl N (DON + NH_4-N) and unfiltered total Kjeldahl N (PON + DON + NH_4-N) concentrations did not change significantly ($p > 0.05$) during the period they remained in the gauge house. Stream discharge was measured continuously with rectangular weirs at the high elevation watersheds since 1963 and with trapezoidal weirs at the low elevation watersheds since 1953.

Chemical analysis

Stream and precipitation samples were filtered in the laboratory prior to analysis. Pre-ashed glass-fiber GF/C filters (1.2 μm pore size) were used from 1968 until 1983, after which GF/F (0.7 μm pore size) filters were used (Martin and Harr 1989). Filters were pre-washed with deionized water and dried at 65 °C. NO_3-N was measured from 1968 to July 1978 manually using a cadmium reduction column and a Spec 20 spectrophotometer. After July 1978, NO_3-N was measured using the same chemistry on a Technicon Auto-Analyzer II. From 1966 to 1978, NH_4-N was analyzed on macro-Kjeldahl equipment by distillation and Nesslerization. Since 1978, NH_4-N was measured using the phenate procedure on a Technicon Auto-Analyzer II. Macro-Kjeldahl analysis was used to analyze for DON and PON. PON was calculated as the difference between Kjeldahl N content of filtered and unfiltered samples. DON concentration was calculated as the difference between Kjeldahl N and NH_4-N concentration in the filtered samples. Detection limits for NO_3-N, NH_4-N, DON, and PON were 0.001 mg N L^{-1}, 0.005 mg N L^{-1}, 0.01 mg N L^{-1} and 0.01 mg N L^{-1}.

Data description

HJA data were obtained from the Forest Science Databank (FSDB), a database maintained by the Department of Forest Science at Oregon State University in Corvallis, Oregon. Patterns of N in streamwater and precipitation were examined as three-week, volume-weighted concentrations and as three-week mass fluxes (kg N ha^{-1}). Three-week mass fluxes (kg N ha^{-1}) were calculated by multiplying each three-week flow-weighted concentration by the total volume of discharge for the three-week interval. Annual N fluxes were calculated by summing three-week mass flux data over the water year (October 1–September 30). Annual concentration was calculated by dividing the annual flux by total precipitation or discharge per year. Annual wet precipitation NO_3-N input data were obtained from the National Atmospheric Deposition Program's database (National Atmospheric Deposition Program (NADP) 1999).

Six watersheds were used for the analysis of annual stream discharge and annual N export. WS6, WS7, and WS10 were harvested in the 1974 and 1975, and the years directly following harvest were not used to derive annual relationships because the disturbance increased annual discharge and altered nutrient export (Martin and Harr 1989). The years included in the analyses (Table 2) were determined by examining plots of NO_3-N and filtered Kjeldahl N export and estimating the year when export returned to pre-disturbance levels. Nitrate returned to pre-disturbance levels within six years after harvest, while harvest had little impact on filtered Kjeldahl N (DON + NH_4-N) values (Martin and Harr 1989). NH_4-N and PON data were not collected during the first few years following harvest, and other years lack a complete stream chemistry record and were also excluded from the annual analysis.

Seasonal analysis was intended to examine subtle responses to changes in watershed hydrology, so only watersheds completely unaffected by harvest–WS2, WS8, and WS9–were used. The three-week interval of data collection was converted to monthly data for graphs by averaging together all data points collected in each month across all years.

Because hydrology-driven patterns in N stream chemistry may vary by season, three intervals were defined for analysis based on precipitation and forest biological activity: fall, winter, and spring/summer. Fall was defined as the months of September, October, and November. Stream low flows occur in August and September, and fall storms begin to increase stream discharge in October. Stream discharge rises dramatically in November. Winter included December, January, February, and March, when soils are generally saturated (Perkins 1997) and precipitation, soil water flux, and stream flow are high. The spring/summer interval extended from April through August. Precipitation decreases and soil moisture drops below saturation in April or May (Perkins 1997).

Statistical analysis

Annual N inputs and outputs (kg N ha^{-1} yr^{-1}) of NO_3-N, NH_4-N, DON and PON were regressed against annual precipitation and stream discharge. Pearson correlation coefficients were calculated for all combinations of seasons, three-week concentrations of NH4-N, DON and PON and three-week precipitation and three-week stream discharge. Precipitation and discharge required a log transformation to linearize the relationship between response and explanatory variables. N concentrations were log transformed to equalize variance of residuals.

Logistic regression was used to regress three-week NO_3-N concentrations against stream discharge and precipitation because many of the values for NO_3-N concentration were below detection. The data were recoded as 1 if a concentration other than zero was recorded, and 0 if a concentration below detection was recorded. All statistical analyses were done using SAS (SAS Institute, Inc. 1990).

Table 2. Years included in annual discharge/export analysis.

	WS2	WS6	WS7	WS8	WS9	WS10
NO_3-N	1982–1995	1972–1974, 1981–1995	1972–1974, 1981–1995	1972–1974, 1976–1995	1969–1995	1969–1975, 1982–1995
NH_4-N	1982–1995	1972–1973, 1979–1995	1972–1973, 1979–1995	1973, 1979–1981, 1988–1995	1972–1973, 1979–1995	1969, 1972–1973, 1979–1995
DON	1982–1995	1972–1973, 1979–1995	1972–1973, 1979–1995	1972–1973, 1979–1995	1969–1977, 1979–1995	1969–1973, 1982–1995
PON	1986–1995	1979–1995	1979–1995	1979–1995	1979–1995	1979–1995

Results

Annual precipitation N inputs

At the low-elevation collector, total annual bulk N input averaged 1.63 kg N ha^{-1} yr^{-1}; at the high elevation collector total annual bulk N input averaged 2.01 kg N ha^{-1} yr^{-1} and wet-only input averaged 1.60 kg N ha^{-1} yr^{-1}. Inputs and concentrations of specific N species followed similar patterns: DON was the largest component of N input at the low-elevation collector, followed by PON, NO_3-N, and NH_4-N (Table 3). At the high-elevation collector, NO_3-N input was higher than at low elevation and was the largest component of N in bulk and wet-only inputs, followed by NH_4-N, DON, and PON.

Of all four N solutes, only annual input of NO_3-N in bulk precipitation has increased significantly ($r^2 = 0.35$; $p = 0.001$) since 1970 (Figure 2) at the low elevation bulk precipitation collector. In contrast, the NADP wet precipitation NO_3-N record from a collector co-located with the HJA bulk precipitation collector showed no significant trend ($p > 0.05$) for the period between 1980 and 2000. Annual bulk inputs of NO_3-N, NH_4-N, DON and PON were not correlated with annual precipitation at the low elevation bulk precipitation collector.

No long-term trends in annual inputs of any form of N were found at the high elevation site. Annual inputs of DON and PON in bulk and wet-only deposition at high elevation were not correlated with annual precipitation ($p > 0.05$). Annual precipitation was, however, a significant predictor of annual bulk NO_3-N input ($r^2 = 0.242$, $p = 0.0529$), annual wet-only NO_3-N input ($r^2 = 0.607$, $p = 0.0390$) and annual bulk NH_4-N input ($r^2 = 0.42$, $p = 0.0380$) at the high elevation site.

While little intra-annual variability in concentrations or inputs of NH_4-N, DON, and PON (Figure 3) occurs, August peaks in NO_3-N concentrations are much more pronounced at the high elevation bulk precipitation collector than at the low elevation bulk precipitation collector. Peaks in DON inputs occur in September and April/May at both elevations.

Annual stream N outputs

On average, DON comprised the largest fraction of total annual N output from HJA watersheds (Table 4). PON was the second largest fraction of annual N output, followed by NH_4-N and then NO_3-N. Average annual concentrations reflected the annual trends in N output; that is, the order of concentration was DON > PON > NH_4-N > NO_3-N.

Annual N output versus annual stream discharge

Total annual discharge was a positive predictor of annual DON export in all watersheds (Figure 4) with r^2 values ranging from 0.42 to 0.79. DON-discharge regression line slopes are not significantly different from each other ($p > 0.05$). In contrast to DON, significant relationships ($p < 0.05$) between annual stream dis-

Table 3. Average annual N inputs (kg N ha^{-1} yr^{-1}), N concentrations (mg N L^{-1} yr^{-1}) and precipitation (cm $year^{-1}$) collected at the low elevation precipitation collector and the high elevation precipitation collector. Bulk deposition was collected at the low elevation site from 1969 to 1995. Bulk deposition was collected at the high elevation site from 1973 to 1988. Wet deposition was collected at the high elevation site from 1989 to 1995.

