

Nitrate variability in hydrological flow paths for three mid-Appalachian forested watersheds following a large-scale defoliation

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[1] Nitrate (NO_3^-) leakage from forested watersheds due to disturbance is a well documented but not well understood process that can contribute to the degradation of receiving waters through eutrophication. Several studies have shown that large-scale defoliation and deforestation events in small forested watersheds in the eastern United States cause immediate and dramatic increases in NO_3^- flux to streams, with large differences in recovery time. Water quality and discharge data collected from 1992 to 2004 following a large-scale gypsy moth defoliation were used to investigate hydrological controls on long-term NO_3^- leakage from three forested watersheds in Shenandoah National Park, Virginia. During storm events, a conventional two-component hydrograph separation in conjunction with an inverse solution technique was employed to determine the concentrations of NO_3^- in groundwater and soil water. Following defoliation, groundwater NO_3^- concentrations declined exponentially with a distinct seasonal pattern. A rank-order relationship between the rate constants associated with the exponential declines in groundwater NO_3^- concentrations and groundwater recession constants indicates a hydrological control on long-term watershed recovery for these defoliated systems. Comparisons to deforested systems in Hubbard Brook, New Hampshire, and Coweeta, North Carolina, indicate hydrological controls are similarly present. Biogeochemical differences, however, need to be considered to account for the more attenuated recovery observed in defoliated systems. No long-term trend was found in the model-derived soil water NO_3^- concentrations, which suggests the presence of some form of rate limitation on the transformation of the nitrogen pool introduced during the disturbance and/or reduced nutrient uptake due to tree mortality.

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1. Introduction

[2] Nitrogen (N) is an essential element for the growth of all living plant material, but an excess of this nutrient can have deleterious impacts on receiving waters. Abnormally high levels of N can lead to eutrophication, a process by which excess nutrients act as fertilizer resulting in over-stimulated plant growth, eventual plant death, and bacterial decomposition resulting in anoxic conditions. Quantification of NO_3^- fluxes from various point and nonpoint sources therefore is critical for management strategies to avoid impairment of receiving waters. Since N is often a limiting macronutrient in temperate forests, export from forested watersheds, typically in the form of nitrate (NO_3^-), is usually found to be relatively minor [Bormann and Likens, 1994]. However, nitrogen saturation and ‘leakage,’ in which the inputs of nitrogen exceed the demand by the floral and

microbial communities, may occur in forests affected by chronic atmospheric deposition [Aber *et al.*, 1989, 1998], and has been documented in forests affected by disturbance such as forest harvest [Likens *et al.*, 1969, 1978], fire [Knoepp and Swank, 1993], and insect defoliation [Swank *et al.*, 1981; Swank, 1988; Swank and Vose, 1997; Eshleman *et al.*, 1998; Lewis, 1998; Bernhardt *et al.*, 2003; Lewis and Likens, 2007]. Prior studies addressing the effects of disturbance on N cycling in forested watersheds have focused on comparisons between in-stream NO_3^- concentrations prior to and immediately after disturbance, but alterations to concentrations within individual flow pathways have not yet been examined. In an analysis of stream chemistry and discharge data, we examine the behavior of NO_3^- concentrations in groundwater and soil water over the course of 12 years following a major defoliation event in three forested watersheds.

[3] The effects of human-induced and natural forest disturbance on watershed N export have previously been examined within the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire. An experimental deforestation in HBEF Watershed 2 from 1965 through 1968 immediately resulted in elevated NO_3^- con-

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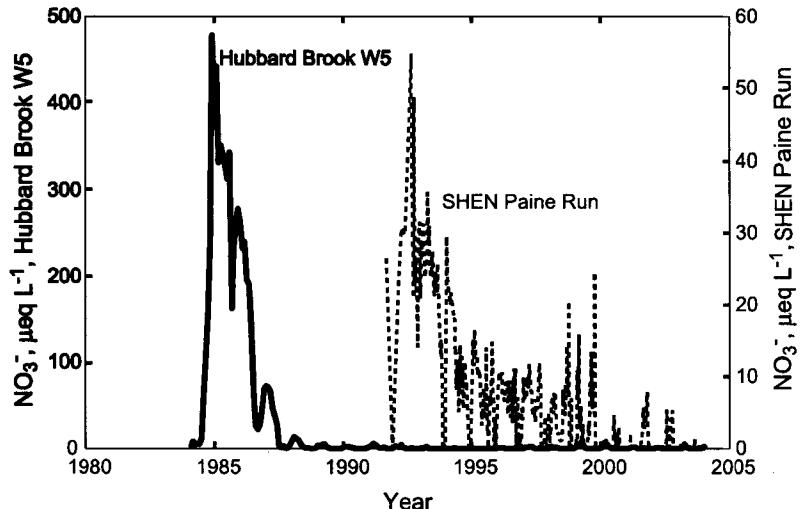


Figure 1. Nitrate concentrations at Hubbard Brook Experimental Forest (HBEF), Watershed 5, and Shenandoah National Park (SHEN), Paine Run. Note the separate y axis for the HBEF and SHEN data sets. Recovery of nitrate levels to baseline conditions took 3–4 years at Watershed 5 but has taken over a decade at Paine Run.

centrations in stream water of several orders of magnitude, returning to baseline conditions by 1972. Rapid return of NO_3^- concentrations to baseline conditions in this setting was attributed to accelerated vegetation regrowth due to high soil temperature, increased light, soil moisture, and nutrients [Likens *et al.*, 1978]. Similar stream water NO_3^- behavior was observed after an experimental deforestation in HBEF Watershed 5 (1981–1985) returning to baseline conditions by 1988. In January 1998, a severe ice storm caused extensive crown damage (30% canopy loss) in an elevation band across several experimental watersheds (Watershed 1 and Watershed 6) in the Hubbard Brook ecosystem. Similar to experimental deforestations, NO_3^- concentrations were elevated in these systems for two years after the storm event [Bernhardt *et al.*, 2003] before returning to baseline conditions.

