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

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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 rate limitation on the transformation of the nitrogen pool introduced during the disturbance and/or reduced nutrient uptake due to tree mortality.


1. Introduction

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.

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-
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.

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].

A single season of defoliation in a Pennsylvania hemlock-hardwoods forest by the elm spanworm (Ennomos subsignaria) 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].

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.

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 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.
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.

[6] 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 steams 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

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Area (km$^2$)</th>
<th>Stream Gradient (%)</th>
<th>Primary Lithology</th>
<th>Mean pH</th>
<th>Mean ANC (μeq L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piney River</td>
<td>12.6</td>
<td>9</td>
<td>basaltic</td>
<td>7.1</td>
<td>229</td>
</tr>
<tr>
<td>Staunton River</td>
<td>10.5</td>
<td>10</td>
<td>granitic</td>
<td>6.7</td>
<td>86</td>
</tr>
<tr>
<td>Paine Run</td>
<td>12.4</td>
<td>9</td>
<td>siliciclastic</td>
<td>5.8</td>
<td>7</td>
</tr>
</tbody>
</table>

*Stream 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

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Piney River</td>
<td>3.8</td>
<td>32.3</td>
<td>34.0</td>
<td>15.2</td>
<td>0.0</td>
<td>14.2</td>
<td>0.0</td>
<td>99.5</td>
</tr>
<tr>
<td>Staunton River</td>
<td>0.0</td>
<td>0.0</td>
<td>31.4</td>
<td>59.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>90.7</td>
</tr>
<tr>
<td>Paine Run</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>8.8</td>
<td>63.4</td>
<td>85.2</td>
<td>0.0</td>
<td>157.4</td>
</tr>
</tbody>
</table>

*Adapted 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 NO₃⁻ 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 NO₃⁻ 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 “signature” 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:

\[
\begin{bmatrix}
  C_{gw,Na^+} & C_{sw,Na^+} \\
  1 & 1
\end{bmatrix}
\begin{bmatrix}
  Q_{gw} \\
  Q_{sw}
\end{bmatrix}
= \begin{bmatrix}
  C_{Na^+} \\
  Q_{total}
\end{bmatrix}
\]

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.
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 $C_0$ 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
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.

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 μeq 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 ($p < 0.05$).

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 μeq L$^{-1}$ each year at all sites.

4.3. Monthly Residuals in Nitrate Concentrations

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

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, respectively, were used to determine the rate of NO$_3^-$ decline in each watershed.
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 $Q_t = Q_0e^{-ct}$ 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 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 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.

Figure 10. Groundwater master recession curves for Piney River, Staunton River, and Paine Run. The recession constant, $c$, is taken from the equation $Q_t = Q_0e^{-ct}$. 

Piney River

$c = 0.07 \text{ days}^{-1}$

Staunton River

$c = 0.11 \text{ days}^{-1}$

Paine Run

$c = 0.17 \text{ days}^{-1}$
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 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 predenitrification 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 decay 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 and Vose, 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 discharge 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 readsorption by trees, which occurs shortly preceding senescence under normal circumstances. Exshleman [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 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$_3^-$
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 NO$_3^-$ from this earlier flushing.

5.3. Factors Affecting Time of Recovery of Nitrate From Disturbance

To investigate the possibility that differences in hydrology influence stream water recovery times between watersheds, the NO$_3^-$ and groundwater recession constants were compared (Figure 11). For the SHEN watersheds, the groundwater recession constants exhibited a rank-order relationship with the NO$_3^-$ recession constants. Longer hydrological residence times in the groundwater, as inferred from slow base flow recessions, are associated with slower recovery from elevated NO$_3^-$ levels. A larger proportion of the NO$_3^-$ introduced into the groundwater zone through recharge remains there from year to year in systems characterized by slower groundwater recessions. As groundwater NO$_3^-$ 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.

To place our results in a broader context, we obtained comparable data from four disturbed watersheds within HBEF and one within Coweeta, 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 Coweeta was subject to clear-cutting and logging in 1977 [Swank, 1988]. For the periods after disturbance, groundwater and NO$_3^-$ 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 NO$_3^-$ 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 Coweeta sites, so no adjustment were made to account for trends in background concentrations. Defoliated watersheds in Coweeta (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.

The deforested watersheds exhibit the same trends as defoliated watersheds, only with more rapid system recovery from elevated NO$_3^-$ levels for similar hydrological recession constants. The crown-damaged watersheds have recovery rates between those exhibited by the defoliated and deforested systems. The higher NO$_3^-$ recession constants in the defoliated and damaged watersheds may reflect various biogeochemical disparities within both the terrestrial and stream 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 NO$_3^-$ 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 NO$_3^-$ 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

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 groundwaer 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.

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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