		Low Elevation Bulk Deposition Collector		High Elevation Bulk Deposition Collector		High Elevation Wet-Only Deposition Collector	
		n	Mean (SE)	n	Mean (SE)	n	Mean (SE)
Inputs (kg N ha-$^{-1}$ yr^{-1})	NO_3-N	27	0.46 (0.042)	16	0.68 (0.038)	7	0.69 (0.027)
	NH_4-N	21	0.33 (0.060)	11	0.56 (0.055)	7	0.41 (0.044)
	DON	21	0.6 (0.06)	11	0.5 (0.06)	7	0.2 (0.05)
	PON	18	0.5 (0.06)	10	0.4 (0.12)	7	0.5 (0.08)
	Total N	18	1.62 (0.124)	10	2.01 (0.282)	7	1.60 (0.143)
Concentration (mg N L^{-1})	NO_3-N	27	0.021 (0.002)	16	0.032 (0.002)	7	0.034 (0.001)
	NH_4-N	21	0.016 (0.002)	11	0.026 (0.002)	7	0.020 (0.002)
	DON	21	0.03 (0.003)	11	0.02 (0.003)	7	0.01 (0.002)
	PON	18	0.03 (0.006)	10	0.02 (0.006)	7	0.01 (0.004)
Precipitation (cm $year^{-1}$)		27	247.7 (44.7)	16	208.3 (39.1)	7	199.5 (31.0)

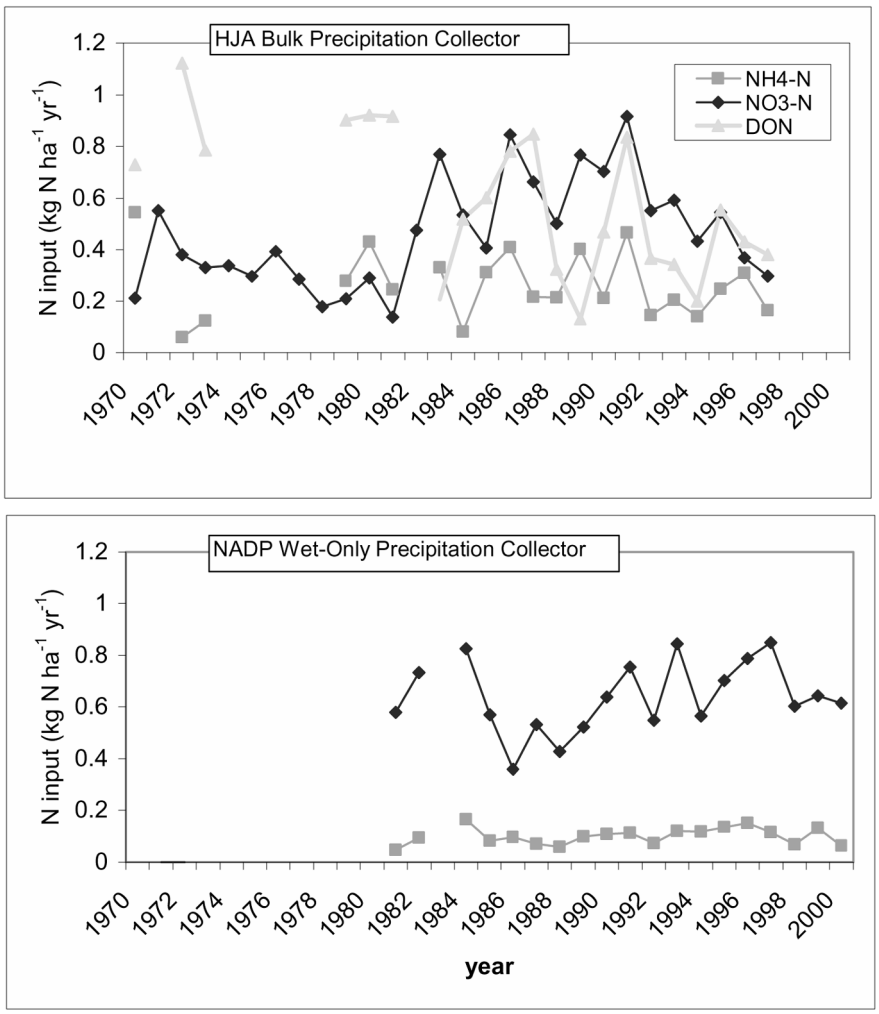

Figure 2. Annual inputs of NO_3-N, NH_4-N and DON (kg N ha^{-1} yr^{-1}) from the low elevation bulk precipitation collector and the co-located NADP collector. Data points not shown were omitted because of missing data.

charge and annual export of NO_3-N, NH_4-N, and PON were not found in all watersheds. Annual NO_3-N export increased with annual stream discharge only in WS2 (r^2 = 0.51). Annual NH_4-N increased with annual stream discharge in WS2 (r^2 = 0.41), WS6 (r^2 = 0.60) and WS10 (r^2 = 0.51), and annual PON export increased with annual stream discharge in WS6 (r^2 = 0.44), WS8 (r^2 = 0.36), and WS10 (r^2 = 0.35).

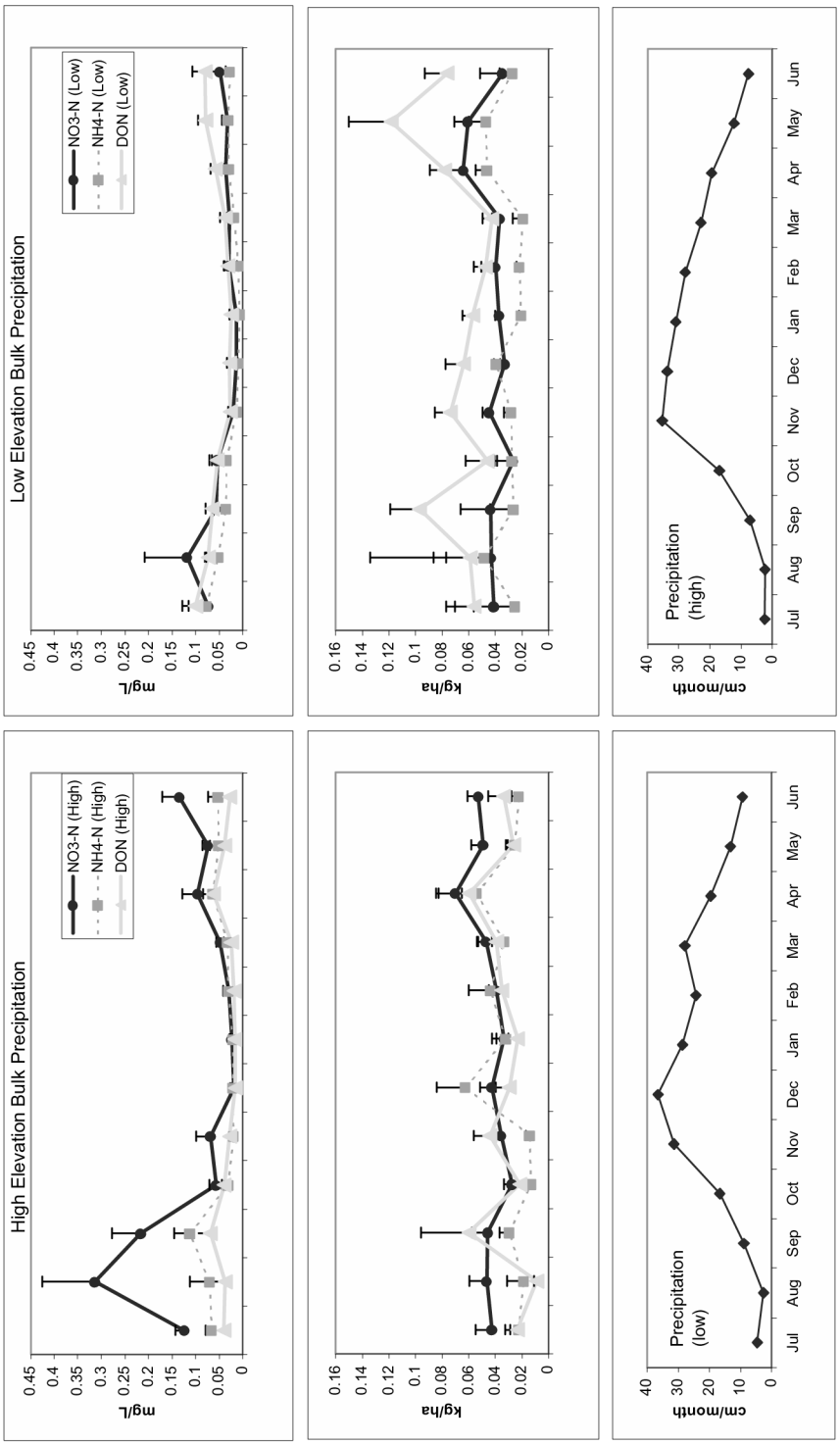

Figure 3. Mean monthly concentrations (mg N L^{-1}) and inputs (kg N ha^{-1}) of NO_3-N, NH_4-N and DON (+1 SE) in bulk precipitation from low and high elevation collectors for water years 1979–1988.

Table 4. Average annual N outputs (kg N ha^{-1} yr^{-1}), N concentrations (mg N L^{-1}), and stream discharge (cm $year^{-1}$) for three HJA watersheds dominated by mature or old-growth Douglas-fir forest.