[4] At the Coweeta forested watersheds in the southern Appalachians of North Carolina, the effects of several defoliation outbreaks on stream water NO_3^- concentrations have been documented. In Watershed 27, an outbreak of the fall cankerworm (*Alsophila pometaria*) began in 1970 and continued with varying levels of defoliation each year until 1978. Stream measurements revealed an immediate increase in NO_3^- concentrations after onset with a rapid return to baseline NO_3^- levels immediately following the end of the outbreak in 1979 [Swank *et al.*, 1981; Swank, 1988; Swank and Vose, 1997]. An infestation of the locust stem borer (*Megacyllene robiniae*) in 1979 resulted in mortality of 21% of all trees within Watershed 6 in Coweeta [Swank and Vose, 1997]. At the time of infestation an abrupt increase in NO_3^- was documented, followed by concentrations which fluctuated around predefoliation levels for several years. Elevated NO_3^- concentrations were again observed in Watershed 6 in subsequent years, peaking in 1990–1993. Increases were attributed to the continued reductions in the density of the black locust (greater than 75%) and the biomass of ground flora (76%) which reduced the N uptake within the watershed [Swank and Vose, 1997].

[5] A single season of defoliation in a Pennsylvania hemlock-hardwoods forest by the elm spanworm (*Ennomos subsigillariu*) in the summer of 1993 resulted in elevated NO_3^- concentrations within 2 months after the end of the defoliation [Lewis and Likens, 2007]. Concentrations returned to predefoliation levels by the summer of 1995. To date, studies of nitrogen leakage after disturbance have documented the typical pattern of a large nitrogen pulse immediately following a disturbance with a relatively rapid system recovery. The primary causes of elevated stream NO_3^- concentrations have been variously attributed to a number of factors including decrease or absence of nutrient uptake by vegetation, accelerated rates of N mineralization from organic matter, increased rates of nitrification, increased N in the form of insect biomass, frass (defined as debris or excrement produced by insects) and uneaten green leaf fragments, and less translocation of nutrients back into the woody debris from the leaves resulting in increased nutrient content in litter [Swank *et al.*, 1981; Bernhardt *et al.*, 2003; Lewis and Likens, 2007].

[6] During the late 1980s to early 1990s within Shenandoah National Park (SHEN), a gypsy moth defoliation moved along a north to south gradient through a variety of regularly monitored forested watersheds. Both biweekly and high-frequency event water chemistry samples were collected during and subsequent to defoliation. Analyses of NO_3^- trends have shown elevated stream concentrations immediately following disturbance [Eshleman *et al.*, 1995; Webb *et al.*, 1995; Eshleman *et al.*, 1998], as is typical for such ecosystems.

[7] Timescales associated with N cycle recovery from disturbance are typically on the order of 0–3 years, although notable exceptions are found at Shenandoah National Park. Recovery of the NO_3^- to predefoliation concentrations in SHEN compared with other systems such as Hubbard Brook, (Figure 1) has been slow, extending more than a decade since the end of the last major defoliation. The primary causes for differences in rates of

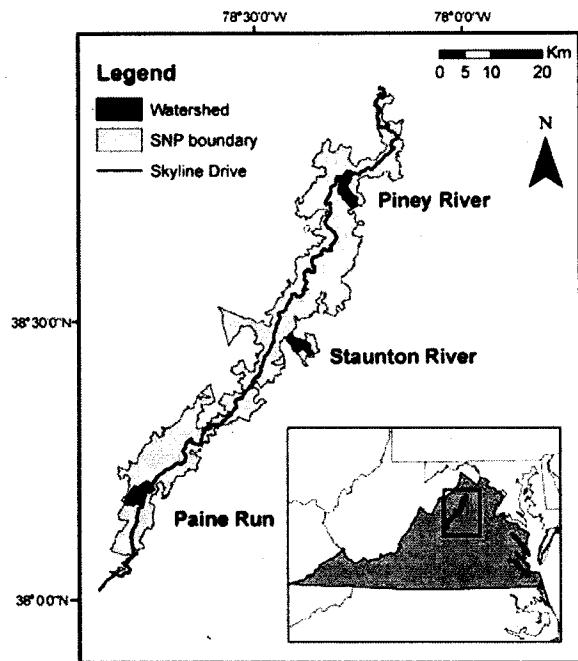


Figure 2. Locations of study watersheds in Shenandoah National Park.

recovery from disturbed systems have not been examined. Physical differences between the watersheds as well as hydrological and biogeochemical differences resulting from the disturbance itself likely contribute to the variability in recovery times between systems. A first step in understanding the recovery process is quantifying variability in recovery rates in systems subject to similar types of disturbance. Only then can the relative role of hydrological and biogeochemical influences be addressed.

[8] Over the course of the long-term recovery following defoliation in SHEN, we examine NO_3^- dynamics within three watersheds that are characterized by distinct hydrological behavior. Our specific objectives are (1) to define NO_3^- concentrations in the distinct hydrologic pathways of groundwater and soil water and to quantify long-term recovery rates and identify seasonal trends, (2) to determine if hydrological controls contribute to differences in recovery rates between the three SHEN watersheds, and (3) to place these results within the broader context of watersheds that have experienced other types of disturbance and in doing so provide insight into the relative role of hydrology and biogeochemistry in accounting for differences in recovery.

2. Site Description

[9] The three study watersheds, which are denoted by the streams that drain them (Piney River, Staunton River, and

Paine Run) are located within the boundaries of Shenandoah National Park (SHEN) in central Virginia within the Appalachian Highlands physiographic region (Figure 2). SHEN contains portions of the headwaters for three major watersheds in Virginia: the Rappahannock, the Shenandoah, and the James Rivers, each of which eventually flow into the Chesapeake Bay. Precipitation in SHEN is approximately evenly distributed throughout the year [Lynch, 1987] with an annual mean during the 1992–2004 study period of approximately 146 cm. The three study watersheds are similar in size and have similar stream gradients. Each is a forested headwater ecosystem, characterized by second- to third-growth mixed hardwoods [Ryan *et al.*, 1989; Young *et al.*, 2006]. While similar in some basic physical characteristics, bedrock type differs between watersheds, with metabasaltic, granitic, and siliciclastic underlying Piney River, Staunton River, and Paine Run, respectively [Gathright, 1976]. The underlying bedrock render soils with differences in clay content and permeability, and contribute to distinctions in hydrologic behavior ranging from attenuated hydrograph peaks and recessions in Piney River to rapid responses to rainfall in Paine Run [Rice *et al.*, 2004]. Bedrock differences are also manifest in the stream water geochemistry. Selected characteristics for the three watersheds are presented in Table 1.