		WS2		WS9		WS8	
		n	Mean (SE)	n	Mean (SE)	n	Mean (SE)
Outputs (kg N ha^{-1} yr^{-1})	NO_3-N	14	0.02 (0.002)	27	0.03 (0.006)	22	0.04 (0.009)
	NH_4-N	14	0.09 (0.012)	21	0.08 (0.011)	18	0.09 (0.016)
	DON	14	0.3 (0.02)	21	0.4 (0.05)	18	0.2 (0.04)
	PON	7	0.2 (0.05)	17	0.3 (0.04)	16	0.1 (0.02)
	Total N Export	7	0.46 (0.065)	17	0.83 (0.070)	16	0.48 (0.048)
	Total Dissolved N (TDN)	7	0.31 (0.03)	27	0.62 (0.04)	22	0.43 (0.05)
	% Organic N/Total N	7	81	17	85	16	73
	% DON/TDN	14	69	21	81	19	66
Concentration (mg N L^{-1})	NO_3-N	14	0.001 (0.001)	27	0.003 (0.001)	22	0.004 (0.001)
	NH4-N	14	0.007 (0.001)	21	0.008 (0.001)	18	0.009 (0.001)
	DON	14	0.02 (0.002)	21	0.04 (0.002)	18	0.02 (0.003)
	PON	7	0.02 (0.003)	18	0.02 (0.004)	16	0.01 (0.001)
Stream discharge (cm)		15	110.35 (10.75)	27	123.16 (7.92)	23	114.83 (8.72)

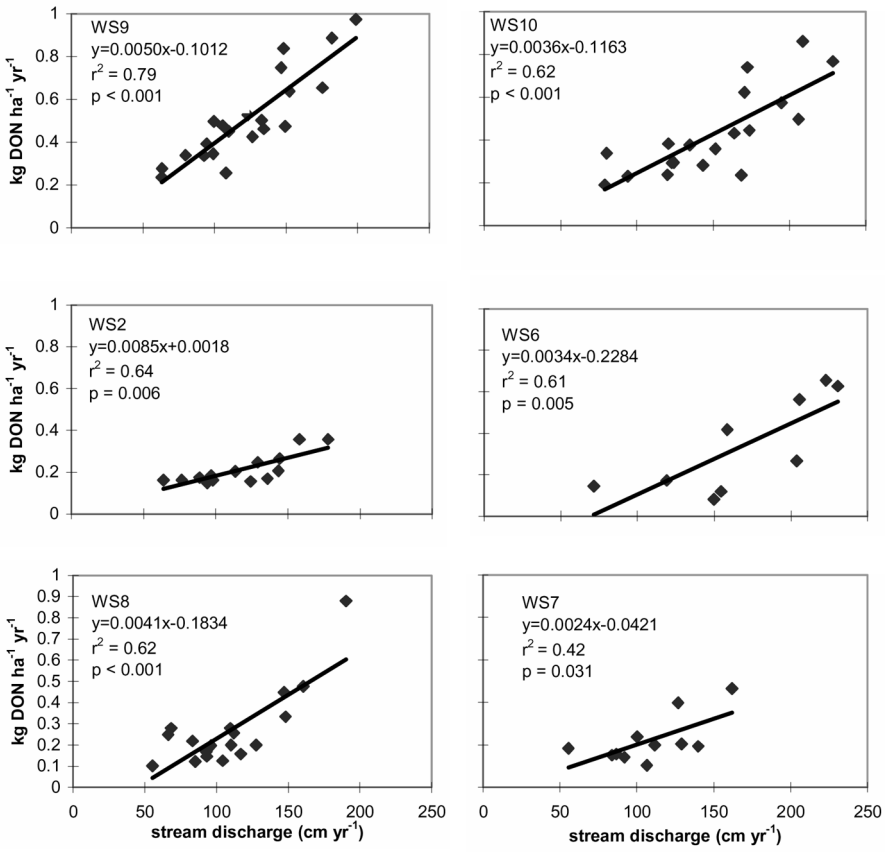

Figure 4. Annual DON output (kg N ha^{-1} yr^{-1}) versus annual stream discharge (cm $year^{-1}$) in six HJA watersheds.

Seasonal variation in stream N chemistry

No systematic long-term average seasonal trends were observed for NO_3-N (Figure 5) or PON concentrations. Elevated concentrations of NH_4-N occurred in spring and early summer in all three watersheds, although they are not convincingly synchronous. However, DON concentrations increased in the fall in every watershed (Figure 6). The increase in concentration began in July or August with the earliest rain events, and peak DON concentrations occurred in October through December before the peak in the hydrograph. DON concentrations then declined during the winter months. DON concentrations follow a hysteresis loop when DON concentration is plotted as a function of discharge at three-week intervals (Figure 7).

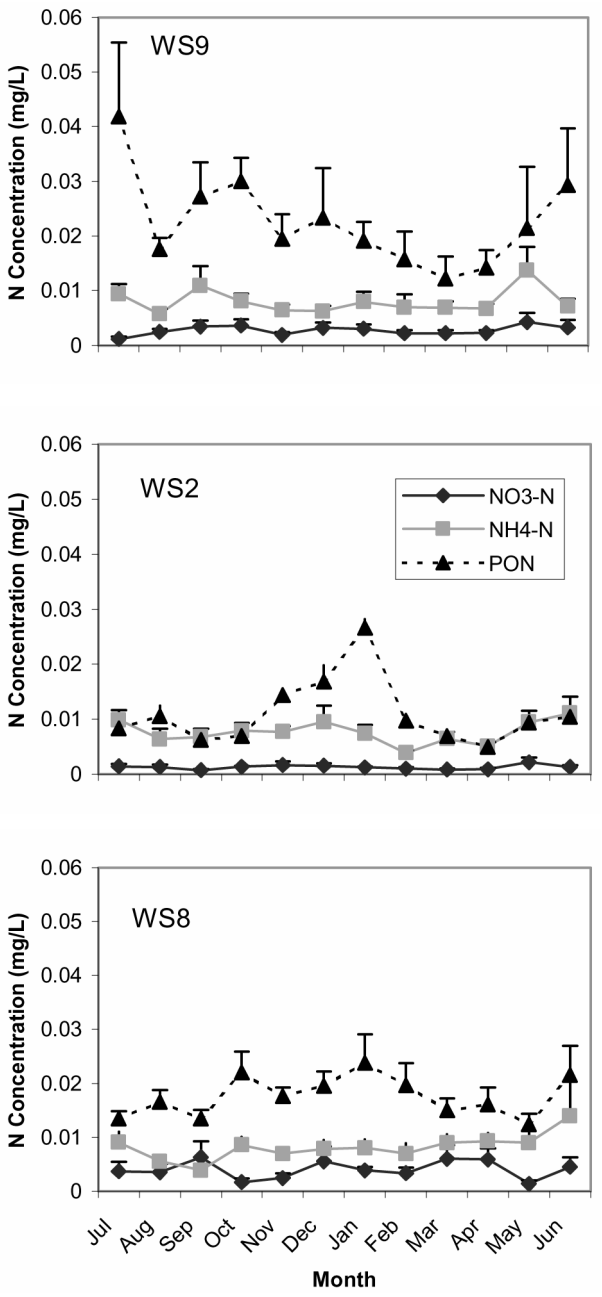

Figure 5. Mean monthly concentrations (mg N L^{-1}) of NO_3-N, NH_4-N and PON in streamwater (+1 SE) in three watersheds dominated by old-growth or mature Douglas-fir forest.

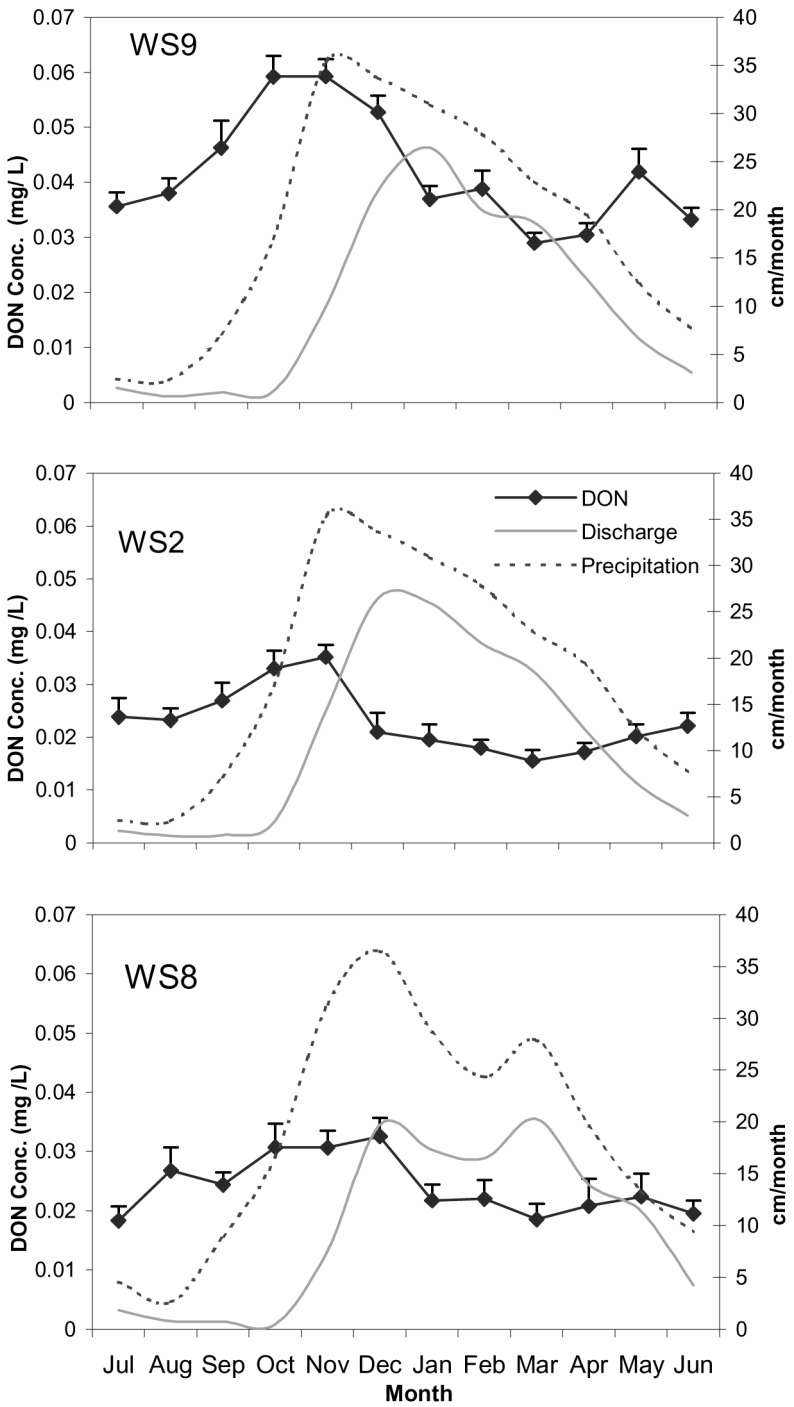

Figure 6. Mean monthly DON concentrations (mg N L^{-1}) in streamwater (+1 SE) in three watersheds at HJA dominated by old-growth or mature Douglas-fir forest. Average monthly stream discharge (cm $month^{-1}$) and average monthly precipitation (cm $month^{-1}$) are also shown.

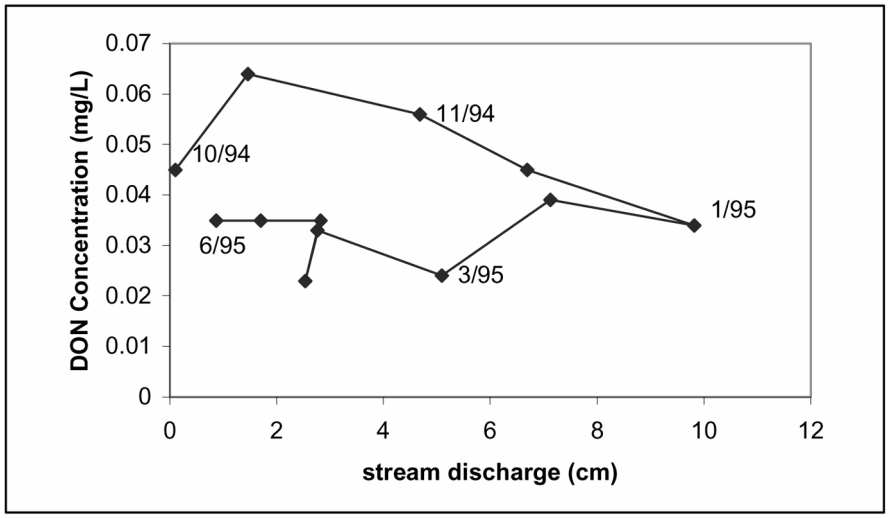

Figure 7. DON concentrations plotted as a function of discharge at three-week intervals follows a clock-wise hysteresis loop. Data are from WS9, October 1994–June 1995.

Relationship between hydrology and seasonal variations in N concentration

For seasonal analyses, only those instances where correlations were observed in all three undisturbed watersheds were noted. DON concentrations were positively correlated with precipitation in all watersheds in Fall and Winter, but not in Spring/Summer. NH_4-N and PON concentrations were not significantly correlated to either precipitation or discharge in all watersheds in Fall, Winter, or Spring/Summer (Table 5). The probability of a detectable NO_3-N concentration was not related to discharge or precipitation in all three watersheds in any season. The odds of a detectable NO_3-N concentration occurring did decrease significantly with increasing precipitation (odds ratio = 0.90, n = 136) and stream discharge (odds ratio = 0.89, n = 136) in Winter in WS8.

Discussion

Precipitation inputs and concentrations

Annual patterns in precipitation

Average annual DIN inputs in bulk precipitation at HJA (0.79 kg N ha^{-1} yr^{-1} at the low elevation site and 1.24 kg N ha^{-1} yr^{-1} at the high elevation site) are small relative to sites in the Eastern US where deposition of atmospheric pollutants is higher. Typical values of DIN inputs in bulk input for forested sites in the eastern US were 7.1 kg N ha^{-1} yr^{-1} during 1995–1997 (Campbell et al. 2000) at the Hubbard Brook Experimental Forest, New Hampshire and 12.8 kg N ha^{-1} yr^{-1} in the

Table 5. Pearson correlation coefficients for the relationship between N solute concentration and precipitation or stream discharge in each season and watershed.

		WS2				WS8				WS9			
		Variable	r	p	n	Variable	r	p	n	Variable	r	p	n
Fall	NH4-N	—				Discharge	0.251	0.047	63	Precipitation	−0.272	0.012	84
	DON	Precipitation	0.314	0.015	59	Precipitation	0.491	0.000	69	Precipitation	0.286	0.006	92
						Discharge	0.254	0.034	70				
	PON	Discharge	0.339	0.048	30	—				—			
Winter	NH_4-N	—				—				—			
	DON	Precipitation	0.245	0.027	82	Precipitation	0.289	0.004	100	Precipitation	0.282	0.003	107
	PON					Discharge	0.298	0.005	88	Discharge	0.233	0.019	101
						Precipitation	0.301	0.004	88				
Spring/Summer	NH_4-N	Precipitation	0.228	0.012	104	—				—			
	DON	Discharge	−0.238	0.014	107	—				—			
	PON	—				—				Discharge	−0.192	0.03	131

mountains of eastern Tennessee (Boring et al. 1988). Wet DIN input alone was 4.0 and 7.1 kg N ha^{-1} yr^{-1} at two forested sites in Georgia (Lovett and Lindberg 1993), while wet DIN input at the high elevation site at HJA was 1.1 kg N ha^{-1} yr^{-1}. Even compared to annual bulk input of total N (DIN + DON + PON) in Olympic National Park, Washington, which ranged from 3.11 to 3.42 kg N ha^{-1} yr^{-1} (Edmonds et al. 1998), annual bulk input of total N at HJA is low, averaging 1.6 and 2.0 kg ha^{-1} yr^{-1} at the low and high collectors, respectively.

The average annual quantity of DON in bulk input at HJA (0.5 kg N ha^{-1} yr^{-1} at the high elevation collector, and 0.6 kg N ha^{-1} yr^{-1} at the low elevation collector) is smaller than values reported elsewhere. Seely et al. (1998) measured 1.9–2.3 kg N ha^{-1} yr^{-1} DON in bulk precipitation on Cape Cod, and Campbell et al. (2000) reported 1.3 to 2.4 kg N ha^{-1} yr^{-1} DON in bulk precipitation at forested watersheds in New Hampshire and Vermont. Total bulk organic N input at HJA (1.1 kg N ha^{-1} yr^{-1} at the low elevation collector and 0.9 kg N ha^{-1} yr^{-1} at the high elevation collector) is lower than in the Sangre de Cristo Mountains of New Mexico, where Gosz (1980) measured total organic N inputs of 1.9–3.3 kg N ha^{-1} yr^{-1}, and in Walker Branch watershed, Tennessee, where Moore and Nuckols (1984) measured total organic N inputs of 1.6 kg N ha^{-1} yr^{-1}. Storms at HJA are from the west, off the Pacific Ocean, and may carry less organic N than precipitation at the other sites where more organic N inputs may originate from terrestrial sources.

Mean annual DON concentrations in precipitation at HJA (0.02–0.03 mg N L^{-1}) are lower than DON concentrations found in precipitation at remote oceanic sites, which generally range from 0.084 to 0.224 mg N L^{-1} (Cornell et al. 1995). N in dust and pollen may be so refractory that the Kjeldahl analysis used at HJA does not break it down into NH_4-N, while the ultraviolet photo-oxidation method used by Cornell et al. (1995) may more accurately measure total DON inputs.