[10] All watersheds are dominated in varying degrees by oak species and were partially defoliated by a southward moving gypsy moth (*Lymantria dispar L.*) infestation from 1987 through 1992. Approximate timing and magnitude of the mapped defoliation for each study watershed are presented in Table 2. The proportion of defoliation in each watershed is based on reported estimates from aircraft surveys for each year [Eshleman *et al.*, 1998].

3. Methods

3.1. Field Methods

[11] Stream chemistry data, at weekly intervals and higher frequency during storm events (typically every 4 h) have been collected at the study watersheds since 1992 as part of the Shenandoah Watershed Study (SWAS) and Virginia Trout Stream Sensitivity Study (VTSSS). Sodium (Na^+) and NO_3^- concentrations were measured by atomic absorption spectrophotometry and ion chromatography, respectively. Detailed descriptions of field methods and laboratory procedures are documented in the Laboratory Procedure Manual [*University of Virginia*, 1996] available on the SWAS website (<http://swas.evsc.virginia.edu>). Stream stage was measured by a float and pulley within a stilling well at each watershed outlet. Routine manual discharge measurements were made to establish rating curves to calculate discharge at hourly intervals. Soil water chemistry data, for each of the three study watersheds, were available for each season of the 2000 water year [Rice *et al.*, 2001]. Samples were obtained from tension lysimeters at

Table 1. Selected Characteristics of Study Watersheds in Shenandoah National Park^a

Watershed	Area (km^2)	Stream Gradient (%)	Primary Lithology	Mean pH	Mean ANC ($\mu\text{eq L}^{-1}$)
Piney River	12.6	9	basaltic	7.1	229
Staunton River	10.5	10	granitic	6.7	86
Paine Run	12.4	9	siliciclastic	5.8	7

^aStream chemistry data for pH and acid neutralizing capacity (ANC) are based on weekly grab samples taken from 1992 to 2004.

Table 2. Year and Percent Area of Gypsy Moth Defoliation in Study Watersheds^a

Watershed	Area of Mapped Defoliation (%)							
	1987	1988	1989	1990	1991	1992	1993	Cumulative
Piney River	3.8	32.3	34.0	15.2	0.0	14.2	0.0	99.5
Staunton River	0.0	0.0	31.4	59.3	0.0	0.0	0.0	90.7
Paine Run	0.0	0.0	0.0	8.8	63.4	85.2	0.0	157.4

^aAdapted from Eshleman *et al.* [1998]. Piney River was subject to the most frequent defoliation, while Paine Run was subject to the most extensive defoliations with respect to cumulative area.

three locations at three depths (nine total) within each watershed. Field methods and laboratory analysis for soil water samples are documented in detail by Rice *et al.* [2001]. Rainfall chemistry data, available as weekly averages, were obtained from a National Atmospheric Deposition Program (accessed at <http://nadp.sws.uiuc.edu/>) monitoring station at Big Meadows (VA28) in SHEN.

3.2. Modeling Methods

[12] To achieve our objective of determining how NO_3^- concentrations associated with the specific hydrologic flow paths change over the course of the long-term time series, we employ a two-part hydrograph separation technique. The first step uses a conservative tracer to perform a traditional hydrograph separation. A Monte-Carlo procedure is applied to this step, in which end-member concentrations for soil water and groundwater are given some degree of flexibility. Using the results of the hydrograph separation, we determine the NO_3^- concentrations of the end-members for groundwater and soil water that best reproduce the observed chemograph for the individual storm. Here we use the aggregate term "soil water" to refer to the component that is comprised of both shallow subsurface and overland flow.

3.2.1. Forward Hydrograph Separation

[13] In undertaking the standard hydrograph separations we apply the standard assumptions: time invariance of end-members throughout a storm and unique geochemical "sig-

natures" associated with the hydrological flow paths. We also assume that the soil concentrations of Na^+ , our conservative tracer, measured in each of the four seasons of the 2000 water year are valid approximations for the range in concentrations during the study period. Insight into the latter two assumptions can be obtained by observing the available grab sample, rainfall, and soil water data for our chosen tracer. There are significant differences between rainfall and base flow Na^+ concentrations (Figure 3) for each watershed, while soil water Na^+ concentrations (Figure 4) do approach base flow concentrations at times. It is possible to have similar Na^+ end-member concentrations. However, owing to the selection of end-members from a range of concentrations, the majority of hydrograph separations for each storm event will adhere to the standard assumption of a unique geochemical signature. There are no long-term trends in base flow Na^+ concentration at any site (Figure 3), only a seasonal component, supporting our assumption that soil water Na^+ concentrations in the 2000 water year are representative of all years within our study period.

[14] By applying two-component mixing, we minimize the inconsistencies often associated with three-component separations [Rice and Hornberger, 1998]. The equations for the separation expressed in matrix form are:

$$\begin{bmatrix} C_{sw.\text{Na}^+} & C_{gw.\text{Na}^+} \\ 1 & 1 \end{bmatrix} \begin{bmatrix} Q_{sw} \\ Q_{gw} \end{bmatrix} = \begin{bmatrix} C_{\text{Na}^+} * Q_{total} \\ Q_{total} \end{bmatrix} \quad (1)$$

where C is concentration and Q is discharge, the subscripts gw , sw , represent groundwater and soil water, respectively and the subscript Na^+ represents sodium. For each storm that was analyzed, the groundwater end-member concentrations were characterized by the last sample collected prior to the storm. Soil water end-member concentrations were characterized by the mean of nine soil samples (three spatial locations and three depths at each location) for the respective season and the weekly rainfall concentrations at each site.

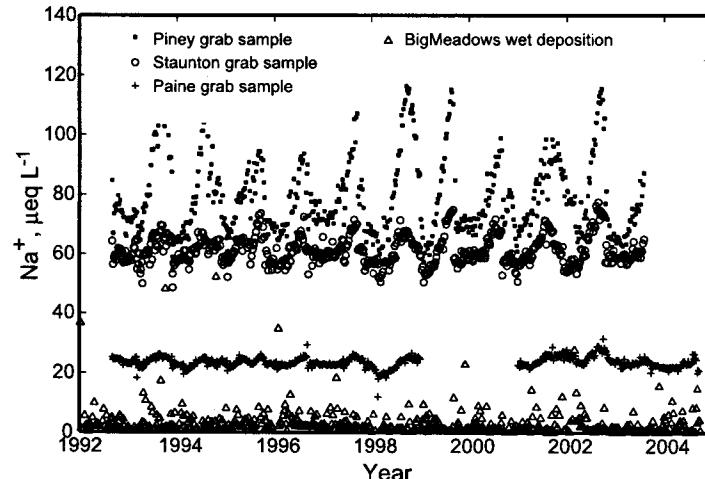


Figure 3. Sodium (Na^+) concentrations in weekly grab samples at Piney River, Staunton River, and Paine Run and weekly composite samples of wet deposition at Big Meadows in SHEN for 1992–2004. Na^+ concentrations in precipitation are significantly lower than in the stream water grab samples.