The long-term trend in bulk NO_3-N input at the low elevation collector results from an increase in NO_3-N input between the 1982 and 1992 relative to earlier years (Figure 2). This increase cannot be explained by increased precipitation, and the trend is absent from NADP wet-only input data, suggesting that there was a source of dry deposition to the bulk collector during those years. Local forest management or construction activities at the HJA Headquarters site, where the precipitation collectors are located, could be the explanation. Several trailer homes were moved on to the HJA Headquarters site beginning in 1980 after which the amount of activity in the area increased dramatically. Permanent structures at HJA Headquarters site were constructed between 1990 and 1994. The increased site usage and construction could account for the increased NO_3-N concentration between 1982 and 1994 relative to the 1969–1981 period. The decrease in NO_3-N concentration between 1994 and 1997 may be due to the reduction in logging and slash burning that began in 1991 as a result of lawsuits about the harvesting of old-growth forests used by the endangered Spotted Owl.

Seasonal patterns in precipitation

Due to the concentrating effects of reduced precipitation during the summer months, input of NO_3-N, NH_4-N, and DON is relatively level throughout the year. DON

input is consistently higher at the low elevation bulk collector than in the high elevation collector, suggesting that the forested slopes surrounding the low elevation collector may be a source of DON. More pollen, for example, may settle into the low elevation collector, and could be a substantial source of DON since as much as forty-nine percent of water-soluble N from pollen is amino-N (Greenfield 1999).

Annual outputs

Outputs of N in stream water at HJA are low compared to other locations, and much of the export is organic N. At Hubbard Brook, output of total dissolved nitrogen (DON + DIN) averaged 2.4 kg N ha^{-1} yr^{-1} during 1995–1997, 59% of which was DON (Campbell et al. 2000). Total dissolved nitrogen at HJA averaged only 0.45 kg ha^{-1} yr^{-1}, 72% of which was DON. Total inorganic and organic (DIN + DON + PON) outputs at HJA averaged 0.59 kg N ha^{-1} yr^{-1}, 80% ofwhich was organic. Other studies quantifying organic N losses in stream water also suggest that organic N may be the major form of N export in some forested ecosystems. Hedin et al. (1995) estimated that 95% of all dissolved N outputs from old-growth forests in southern Chile were DON. PON and DON accounted for 60–70% of the 4–9 kg N ha^{-1} yr^{-1} N exported from Luquillo Experimental Forest watersheds in Puerto Rico (McDowell and Asbury 1994). Fifty percent of exports from 25 tropical watersheds was DON, and 75% was organic N (DON + PON) (Lewis et al. 1999). Ninety percent of total nitrogen outputs of 1.15 kg ha^{-1} yr^{-1} from small watersheds in the Sierra Nevada were DON and PON (Coats and Goldman 2001).

At HJA, NH_4-N output was roughly twice NO_3-N output. Andrews Forest is one of several old-growth forests having ratios of NH_4-N:NO_3-N outputs exceeding 1 (Hedin et al. 1995). The low level of NO_3-N relative to NH_4-N in streams HJA may be due to low populations of nitrifiers and/or to denitrification in the soil or stream. Denitrification rates at upland sites in the Andrews are low, with the latter measuring less than 0.07 kg N ha^{-1} $year^{-1}$ (Vermes and Myrold 1992). Denitrification in the stream or riparian zone has not been measured, so the in-stream influence of denitrification is unknown. Sollins et al. (1980) found, however, that soil solution samples collected in WS10 at depths of 30–200 cm had NO_3-N concentrations averaging between 0.013 and 0.020 mg N L^{-1}, slightly higher than mean concentrations of NO_3-N in the stream, suggesting some minimal in-stream or riparian zone NO_3-N uptake or denitrification. Sollins and McCorison (1981) measured annual NH_4-N concentrations in the rooting zone of WS9 ranging between 122 and 200 mg N L^{-1}, and below the rooting zone as 38 mg N L^{-1}, while mean concentrations of NH_4-N in streamwater ranged from 0.007 to 0.009 mg N L^{-1}. These results imply that groundwater entering the stream has higher concentrations of NH_4-N than NO_3-N, and that some assimilation or nitrification of NH_4-N occurs within the stream or riparian zone. Based on an isotope addition experiment, Peterson et al. (2001) reported that nitrification rates in a third-order stream at the Andrews accounted for roughly 40% of NH_4-N removal, and that ammonium and nitrate uptake rates in the stream were about equal. Even though nitrate is produced

in HJA streams, demand for all forms of N is evidently so high that very little nitrate is exported from HJA watersheds.

Annual output related to stream discharge

Nitrate

The lack of correlation between annual NO_3-N output and annual stream discharge in five of the six watersheds may be a function of multiple controls on labile DIN. First, high terrestrial biological demand for NO_3-N would create low availability of NO_3-N for flushing. Vegetation demand for N is substantial in HJA where rainfall is quite high but N inputs are low (Sollins et al. 1980). Further, Hart et al. (1994) found that gross rates of nitrification at an old-growth site in the HJA were significant, but that net rates were low because of swift microbial assimilation of nitrate. Pulses of NO_3-N in streamwater have been observed during early fall storms (Gregory unpub. data) at HJA, but the pool of NO_3-N in the soil may be so small that further increases in stream discharge may not result in any measurable increase in NO_3-N output. Nitrate concentrations may damped due to high riparian zone (Ashby et al. 1998) and in-stream (Peterson et al. 2001) uptake of this limiting nutrient in a high carbon-availability environment. In a study of 25 watersheds of the American tropics, Lewis et al. (1999) found that annual output of all N fractions increased with runoff. However, almost all of their sites had significantly higher N exports than found at HJA, again suggesting that the strong N limitation seen at HJA caused the lack of a correlation between runoff and output.

DON

In contrast to DIN export, annual DON export is related to annual stream discharge in all watersheds, suggesting that there may be less biological processing of DON in soils, the riparian zone, and stream water compared to NO_3-N and NH_4-N. Although some plants may take up specific labile forms of DON (Nasholm et al. 1998), DON in streams may be dominated by refractory fulvic acids, and may be little affected by stream biota. Qualls and Haines (1992) reported that most DON decomposed very slowly in an Appalachian stream, and concluded that stream DON is largely composed of refractory compounds. Hedin et al. (1995) also presented evidence from watersheds in southern Chile suggesting that most hydrologic DON losses are fulvic acids from soil organic matter.

Annual DON export and annual stream discharge have been shown to be strongly positively related in other sites. For example, fifty-five percent of the variation in annual DON export from 25 tropical watersheds was explained by annual stream discharge (Lewis et al. 1999). This study was a survey over many sites, however, whereas the results from the HJA underscore the consistency of the mechanism influencing DON export at a single site.

PON

Annual PON export increased significantly with annual stream discharge in four of the six watersheds. Greater discharge results in an increase in the wetted area of the streambank as the stream comes in contact with more detritus, potentially increasing PON concentration. Overland flow, although minor at HJA, may also move organic matter into streams during intense storms. Other processes, including dry ravel, raindrop impact, needle ice, and animal movements (Swanson et al. 1982) introduce particles into the channel throughout the year. Even a light rain may wash particles from the forest canopy in throughfall into the stream, increasing PON concentration.

Seasonal hydrologic controls on N concentrations

Correlation between precipitation or discharge and N solute concentrations was rarely consistent across watersheds in a given season, and correlation coefficients were low, ranging between 0.2 and 0.4. Much of the variation in streamwater N concentrations may be obscured by the coarse resolution of the data. The flow-weighted N concentration data reflect changes in concentration over a three-week period, during which concentration may have changed dramatically more than once. Concentrations of DIN and DON, for example, have been observed to differ between rising and falling limbs of a storm hydrograph at the HJA (Fredriksen 1972; Wondzell and Swanson 1996) and elsewhere (Henderson et al. 1977; Bond 1979). Bakke (1993) also reported low correlations between NO_3-N concentrations and stream discharge for a long-term data set at another site in Oregon, and concluded that grab samples taken at two-week intervals also lacked the resolution to adequately capture fluctuations in NO_3-N concentrations. Interpretation of plots of nutrient concentrations and hydrologic mechanisms controlling seasonal N stream chemistry based on consistent statistical results across all three watersheds are discussed below.

Fall and winter

Precipitation was positively correlated with DON concentrations at the three-week interval in all three watersheds in Fall and Winter. A precipitation-related mechanism for the increase in DON observed in the fall is suggested by the data of Sollins and McCorison (1981) who observed an increase in DON at the 2.0 m depth in WS10 that began in August 1976 with the first fall rains and peaked in November 1976. Decomposer activity may be stimulated as soils wet up in the fall, resulting in increased DON in soil solution. Some of the fall increase in DON concentration in stream water may be a function of elevated DON in groundwater seeping into the stream.

Evidence from other studies suggests that flushing from the upper soil horizons results in the increased concentration of DON in streamwater. For example, DOC concentrations peak before spring stream discharge peaks in the Snake River (Horn-

berger et al. 1994) and in a small headwater catchment in Colorado (Boyer et al. 1996), in a pattern similar to that observed for DON in HJA watersheds. These responses were hypothesized to be the result of increased flows through the upper soil horizon during snowmelt (analogous to rainfall at HJA), which flushed DOC enriched interstitial water, built up during low flow periods, to the stream. Because DOC fluxes were highly correlated with DON fluxes in 42 case studies of forested ecosystems (Michalzik et al. 2001) this mechanism may be applied to DON, as well. The hysteresis loop (Figure 7) exhibited by seasonal DON concentrations illustrates that the sources of DON are depleted in the spring relative to the fall and that total DON export is supply limited.