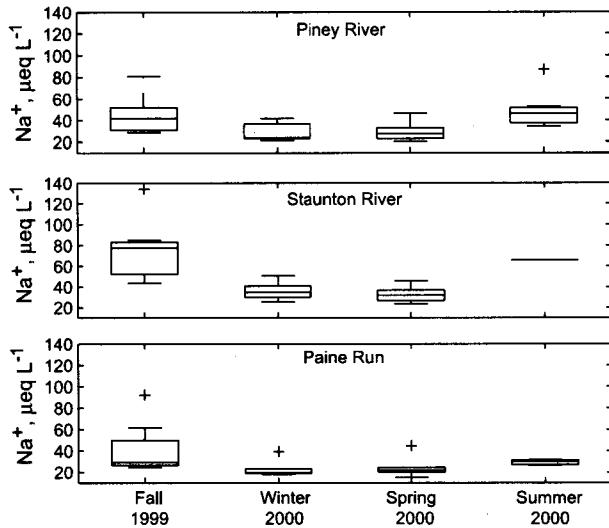


Figure 4. Box plots showing Na^+ concentrations in soil water samples collected from tension lysimeters at three depths, at three locations within Piney River, Staunton River, and Paine Run in each season, fall 1999, winter 2000, spring 2000, and summer 2000 [Rice *et al.*, 2001].

[15] The inherent uncertainty in the end-member concentrations was accounted for through the use of a Monte Carlo approach. Similar to Bazemore *et al.* [1994], a range of possible end-member concentrations was used to evaluate 10,000 possible solutions to the hydrograph separation. Groundwater end-members were selected from a normal distribution. The mean of the distribution was defined by the last base flow sample prior to the storm and the standard deviation was defined as $\pm 10\%$, similar to the approach by Rice and Hornberger [1998]. Soil water end-members were randomly selected from a uniform distribution defined by the mean weekly rainfall concentration as the lower bound and seasonal soil water concentrations as the upper bound. This upper bound was defined by random selection from a distribution based on the mean and standard deviation of the nine soil water samples measured for each season.

3.2.2. Inverse Solution for Nitrate End-Members

[16] The NO_3^- end-members were determined by a least squares optimization with the NO_3^- time series. This inverse solution technique solves for NO_3^- end-members by minimizing the root mean square error between measured and model-derived NO_3^- over the course of a storm. The equations in matrix form are expressed as:

$$\begin{bmatrix} Q_{sw,1} & Q_{gw,1} \\ Q_{sw,2} & Q_{gw,2} \\ \vdots & \vdots \\ Q_{sw,n} & Q_{gw,n} \end{bmatrix} \begin{bmatrix} C_{sw,\text{NO}_3^-} \\ C_{gw,\text{NO}_3^-} \end{bmatrix} = \begin{bmatrix} C_{\text{NO}_3^-,1} * Q_{total,1} \\ C_{\text{NO}_3^-,2} * Q_{total,2} \\ \vdots \\ C_{\text{NO}_3^-,n} * Q_{total,n} \end{bmatrix} + \varepsilon_i \quad (2)$$

where C is concentration, Q_{total} is stream discharge, n is the number of observations, and ε_i is the error between

measured and simulated NO_3^- concentrations for each observation i . The inverse solution was performed for each of the 10,000 Monte Carlo hydrograph realizations and the NO_3^- end-members were selected based on the minimum root mean squared error. No constraints were placed upon the NO_3^- end-members solved by this manner, and we assume time-invariant NO_3^- concentrations over the course of a storm.

4. Results

4.1. Hydrograph Separations

[17] For water years 1992–2004, water chemistry and discharge data were available for a total of 64, 62, and 57 storm events for Piney River, Staunton River, and Paine Run, respectively. Of these, only storms for which samples were available throughout the storm, on both rising and falling limbs of the hydrograph, were used in the analysis. Hydrograph separations were performed for 50, 52, and 45 “complete” storms at Piney River, Staunton River, and Paine Run, respectively. For each storm, Monte Carlo simulations were conducted for the given range of parameters until 10,000 realizations were generated. Any realization which yielded a negative discharge component was considered invalid and not counted toward the final solution set. All sites were able to accrue 10,000 realizations for the final analysis. For the optimal hydrograph separations (selected by the NO_3^- error minimization described previously), the discharge composition at peak flow was on average 64% groundwater and 36% soil water for Piney River; 57% groundwater and 43% soil water for Staunton; and 72% groundwater and 28% soil water for Paine Run.

4.2. Inverse Solution Results for Nitrate End-Members

[18] Inverse solutions to the mixing model determined NO_3^- concentrations associated with the groundwater and soil water reservoirs. To evaluate the quality of results and gain more insight into the behavior of the measured NO_3^- time series and corresponding simulated NO_3^- time series, plots were generated for each storm. Figure 5a illustrates a ‘good’ fit, and Figure 5b illustrates a ‘poor’ fit between measured and derived NO_3^- time series. Note the irregular shape of the observed chemograph for the ‘poor’ fit (Figure 5b). No basic hydraulic parameters, including mean discharge, maximum discharge, length of storm, or season, were found to be significantly correlated ($p > 0.05$) with the root mean squared error of the model fit. Data from ‘poor’ fits were included in analysis, as they are the best representation of the mean groundwater and soil water concentrations for the time series given our assumptions.