DON concentrations observed during fall storm events at HJA indicate that the three-week level of observation does not adequately capture the variability of DON concentrations in discharge, at least partially accounting for the low correlation coefficients. Fredriksen (1972) reported that DON concentration in streamwater peaked before the hydrograph peaked during a storm in Andrews Forest WS10. Wondzell and Swanson (1996) also found that DON concentrations were highest on the rising limb of the hydrograph during fall storms in a small tributary emptying into a 4th order HJA stream.

The positive correlation between fall DON concentrations and precipitation, rather than stream discharge, at the three-week scale of measurement may be observed because early fall storms flush near-stream pools of DOC and DON from the soil and litter into the stream causing the increased DON concentration with little effect on the hydrograph. Leaf litter can be a major source of DOC in stream water. For example, in headwater streams at Coweeta and Hubbard Brook leaf litter in the stream contributed as much as 30% to 40% of daily DOC export (McDowell and Fisher 1976; Meyer et al. 1998). Peak litterfall occurs at the same time as peak DON concentrations in streamwater in WS10 (Triska et al. 1984). Hongve (1999) concluded that leaching of DOC from coniferous or deciduous litter could explain the markedly increased concentration of DOC in autumnal storm events in forested catchments. Precipitation may leach organic material from litter near the stream during storms or deliver litter into the stream itself, resulting in the observed precipitation-concentration seasonal pattern. In a study of 14 small HJA streams, Bonin et al. (2000) observed a dramatic reduction in C:N ratio and increases in microbial respiration and enzyme activity of fine particulate organic matter following an October storm. They attributed these changes to inputs of litter with high concentrations of organic N, which supports the idea that the fall increases in DON concentration at HJA may be due to litter inputs. Another possible source of DON to the stream related to precipitation in the fall is throughfall, which was identified as a major source of DON to streams in a watershed in Switzerland (Hagedorn et al. 2000).

Spring/Summer

There were no consistent relationships between N concentrations and precipitation or discharge across all watersheds in spring/summer. Biological demand by stream

organisms probably plays a strong role in regulating stream N chemistry during this season. Diel fluctuations in NO_3-N were observed during three summer low-flow days in a first-order stream in HJA (Vanderbilt, unpublished data) with highest concentrations occurring during the night, presumably because of microbial uptake during the day. Biological uptake of DIN in HJA streams has been shown to be light-limited (Gregory 1980). Stable isotope tracer studies conducted in a third-order HJA stream clearly illustrate the high within-stream biological demand for NH_4-N and NO_3-N during the summer (Peterson et al. 2001).

Seasonal patterns at HJA compared to other sites

Relatively few studies examine the relationship between seasonal variation in stream discharge and DON concentration (Table 6). A relationship between stream discharge and DOC has been more frequently detected, however, and DON and DOC response to discharge will probably be similar (Hedin et al. 1995; Michalzik et al. 2001). Consistent with results of this study, most others report that at the scale of seasons or individual storms DOC concentration increases with increasing discharge. The variability detected in DOC or DON responses to increasing stormflow between sites may be a function of differing flowpaths. Hinton et al. (1998) found that DOC concentrations were positively correlated with stream discharge during storms in some small catchments in central Ontario, but not in others, and concluded that the difference in response was due to different DOC sources and flowpaths in riparian, hillslope and wetland areas. The importance of flowpaths in determining stream nitrogen chemistry is widely recognized (Mulholland 1993; Hill et al. 1999; Cirmo and McDonnell 1997). The relative amounts of pre-event "old" water that has had long contact with the soil and "new event" water flowing through macropores at least partially determine the concentration-discharge response of nitrogen solutes. Hagedorn et al. (2000) were able to explain temporal variations in DOC and DON concentrations during storms based on changing contributions of water from topsoil, throughfall, and subsoil during stormflow.

While no seasonal changes in NO_3-N concentrations were observed at the HJA, many other studies have reported seasonal fluctuations in NO_3-N (Williams and Melack 1997; Feller and Kimmins 1979; Stottlemyer and Troendle 1992). Edmonds et al. (1995) found highest NO_3-N concentrations in the fall in a stream in an old-growth forested watershed in Olympic National Park, Washington, where precipitation patterns are similar to those at the HJA. More commonly, NO_3-N pulses in stream water have been reported during snowmelt (Hubbard Brook, NH: ??; Isle Royale National Park, MI: Stottlemyer et al. (1998) and Stottlemyer and Toczydlowski (1999); Turkey Lakes, Ontario: Creed and Band (1998); Sierra Nevada, CA: Johnson et al. (1997)). This pattern is attributed to the flushing from the soil of NO_3-N built-up from decomposition during the winter (Rascher et al. 1987) and release of NO_3-N stored in the snowpack (Williams and Melack 1991). Similar pulses of NO_3-N concentration in streamwater have been observed when fall rains flush soils of decomposition products built up during a dry summer (Edmonds et al. 1998; Fenn and Poth 1999). Winter, or dormant season, increases in NO_3-N in

Table 6. Relationship between stream discharge and N or DOC concentrations at tropical and temperate forested sites. NA means data not reported.

	Bear Brook, NH (in Hubbard Brook Exp. Forest)*	Turkey Lakes, Ontario	Como Creek, CO*	Walker Branch, TN*	Coweeta Hydrologic Lab, NC	Northwest Costa Rica	New England (New Hampshire and Vermont)	Lake Tahoe, California Nevada	Luquillo, Puerto Rico
WS size (ha)	130	2.3–62.7	664	38.4, 59.1	13, 61	37, 36, 55, 264, 311, 319	13–163 (9 watersheds)	539–14,219	16.2, 262, 326
Sampling interval	Weekly and individual storms	Two week interval	Weekly for three years	Individual storms and weekly samples	Weekly	Monthly	Weekly and biweekly	Weekly and monthly	Weekly
Stream Order	2	1	2	1	2	NA	NA	NA	NA
NO_3-N	+	0	–	–	0	+	+/0	+	0
NH_4-N	NA	NA	0	–	0	NA	0	NA	0
DOC	+	NA	+	+	+	+	NA	NA	+
DON	+	0	0	NA	NA	+	+/0	+/0	NA
POC	+	NA	NA	NA	+	NA	NA	NA	+
PON	NA	NA	NA	+	NA	NA	NA	+/0	NA
TN	NA	NA	NA	+/–	NA	NA	NA	+/0	NA
Reference	Fisher and Likens (1973) and McDowell and Likens (1988), Johnson et al. (1969)	Nicolson (1988) and Creed and Band (1998)	Lewis and Grant (1979)	Mulholland (1992) and Elwood and Turner (1989), Henderson et al. (1977), Nuckols and Moore (1982)	Meyer and Tate (1983) and Swank and Vose (1997)	Newbold et al. (1995)	Campbell et al. (2000)	Coats and Goldman (2001)	McDowell and Asbury (1994)

*adapted from Meyer et al. (1998)

these ecosystems are frequently followed by low growing season NO_3-N concentrations that are attributed to high NO_3-N uptake by soils and vegetation (Foster et al. 1989; Edmonds et al. 1995; Lajtha et al. 1995). Where vegetation demand for N is low, such as in mature deciduous forests, the summer-time low may not be observed (Vitousek and Reiners 1975; Martin 1979).

In contrast to the winter-maxima, summer-minima NO_3-N concentration pattern observed at many sites in the northeastern US and Canada, streams at Coweeta Hydrologic Lab, NC (Swank and Vose 1997) and at Walker Branch, TN (Mulholland 1992) have the opposite seasonal NO_3-N pattern. Mulholland (1992) posited that in areas where streamwater temperatures remain above 0 °C during the dormant season rates of N immobilization from autumn leaf litter by soil and streamwater organisms may be high throughout the fall and winter. The winter-minima, summer-maxima pattern of NO_3-N in southern forest streams is influenced by year-round nitrogen uptake in soils and by microbes and algae in the streams (Mulholland and Hill 1997). This pattern might be expected at HJA, as well, where soil and streams remain unfrozen throughout the year. There is evidently so little NO_3-N available in this high carbon, low nitrogen ecosystem that the pattern is not expressed.

Conclusion

The long-term precipitation and stream N chemistry datasets at HJA offer a valuable record with which to examine temporal patterns of organic and inorganic N dynamics in forested watersheds in an area free from atmospheric N pollution. Our analyses suggest that different factors may control organic vs. inorganic N export. Annual DON export is closely tied to annual stream discharge, in contrast to annual DIN export. At the seasonal scale, DON concentrations in streamwater increased with precipitation in the fall and winter, while variations in NO_3-N and NH_4-N concentrations at the seasonal scale were unrelated to precipitation or stream discharge in all watersheds. These results suggest that terrestrial or within-stream biotic controls may strongly influence streamwater concentrations of DIN, while DON may be much less sensitive to biological demand and more strongly tied to climate. High biological demand for NO_3-N in this ecosystem may result in stream concentrations of NO_3-N too low to detect seasonal patterns. Our results imply that DON in streams may be recalcitrant, and largely unavailable to stream organisms. Research characterizing DON compounds in streamwater and tracing DON to its source as root exudates, leaf leachate, or decomposition products will help clarify what drives the seasonal DON patterns observed in this study.