[19] Groundwater NO_3^- concentrations determined for each storm event were combined with all weekly grab samples taken during base flow conditions (i.e., not taken during a storm based on visual inspection of the hydrograph). Long-term trends in groundwater NO_3^- concentrations derived from the storm analysis and base flow samples can be approximated by exponential declines for each watershed. The NO_3^- data and best fit exponentials are illustrated in Figure 6 with their corresponding equation in the form $C_t = C_0 e^{-kt}$ where C_t is the concentration at time t , C_0 is the initial concentration ($t = 0$), and k is the rate constant. Nitrate recession constants (k) were determined to

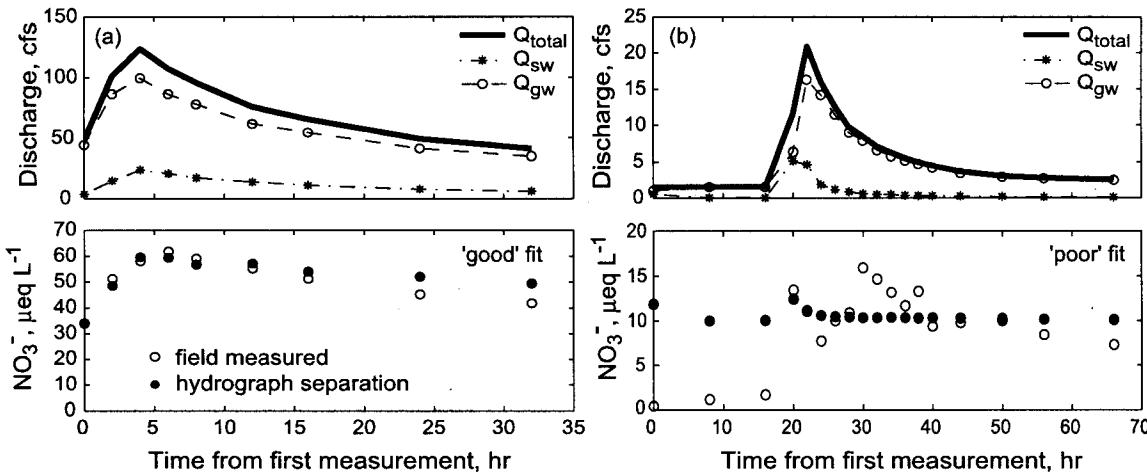


Figure 5. Examples of (top) hydrograph separations and (bottom) NO_3^- concentrations measured and derived from hydrograph separations for storms in Piney River characterized as having (a) a ‘good’ fit on 21–22 March 2001 and (b) a ‘poor’ fit on 15 June 1994.

be 0.0004, 0.0009, and 0.0010 day⁻¹ for Piney River, Staunton River, and Paine Run, respectively. A large-sample, two-sided *t* test was used to determine if the exponential fit to the grab sample data is significantly different from the exponential fit to the model-derived data. The fits to the observed and modeled data were coincident for Paine and Piney ($p < 0.05$). For Staunton, there was no significant difference between the rate constants, but the same could not be established for the initial concentrations.

[20] A clear seasonal imprint is observed for each of these time series. Maximum concentrations occur in the winter and consistently decrease in each subsequent year. Minimum concentrations occur in late fall, consistently approaching 0 $\mu\text{eq L}^{-1}$ each year. Groundwater concentrations inferred from the hydrograph separation technique were generally within the range of variability observed for the direct base flow samples (Figure 6). Considering the storm-derived groundwater concentrations alone, the exponential declines in each watershed were found to be significant ($p < 0.05$).

[21] In contrast to groundwater, soil water exhibited no significant exponential declining trend at Piney River or Paine Run ($p = 0.63$ and 0.76, respectively), but did have a significant trend at Staunton River ($p = 0.0017$) due to the prevalence of near-zero concentrations near the end of the time period. Soil water NO_3^- concentrations for each watershed are illustrated in Figure 7. Soil water concentrations exhibited a wide range of variability within each year, but had no distinct seasonal pattern. Minimum concentrations approach 0 $\mu\text{eq L}^{-1}$ each year at all sites.

4.3. Monthly Residuals in Nitrate Concentrations

[22] Residuals of the groundwater and soil water data with respect to the best fit exponential line were calculated for each watershed and normalized by the standard deviation in concentration for the respective water year. These residuals were averaged for each month to determine if a seasonal pattern was evident. Groundwater NO_3^- residuals demonstrate a clear seasonal pattern for each watershed, with elevated concentrations in December–March, and

depressed concentrations in May–October, which correspond to the high-flow/dormant season and low-flow/growing season, respectively (Figure 8). Soil water residuals did not demonstrate a seasonal pattern at any site (Figure 9).

4.4. Groundwater Discharge Recession Analysis

[23] To compare the behavior of NO_3^- in groundwater between watersheds, the hydrologic behavior of groundwater was characterized for each watershed. Concurrent with times in which rainfall did not influence stream stage, a total of 14, 19, and 9 individual recessions (obtained from 1992 to 2004) in Piney River, Staunton River, and Paine Run,

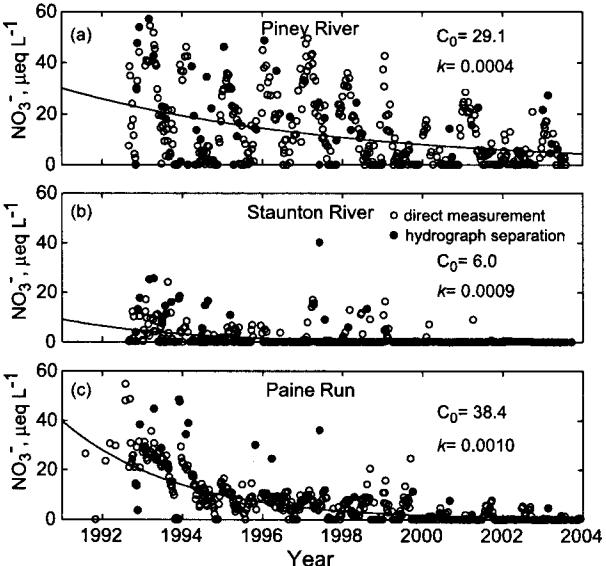


Figure 6. Groundwater nitrate concentrations measured during base flow and generated from hydrograph separations, along with the best exponential fits for combined data sets for (a) Piney River, (b) Staunton River, and (c) Paine Run. The initial concentration, C_0 , and exponential decline rate of NO_3^- , k , are taken from the equation $C_t = C_0 e^{-kt}$.

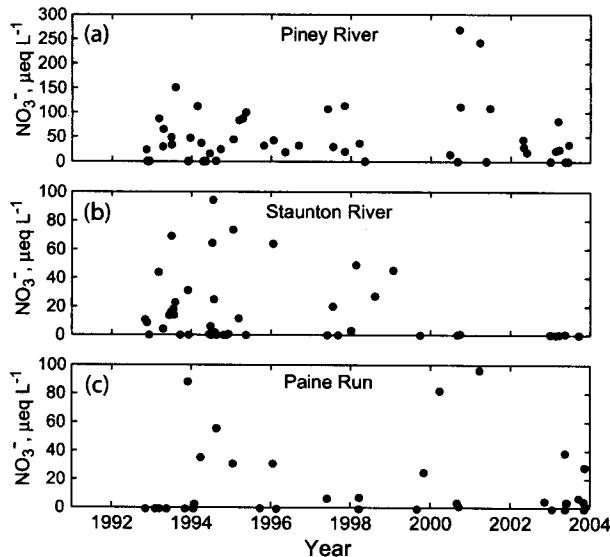


Figure 7. Soil water nitrate concentrations derived from hydrograph separations for (a) Piney River, (b) Staunton River, and (c) Paine Run. Statistically significant declines in soil water nitrate concentrations were found only for Staunton River.

respectively, were used to produce a master recession curve for each watershed based on the “matching strip method” [Nathan and McMahon, 1990]. Each master recession curve plotted along a semilog axis conformed to a straight line (Figure 10) at the later portion of each recession. Departures from the straight line in the early portion of the recession segments were due to contributions from overland or shallow subsurface stormflow. The recession equation is expressed as $Q_t = Q_0 e^{-ct}$ where Q is discharge at time t , Q_0 is initial discharge ($t = 0$) and c is the groundwater recession constant. Larger ‘ c ’ values represent rapid drainage while smaller values represent slower drainage. Recessions

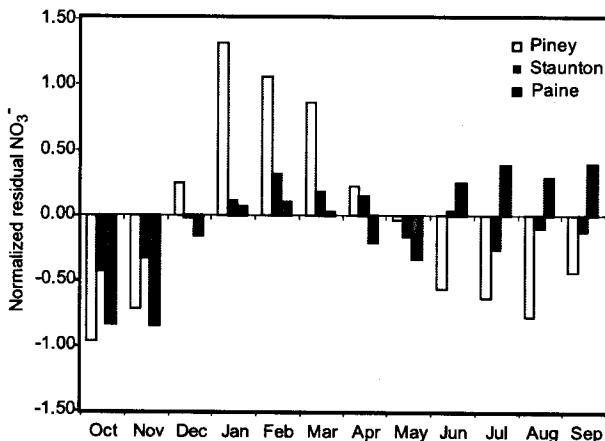


Figure 8. Normalized mean monthly residual nitrate concentrations in groundwater for Piney River, Staunton River, and Paine Run. Lowest concentrations are found in late fall, while the highest concentrations are found in winter at all sites.

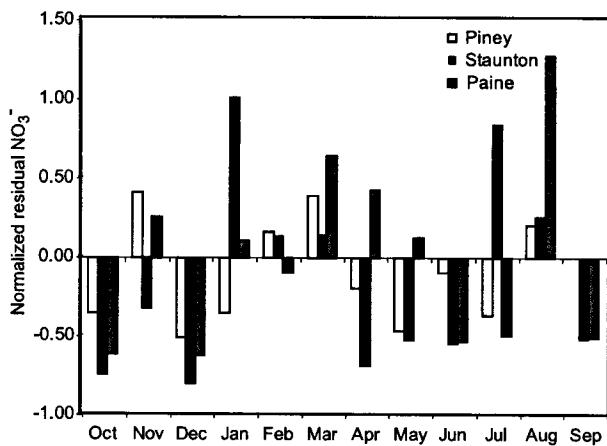


Figure 9. Normalized mean monthly residual nitrate concentrations in soil water for Piney River, Staunton River, and Paine Run. No seasonal trend is apparent.

vary between catchments consistent with expectations from underlying geology, with the most rapid drainage at Paine Run followed by Staunton River and Piney River.

5. Discussion

5.1. Groundwater Nitrate Following Defoliation

[24] Significant exponential declines in groundwater NO_3^- concentrations were observed in each watershed during the time period 1992–2004 based on grab samples and results from the hydrograph separations. Widespread

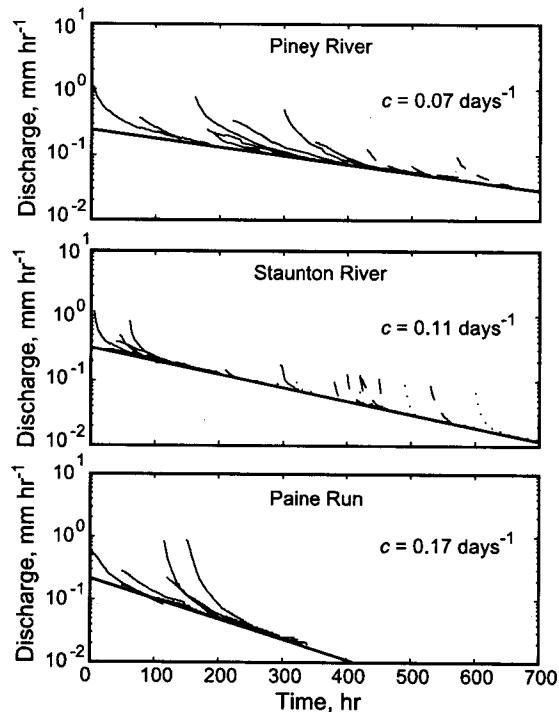


Figure 10. Groundwater master recession curves for Piney River, Staunton River, and Paine Run. The recession constant, c , is taken from the equation $Q_t = Q_0 e^{-ct}$.

declines in “background” levels of NO_3^- have been documented in forested watersheds in New England [Goodale *et al.*, 2003; Huntington, 2005; Bernhardt *et al.*, 2005], which have been attributed to factors such as atmospheric chemistry changes, climate fluctuations, and changes to in-stream processing. While the latter factor in particular, may have contributed to the declines in NO_3^- concentrations reported here, its effect is likely to be second-order relative to the observed tenfold increase and subsequent decline to pre-defoliation conditions. Our analysis focuses on these periods of elevated NO_3^- concentrations that stand apart from the more subtle long-term background dynamics.