Acknowledgements

This research was supported by a cooperative agreement between the Pacific Northwest Research Station of the U.S. Forest Service and Oregon State University, and by NSF OEB-96-32921 (H.J. Andrews Long-Term Ecological Research). The authors gratefully acknowledge the staff of the H.J. Andrews Experimental Forest for their years of effort making this high quality data set available. We thank Don Henshaw and Gody Spycher, managers of the Forest Science Database (FSDB), from which these data came. We thank Cam Jones of the Central Chemical Analytical Lab (CCAL) for his dedication to assuring that high quality data result from the stream and precipitation samples analyzed. Manuela Huso and Lisa Ganio provided valuable statistical advice and Theresa Valentine provided Figure 1. We also thank three anonymous reviewers for their suggestions that greatly improved this manuscript.

References

Ashby J.A., Bowden W.B. and Murdoch P.S. 1998. Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the Catskill Mountains, USA. Soil Biol. Biochem. 30: 853–864.

Bakke P.D. 1993. The spatial and temporal variability of nitrate in streams of the Bull Run Watershed, Oregon. MS thesis, Oregon State University, Corvallis, USA.

Bond H.W. 1979. Nutrient concentration patterns in a stream draining a montane ecosystem in Utah. Ecology 60: 1184–1196.

Bonin H.L., Griffiths R.P. and Caldwell B.A. 2000. Nutrient and microbiological characteristics of fine benthic organic matter in mountain streams. J. N. Am. Benthol. Soc. 19: 235–249.

Boring L.R., Swank W.T., Waide J.B. and Henderson G.S. 1988. Sources, fates, and impacts of nitrogen inputs to terrestrial ecosystems; review and synthesis. Biogeochemistry 6: 119–159.

Boyer E.W., Hornberger G.M., Bencala K.E. and McKnight D. 1996. Overview of a simple model describing variation of dissolved organic carbon in an upland catchment. Ecological Modelling 86: 183–188.

Buffam I., Galloway J.N., Blum L.K. and McGlathery K.J. 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry 53: 269–306.

Burns D.A. 1998. Retention of nitrate in an upland stream environment: A mass balance approach. Biogeochemistry 40: 73–96.

Campbell J.L., Hornbeck J.W., McDowell W.H., Buso D.C., Shanley J.B. and Likens G.E. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49: 123–142.

Cirmo C.P. and McDonnell J.J. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: A review. J. Hydrol. 199: 88–120.

Coats R.N. and Goldman C.R. 2001. Patterns of nitrogen transport in streams of the Lake Tahoe basin, California-Nevada. Water Resour. Res. 37: 405–415.

Cornell S., Rendell A. and Jickells T. 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature 376: 243–246.

Creed I.F. and Band L.E. 1998. Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics. Water Resour. Res. 34: 3105–3120.

Dise N.B. and Wright R.F. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. For. Ecol. Manage. 71: 153–161.

Dyrness C.T. and Hawk G. 1972. Internal Report 43: Vegetation and Soils of the Hi-15 Watersheds, H.J. Andrews Experimental Forest. Coniferous Forest Biome, U.S. Analysis of Ecosystems. University of Washington, Seattle, Washington, USA.

Edmonds R.L., Thomas T.B. and Blew R.D. 1995. Biogeochemistry of an old-growth forested watershed, Olympic National Park, Washington. Water Resour. Bull. 31: 409–419.

Edmonds R.L., Blew R.D., Marra J.L., Blew J., Barg A.K., Murray G. et al. 1998. Vegetation patterns, hydrology, and water chemistry in small watersheds in the Hoh River Valley, Olympic National Park. Scientific Monograph NPSD/NRUSGS/NRSM-98/02. United States Department of the Interior, National Park Service.

Elwood J.W. and Turner R.R. 1989. Streams: Water Chemistry and Ecology. In: Johnson D.W. and Van Hook R.I. (eds), Analysis of Biogeochemical Cycling Processes in Walker Branch Watershed. Springer-Verlag, New York, pp. 301–350.

Feller M.C. and Kimmins J.P. 1979. Chemical characteristics of small streams near Haney in Southwest British Columbia. Water Resour. Res. 15: 247–258.

Fenn M.E. and Poth M.A. 1999. Temporal and spatial trends in streamwater nitrate concentrations in the San Bernardino Mountains, Southern California. J. Environ. Qual. 28: 822–836.

Fenn M.E., Poth M.A., Aber J.D., Baron J.S., Bormann B.T., Johnson D.W. et al. 1998. Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. Ecol. Appl. 8: 706–733.

Fisher S.G. and Likens G.E. 1973. Energy flow in Bear Brook, New Hampshire: An integrative approach to stream ecosystem metabolism. Ecol. Monogr. 43: 421–439.

Foster N.W., Nicolson J.A. and Hazlett P.W. 1989. Temporal variation in nitrate and nutrient cations in drainage waters from a deciduous forest. J. Environ. Qual. 18: 238–244.

Frank H., Schleppi P., Waldner P. and Hannes F. 2000. Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments-the significance of water flow paths. Biogeochemistry 50: 137–161.

Fredriksen R.L. 1969. A battery powered proportional water sampler. Water Resour. Res. 5: 1410–1413.

Fredriksen R.L. 1972. Nutrient budgets of a Douglas-fir forest on an experimental watershed in western Oregon. In: Proceedings-Research on Coniferous Forest Ecosystems-A Symposium. March 23–24, Bellingham, WA, USA., pp. 115–131.

Fredriksen R.L. 1975. Nitrogen, Phosphorus and Particulate Matter Budgets of Five Coniferous Forest Ecosystems in the Western Cascades Range, Oregon. PhD Dissertation, Oregon State University, Corvallis, USA.

Gosz J. 1980. Nutrient budget studies for forests along an elevational gradient in New Mexico. Ecology 61: 515–521.

Greenfield L.G. 1999. Weight loss and release of mineral nitrogen from decomposing pollen. Soil Biol. Biochem. 31: 353–361.

Gregory S.V. 1980. Effects of light, nutrients, and grazers on periphyton communities in streams. PhD Dissertation, Oregon State University, Corvallis, USA.

Gundersen P., Callesen I. and de Vries W. 1998. Nitrate leaching in forest ecosystems is related to forest floor C/N ratios. Environ. Pollut. 102 : 403–407.

Hagedorn F., Schleppi P., Peter W. and Hannes F. 2000. Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments – the significance of water flow paths. Biogeochemistry 50: 137–161.

Harr R.D. 1977. Water flux in soil and subsoil on a steep forested slope. Journal of Hydrology 33: 37–58.

Harr R.D. 1981. Some characteristics and consequences of snowmelt during rainfall in western Oregon. J. Hydrol. 53: 277–304.

Hart S.C., Nason G.E., Myrold D.D. and Perr D.A. 1994. Dynamics of gross nitrogen transformations in an old-growth forest: the carbon connection. Ecology 75: 880–891.

Hedin L.O., Armesto J.J. and Johnson A.H. 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: Evaluation of biogeochemical theory. Ecology 76: 493–509.

Henderson G.S., Hunley A. and Selvidge W. 1977. Nutrient discharge from Walker Branch Watershed. In: Correll D.L. (ed.), Watershed Research in Eastern North America: A Workshop to Compare Results. Chesapeake Bay Center for Environmental Studies, Smithsonian Institution, Edgewater, Maryland, USA, pp. 307–320.

Hill A.R. 1986. Stream nitrate-N loads in relation to variations in annual and seasonal runoff regimes. Water Resour. Bull. 22: 829–839.

Hill A.R. 1993. Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed. Biogeochemistry 29: 19–44.

Hill A.R., Kemp W.A., Buttle J.M. and Goodyear 1999. Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. Water Resourc. Res. 35: 811–821.

Hinton M.J., Schiff S.L. and English M.C. 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry 41: 175–197.

Holland E.A., Dentener F.J., Braswell B.H. and Sulzman J.M. 1999. Contemporary and pre-industrial global reactive nitrogen budgets. Biogeochemistry 46: 7–43.

Hongve D. 1999. Production of dissolved organic carbon in forested catchments. J Hydrol. 224: 91–99.

Hornberger G.M., Bencala K.E. and McKnight D.M. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25: 147–165.

Johnson D.W., Susfalk R.B. and Dahlgren R.A. 1997. Nutrient fluxes in forests of the eastern Sierra Nevada mountains, United States of America. Global Biogeochem. Cycles 11: 673–681.

Johnson N.M., Likens G.E., Bormann F.H., Fisher D.W. and Pierce R.S. 1969. A working model for the variation in stream chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resour. Res. 5: 1353–1363.

Lajtha K., Seely B. and Valiela I. 1995. Retention and leaching losses of atmospherically-derived nitrogen in the aggrading coastal watershed of Waquoit Bary, MA. Biogeochemistry 28: 33–54.