[25] The best fit exponential curve varied between the SHEN sites, with the initial NO_3^- concentrations (C_0 in Figure 6) related to the impact of the gypsy moth defoliation. A rank-order relationship was observed between initial NO_3^- concentrations (Figure 6) and mean defoliation percentage for each watershed (Table 2). This relationship is consistent with findings of Houlton *et al.* [2003], who reported a positive relationship between percent crown damage and volume weighted annual NO_3^- concentrations for five watersheds within the Hubbard Brook ecosystem. In SHEN, the lower initial NO_3^- concentration observed for Staunton River also reflects the timing of defoliation relative to sampling within that watershed. The last defoliation occurred in 1990 (Table 2) and concentrations likely declined during the two years prior to initiation of sampling. Extending the exponential decline back two years, however, would still result in Staunton River having the lowest initial NO_3^- concentration. Exponential decline rates (k in Figure 6), a measure of the rate of stream water recovery from the disturbance, is hypothesized to be influenced by both hydrological factors and biogeochemical factors, a point to be addressed later in this section.

[26] A distinct seasonal pattern was evident for groundwater NO_3^- concentrations in all three watersheds. The lowest concentrations are consistently observed in late fall, which coincides with the end of the growing season. The highest concentrations are typically observed in early to mid winter, which coincides with the dormant season as well as the onset of higher stream flow. Similar seasonal patterns of NO_3^- in stream water have been observed in other watersheds [Martin, 1979; Swank *et al.*, 1981; Groffman *et al.*, 1992; Creed *et al.*, 1996; Swank and Vose, 1997; Lovett *et al.*, 2000]. The seasonal patterns of NO_3^- concentrations in stream water have been attributed to hydrological and biological factors which define transport and transformation mechanisms, respectively.

[27] Elevated NO_3^- concentrations during the dormant season have been attributed to decreased rates of plant uptake and increased rates of nitrification of NH_4^+ , which typically occurs with the addition of organic matter as leaf fall and increases NO_3^- availability [Bormann and Likens, 1979; Swank and Vose, 1997]. Water table levels, which rise during the dormant season due to reduced plant uptake and evaporation, facilitate the mobilization of NO_3^- located in the near-surface soils [Creed *et al.*, 1996]. Depressed NO_3^- concentrations during the growing season, on the other hand, have been attributed to vegetation uptake and microbial transformations including denitrification and microbial immobilization, which reduce NO_3^- availability for transport [Groffman *et al.*, 1992]. Lower rates of groundwater dis-

charge to the stream, along with enhanced microbial activity with the warmer soil temperature, may allow for more complete denitrification of the groundwater that passes through the near-stream sediment.

5.2. Soil Water Nitrate Following Defoliation

[28] An unexpected result from our analysis is that soil water NO_3^- concentrations were found to exhibit no clear trends over the 1992–2004 period of study. Our prior expectation was that the soil water concentrations would demonstrate a declining trend similar to that of the groundwater following the disturbance. The persistence of high NO_3^- levels in the soil water over ten years following gypsy moth defoliation suggests a long-term source of NO_3^- or a sustained absence of a previous N sink.

[29] Two sources of N associated with defoliation could account for a persistent source: N-enriched litterfall and frass deposited by the gypsy moth caterpillar. Litterfall induced by biological disturbance is relatively enriched in N due to the absence of nutrient readorption by trees, which occurs shortly preceding senescence under normal circumstances. Eshleman [2000] remarked that nitrification of mineralized ammonium could proceed at a slow rate in the soils following defoliation, which would lead to a steady source of NO_3^- to the stream. Lovett *et al.* [2002], on the other hand, pointed to the mineralization of the N incorporated in soil organic matter (originally from gypsy moth larvae and excreted as frass) as the rate limiting step in the conversion to NO_3^- . Likewise, Christenson *et al.* [2002] found that a large percentage of N derived from frass becomes incorporated into deeper soils and is largely unavailable to plants and microorganisms. The sustained removal of a sink associated with defoliation could be caused by tree mortality. Lovett *et al.* [2002] proposed that high tree mortality and slow vegetation regrowth in defoliated systems would cause nutrient uptake in the growing season to be reduced. Clearly, mechanisms exist for a long-term source of NO_3^- in soils as well for the removal of an N sink following a defoliation such as the one experienced in SHEN. In situ measurements would be needed to identify the exact processes responsible for the persistence of the relatively high concentrations of NO_3^- inferred for the soil water component of the stream chemistry.

[30] The lack of any seasonal trend in soil water NO_3^- concentrations suggests other factors may be responsible for the variability in this flow path. As articulated by Creed *et al.* [1996], soil water NO_3^- concentrations are variable in time as a result of the cyclical accumulation of mobile N in the soil reservoir and hydrological “flushing” of this zone. The balance between microbial transformations and vegetative uptake, both of which exhibit seasonality, partially determine whether or not the soil water is enriched or depleted in NO_3^- relative to the stream water. During the dormant season, NO_3^- accumulates in the soils at a faster rate than in the growing season, when vegetation uptake can be substantial. The other main factor is the timing of hydrological transport of NO_3^- from the soil reservoir. Long periods of time between flushing events can lead to enhanced levels of available NO_3^- within the soil.

[31] Hydrological influences on the soil water NO_3^- levels can obscure any seasonality that may be present. This could possibly account for the consistently low soil water NO_3^-

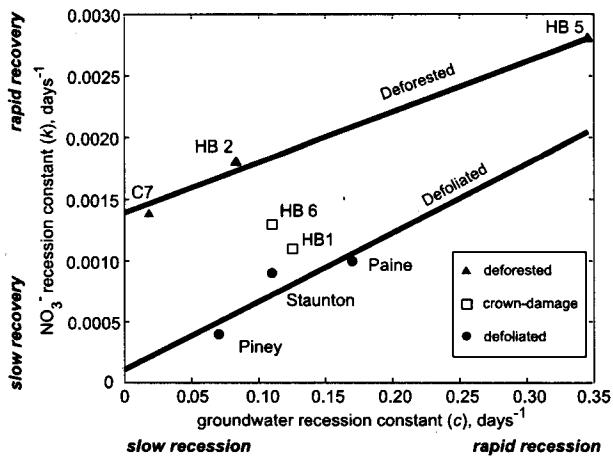


Figure 11. Groundwater and nitrate recession constants for Paine Run, Staunton River, and Piney River in Shenandoah National Park (SHEN) watersheds, along with HB 1, HB 2, HB 5, and HB 6 in Hubbard Brook Experimental Forest and C 7 in Ceweeta Hydrologic Laboratory. All SHEN watersheds were subject to defoliation, HB 2, HB 5, and C 7 were subject to deforestation, and HB 1 and HB 6 were subject to crown damage.

concentrations found for Staunton River near the latter portion of the study period (Figure 7b). Analysis of the storm event samples in conjunction with the discharge record at Staunton River indicate that several storms in the early part of the dormant season were not sampled. Therefore it is likely that the subsequent storms were characterized by soil water that was depleted in NO₃⁻ from this earlier flushing.

5.3. Factors Affecting Time of Recovery of Nitrate From Disturbance

[32] To investigate the possibility that differences in hydrology influence stream water recovery times between watersheds, the NO₃⁻ and groundwater recession constants were compared (Figure 11). For the SHEN watersheds, the groundwater recession constants exhibited a rank-order relationship with the NO₃⁻ recession constants. Longer hydrological residence times in the groundwater, as inferred from slow base flow recessions, are associated with slower recovery from elevated NO₃⁻ levels. A larger proportion of the NO₃⁻ introduced into the groundwater zone through recharge remains there from year to year in systems characterized by slower groundwater recessions. As groundwater NO₃⁻ concentrations result from a mixture of existing reservoir water and inputs from soil water recharge, the residual nitrate concentrations exert some control on long-term rates of nitrate decline.

[33] To place our results in a broader context, we obtained comparable data from four disturbed watersheds within HBEF and one within Ceweeta, all of which were characterized by disturbance followed by uninterrupted recovery. Watershed 2 and Watershed 5 in HBEF were subject to whole tree harvests in 1967–1969 and 1983–1984, respectively. Watershed 1 and Watershed 6 in HBEF were impacted by an ice storm in 1998 which caused extensive crown

damage (>30%) [Bernhardt *et al.*, 2003]. Watershed 7 in Ceweeta was subject to clear-cutting and logging in 1977 [Swank, 1988]. For the periods after disturbance, groundwater and NO₃⁻ recession constants were determined for each watershed by the method previously described for the SWAS data, only without the inclusion of any model-derived concentration data. Recession constants are plotted along with SHEN data for comparison (Figure 11). The long-term declining trend in background NO₃⁻ concentrations within the Hubbard Brook ecosystems [Bernhardt *et al.*, 2005] was removed from those data sets prior to recession analysis. This linear detrending resulted in insignificant changes in the exponential rate constants determined for the deforested watershed, and minor reductions in the rate constants for the damaged watersheds. Similar long-term data were not available for SHEN and Ceweeta sites, so no adjustment were made to account for trends in background concentrations. Defoliated watersheds in Ceweeta (W 27) and Pennsylvania, mentioned in the introduction, were not considered in the analysis due to the extended duration of defoliation and relative infrequency of sampling, respectively.

[34] The deforested watersheds exhibit the same trends as defoliated watersheds, only with more rapid system recovery from elevated NO₃⁻ levels for similar hydrological recession constants. The crown-damaged watersheds have recovery rates between those exhibited by the defoliated and deforested systems. The higher NO₃⁻ recession constants in the deforested and damaged watersheds may reflect various biogeochemical disparities within both the terrestrial and instream environments. For example, the N pool may be more recalcitrant within the soils of the defoliated watersheds due to the presence of N in microbial tissues (originally from decomposed frass), whereas N conversion rates to mobile NO₃⁻ are not inhibited in the deforested or damaged systems, and subsequent export to rivers is relatively rapid. Other biogeochemical explanations include those given by Lovett *et al.* [2002] which include high tree mortality and slow vegetation regrowth in defoliated systems in contrast to deforested systems where increased light penetration may lead to more rapid regrowth. Light penetration would also result in higher temperatures and accelerated rates of nitrification and therefore more rapid N mobilization. Soil N sequestration during forest regrowth through microbial transformations may also play a role in the quick return to baseline conditions for deforested systems [Huntington, 2005]. Watersheds with crown damage represent an intermediate state between defoliated and deforested systems analyzed here, in terms of stream water recovery following disturbance. They do not benefit as much from increased light penetration and vegetative regrowth compared to deforested watersheds, but their recovery to background NO₃⁻ concentrations is not extended by the presence of a relatively immobile pool of N, as is the case for watersheds impacted by gypsy moth defoliation. Differences in instream removal mechanisms between deforested and defoliated systems may also influence system recovery rates. Bernhardt *et al.* [2005] proposed that increases in heterotrophic assimilation of N and increased denitrification can be caused by the formation of new organic debris dams. Although further studies are necessary to identify the specific mechanisms, our results indicate that hydrologic

residence times, together with factors that govern nitrate availability control long-term recovery of NO_3^- in watersheds impacted by disturbance.

5.4. Summary of Observations and Future Direction

[35] For over a decade following a large-scale defoliation, exponential declines with seasonal patterns were observed in groundwater NO_3^- concentrations within three SHEN watersheds. NO_3^- decline rates were significantly different between watersheds. The length of time it takes for stream water NO_3^- levels to return to predisturbance conditions is shown to be influenced by the hydrological residence time of the groundwater reservoir. Watersheds with rapid groundwater recession tend to have shorter recovery times following disturbance. Comparisons to deforested systems indicate hydrological controls are similarly present; however inherent biogeochemical differences need to be considered to account for the more attenuated recovery in defoliated systems.

[36] Neither long-term declines nor seasonal patterns were found in model-derived soil water NO_3^- concentrations. The absence of a comparable pattern compounded by the lack of direct measurements of soil biogeochemical processes makes it difficult to ascertain the specific processes driving N behavior in the soil zone. Understanding soil water NO_3^- dynamics, which influence stream water indirectly from groundwater recharge and directly during storm events, is essential to understanding differences between watershed recoveries. Future investigative steps to determine the biogeochemical processes that contribute to differences in NO_3^- recoveries after a disturbance include characterization of upland soil N accumulation, near-stream and in-stream denitrification rates, as well as documentation of tree mortality and vegetation regrowth during and subsequent to disturbance.

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