Lepisto A., Andersson L., Arheimer B. and Sundblad K. 1995. Influence of catchment characteristics, forestry, activities and deposition on nitrogen export from small forested catchments. Water Air Soil Pollut. 84: 81–102.

Lewis W.M. Jr and Grant M.C. 1979. Relationships between stream discharge and yield of dissolved substances from a Colorado mountain watershed. Soil Science 128: 353–363.

Lewis W.M. Jr, Melack J.M., McDowell W.H., McClain M. and Richey J.E. 1999. Nitrogen yields from undisturbed watersheds in the Americas. Biogeochemistry 46: 149–162.

Likens G.E. and Bormann F.H. 1995. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Lovett G.M. and Lindberg S.E. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. Can. J. For. Res. 23: 1603–1616.

Martin C.W. 1979. Precipitation and streamwater chemistry in an undisturbed forested watershed in New Hampshire. Ecology 60: 36–42.

Martin C.W. and Harr R.D. 1988. Precipitation and streamwater chemistry from undisturbed watersheds in the Cascade Mountains of Oregon. Water Air Soil Pollut. 42: 203–219.

Martin C.W. and Harr R.D. 1989. Logging of mature Douglas-fir in western Oregon has little effect on nutrient output budgets. Can. J. For. Res. 19: 35–43.

McDowell W.H. and Fisher S.G. 1976. Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecology 57: 561–569.

McDowell W.H. and Asbury C.E. 1994. Export of carbon, nitrogen and major ions from three tropical montane watersheds. Limnol. Oceanogr. 39: 111–125.

McDowell W.H. and Likens G.E. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol. Monogr. 58: 177–195.

McHale M.R., Mitchell M.J., McDonnell J.J. and Cirmo C.P. 2000. Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen. Biogeochemistry 48: 165–184.

Meyer J.L. and Tate C.M. 1983. The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecology 64: 33–44.

Meyer J.L., Wallace J.B. and Eggert S.L. 1998. Leaf litter as a source of dissolved organic carbon in streams. Ecosystems 1: 240–249.

Mitchell M.J., Driscoll C.T., Kahl J.S., Likens G.E., Murdoch P.S. and Pardo L.H. 1996. Climatic control of nitrate loss from forested watersheds in the northeast United States. Environ. Sci. Technol. 30: 2609–2612.

Michalzik B., Kalbitz K., Park J.-H., Solinger S. and Matzner E. 2001. Fluxes and concentrations of dissolved organic carbon and nitrogen-a synthesis for temperate forests. Biogeochemistry 52: 173–205.

Moore I.D. and Nuckols J.R. 1984. Relationship between atmospheric nitrogen deposition and the stream nitrogen profile. J. Hydrol. 74: 81–103.

Mulholland P.J. 1993. Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch Watershed. J. Hydrol. 151: 291–316.

Mulholland P.J. 1992. Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes. Limnol. Oceanogr. 37: 1512–1526.

Mulholland P.J. and Hill W.R. 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. Water Resourc. Res. 33: 1297–1306.

Murdoch P.S. and Stoddard J.L. 1992. Role of nitrate in the acidification of streams in the Catskill Mountains of New York. Water Resourc. Res. 28: 2707–2720.

Nasholm T., Ekblad A., Nordin A., Giesler R., Hogberg M. and Hogberg P. 1998. Boreal forest plants take up organic nitrogen. Nature 392: 914–916.

National Atmospheric Deposition Program (NADP) 1999. (NRSP-3)/National Trends Network. NADP Program Office, Illinois State Water Survey.

Newbold J.D., Sweeney B.W., Jackson J.K. and Kaplan L.A. 1995. Concentrations and export of solutes from six mountain streams in northwestern Costa Rica. J. N. Am. Bethol. Soc. 14: 21–37.

Nicolson J.A. 1988. Water and chemical budgets for terrestrial basins at the Turkey Lakes Watershed Can. J. Fish. Aquat. Sci. 45: 88–95.

Nuckols J.R. and Moore I.D. 1982. The influence of atmospheric nitrogen influx upon the stream nitrogen profile of a relatively undisturbed forested watershed. J. Hydrol. 57: 113–135.

Pardo L.H., Driscoll C.T. and Likens G.E. 1995. Patterns of nitrate loss from a chronosequence of clearcut watersheds. Water Air Soil Pollut. 85: 1659–1664.

Perkins R.M. 1997. Climatic and Physiographic Controls on Peakflow Generation in the Western Cascades, Oregon. PhD Dissertation, Oregon State University, Corvallis, USA.

Peterson B.J., Wollheim W.M., Mulholland P.J., Webster J.R., Meyer J.L., Tank J.L. et al. 2001. Control of nitrogen export from watersheds by headwater streams. Science 292: 86–90.

Qualls R.G. and Haines B.L. 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Sci. Soc. Am. J. 56: 578–586.

Rascher C.M., Driscoll C.T. and Peter N.E. 1987. Concentration and flux of solutes from snow and forest floor during snowmelt in the West-Central Adirondack Region of New York. Biogeochemistry 3: 209–224.

Rothacher J., Dyrness T. and Richardson R.L. 1967. Hydrologic and Related Characteristics of Three Small Watersheds in the Oregon Cascades. General Technical Report. U.S. Department of Agriculture, U.S. Forest Service, Pacific Northwest Research Station, Portland, Oregon, USA, 54 pp.

SAS Institute, Inc. 1990. SAS/STAT Users Guide. Version 6. SAS Institute Inc., Cary, NC, USA.

Seely B., Lajtha K. and Salvucci G.D. 1998. Transformation and retention of nitrogen in a coastal forest ecosystem. Biogeochemistry 42: 325–343.

Sollins P., Grier C.C., McCorison F.M., Cromack K. Jr and Fredriksen R.L. 1980. The internal element cycles of an old-growth Douglas-fir ecosystem in western Oregon. Ecol. Monogr. 50: 261–285.

Sollins P. and McCorison F.M. 1981. Nitrogen and carbon solution chemistry of an old growth coniferous forest watershed before and after cutting. Water Resour. Res. 17: 1409–1418.

Stoddard J.L. 1994. Long-term changes in watershed retention of nitrogen. In: Baker L.A. (ed.), Environmental chemistry of lakes and reservoirs. Advances in chemistry series 237. American Chemical Society, Washington, DC, USA, pp. 223–284.

Stohlgren T.J., Melack J.M., Esperanza A.M. and Parsons D.J. 1991. Atmospheric deposition and solute export in giant sequoia-mix conifer watersheds in the Sierra Nevada. Biogeochemistry 12: 207–230.

Stottlemyer R., Toczydlowski D. and Herrmann R. 1998. Biogeochemistry of a Mature Boreal Ecosystem: Isle Royale National Park, Michigan. Scientific Monograph NPS/NRUSGS/NRSM-98/01. United States Department of the Interior, National Park Service.

Stottlemyer R. and Toczydlowski D. 1999. Seasonal relationships between soil precipitation, forest floor and streamwater nitrogen, Isle Royale, Michigan. Soil Sci. Soc. Am. J. 63: 389–398.

Stottlemyer R. and Troendle C.A. 1992. Nutrient concentration patterns in streams draining alpine and subalpine catchments, Fraser Experimental Forest, Colorado. J. Hydrol. 140: 179–208.

Swank W.T. and Vose J.M. 1997. Long-term nitrogen dynamics of Coweeta forested watersheds in the southeastern United States of America. Global Biogeochem. Cycles 11: 657–671.

Swanson F.J., Fredriksen R.L. and McCorison F.M. 1982. Material transfer in a western Oregon forested watershed. In: Edmonds R.L. (ed.), Analysis of coniferous forest ecosystems in the western United States. US/IBP Synthesis Series 14. Hutchinson Ross Publishing Company, Stroudsburg, PA, USA, pp. 233–266.

Triska F.J., Sedell J.R., Cromack K. Jr, Gregory S.V. and McCorison M.F. 1984. Nitrogen budget for a small coniferous forest stream. Ecol. Monogr. 54: 119–140.

Vermes J.-F. and Myrold D.D. 1992. Denitrification in forest soils in Oregon. Can. J. For. Res. 22: 504–512.

Vitousek P.M. 1977. The regulation of element concentrations in mountain streams in the northeastern United States. Ecol. Monogr. 47: 65–87.

Vitousek P.M. and Reiners W.A. 1975. Ecosystem succession and nutrient retention: A hypothesis. Bioscience 25: 376–381.

Wigington P.J. Jr, Church M.R., Strickland T.C., Eshleman K.N. and Van Sickle J. 1998. Autumn chemistry of Oregon Coast Range streams. J. Am. Water Res. Assoc. 34: 1035–1049.

Williams M.R. and Melack J.M. 1997. Atmospheric deposition, mass balances, and processes regulating stormwater solute concentrations in mixed-conifer catchments of the Sierra Nevada, California. Biogeochemistry 37: 111–144.

Williams M.W. and Melack J.M. 1991. Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. Water Resourc. Res. 27: 1575–1588.

Wondzell S.M. and Swanson F.J. 1996. Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. II Nitrogen cycling. J. N. Am. Benthol. Soc. 15: 20–34.