## ASSESSING THE EXTENT OF NITROGEN SATURATION IN NORTHERN WEST VIRGINIA FORESTED WATERSHEDS: A SURVEY OF STREAM NITRATE CONCENTRATIONS

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ABSTRACT.—Twenty-seven forested watersheds in northern West Virginia were sampled for stream nitrate concentrations during summer 1997 and fall 1998 baseflow periods to determine if Fernow watershed 4, an often-cited and studied nitrogen saturated basin, was anomalous or regionally representative in terms of stream nitrate levels. Baseflow stream NO<sub>3</sub>-N concentrations ranged from 0.005 to 1.54 mg L<sup>-1</sup>, with nearly half of the streams being higher than Fernow 4 in both summer and fall. Variations in stream nitrate were related to basin geology, whereas no direct effects of basin physiography could be established. It was concluded that Fernow 4 was representative of regional stream nitrate concentrations and the majority of the watersheds surveyed showed similar signs of nitrogen saturation.

Northern temperate forests have long been considered to be nitrogen limited ecosystems. vielding low concentrations of nitrogen in streamflow. This theory has been challenged by researchers who observed increasing levels of nitrogen export from forested headwater streams (Aber and others 1989, Driscoll and others 1989, Johnson and Lindberg 1992, Murdoch and Stoddard 1992, Stoddard 1994). Researchers have coined the phrase "nitrogen saturation" to describe a forest ecosystem's declining ability to retain nitrogen (Aber and others 1989, Agren and Bosatta 1988). In nitrogen saturated systems, inorganic nitrogen is supplied in excess of microbial and vegetative demand (Aber and others 1989, 1998; Stoddard 1994).

Stoddard (1994) described nitrogen saturation in a series of stages based on seasonal stream nitrate concentrations. In stage 0, stream nitrate-N concentrations are near zero year round. In stage 1, nitrate-N becomes elevated (0.5 to 0.8 mg NO<sub>3</sub>-N L<sup>-1</sup>) in the dormant season due to a lack of microbial and vegetative uptake. Stage 2 is characterized by elevated stream nitrate-N concentrations year round. Watershed 4 at the Fernow Experimental Forest has been cited as the best example of a stage 2 nitrogen-saturated watershed in the northeastern United States, exhibiting elevated year round nitrate-N concentrations ( $0.72 \pm 0.10$  mg NO<sub>3</sub>-N L<sup>-1</sup> from 1997 to 1998) (Peterjohn and others 1996, Fenn and others 1998, Williard 1999).

The Fernow Experimental Forest is located in northern West Virginia, an area that receives high inputs of bulk atmospheric nitrate deposition (5.0 kg NO<sub>3</sub>-N ha<sup>-1</sup> yr<sup>-1</sup> from 1983 to 2001) (P. Edwards – written comm.). Watershed 4 at Fernow is a control watershed that has been exporting high rates of nitrate (5.1 kg NO<sub>3</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>) for the past two decades (Adams and others 1993). On Fernow 4, nitrate-N bulk deposition inputs (5.0 kg ha<sup>-1</sup> yr<sup>-1</sup>) and stream outputs (5.1 kg ha<sup>-1</sup> yr<sup>-1</sup>) are equal and outputs show little seasonal variation. Both of these characteristics are indicators of nitrogen saturation (Gilliam and others 1996, Peterjohn and others 1996).

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Fernow also contains two other control catchments in close proximity (within 1.1 km) to Fernow 4: watersheds 10 and 13. Nitrate-N exports from Watershed 13 (4.0 kg NO<sub>3</sub>-N ha-1 yr-1) and Watershed 10 (1.2 kg  $NO_3$ -N ha-1 yr-1) are lower than Watershed 4, even though they receive similar amounts of atmospheric nitrogen deposition (P. Edwards, written communication). All three of these watersheds contain deciduous vegetation with forest stand ages between 60 and 90 years old. If atmospheric deposition were leading to nitrogen saturation, these watersheds would be expected to export similar amounts of nitrate. This raises the question of whether other factors such as geology/soil chemistry, physiographic parameters, and past land use history are causing differences in stream nitrate export in this localized area.

Our objective was to examine the spatial and temporal variability of stream nitrate concentrations in an area that contains a nitrogen saturated watershed, Fernow 4. The specific null hypotheses tested were:

- 1) growing and dormant season stream nitrate concentrations in 26 surrounding forested watersheds were similar to Fernow 4, and
- 2) dormant season stream nitrate concentrations were greater than growing season nitrate concentrations in 27 forested watersheds.

Assessing the local variability in stream nitrate concentrations in relation to geology and watershed characteristics may aid in the identification of local controls on stream nitrate concentrations in forested watersheds.

# STUDY SITES

Study watersheds were located on the east and west side of Shavers Fork River in close proximity (within 10 km) to the Fernow Experimental Forest to keep climatic conditions and nitrogen deposition rates as uniform as possible (fig. 1). The 27 watersheds were all located between the elevations of 537 m and 1,136 m, which was the range of elevation on one of the largest watersheds (Canoe Run). Gilliam and Adams (1996) found that wet ammonium and nitrate deposition rates were not significantly different at three sampling sites (689 to 838 m elevation) within and near the Fernow Experimental Forest.

The watersheds selected for the study were all 100 percent forested. Predominant overstory species found on the study watersheds were red oak (*Quercus rubra* L.), sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), yellow-poplar (*Liriodendron tulipifera* L.), and American beech (*Fagus grandifolia* Ehrh.). West and south facing slopes contained white oak (*Quercus alba* L.) instead of red oak. Eighteen of the twenty-seven study watersheds contained actively managed stands, which have experienced timber harvesting, but none have been completely clearcut. The most recent partial cutting on any of the study watersheds was 4 years prior to sampling.

# METHODS

# **Field Measurements**

Stream water grab samples were taken on June 17, 1997, from 9:00 a.m. to 6:00 p.m. and on October 23, 1998, from 9:45 a.m. to 5:00 p.m. near the mouth of the watersheds during baseflow conditions. The samples were immediately put on ice for transport to the Water Analysis Laboratory at The Pennsylvania State University where they were analyzed within 48 hours for dissolved nitrate and ammonium using cadmium reduction and automated phenate methods, respectively (American Public Health Association 1995). Stream ammonium concentrations were near or below the detection limit (0.005 mg L<sup>-1</sup>) in the study watersheds, which was expected given the lack of ammonium leaching through the soil matrix. Stream pH and specific electrical conductance (SEC) also were taken at each watershed using calibrated, portable meters (pHTestr 3 and TDSTestr, both by Oakton Inc., Singapore).

The 27 sampled watersheds were delineated on topographic maps (Parsons, Bowden, Elkins, and Montrose, WV 7.5 minute USGS quadrangles) and their bedrock geology types were determined with the use of quadrangle geology maps (Reger 1923, 1931). Represented bedrock types were grouped into two categories [(1) Catskill/Chemung/Pocono shale and sandstone, and (2) Mauch Chunk shale/Greenbrier limestone] based on relative differences in published aquifer pH values (Ponce and others 1979; Gever and Wilshusen 1982; Taylor and others 1982, 1983). The catchment area, relief ratio, and average basin slope were calculated using the delineated watershed boundaries. Watershed area was determined using a digital planimeter (Sokkia Corp., Overland Park, KS). Relief ratio was calculated as the maximum elevation difference divided by the basin length measured along the long axis of the basin. Average basin slope was calculated using the Wentworth (1930) line-intersection method.



Figure 1.—Locations of the 27 study watersheds in northern West Virginia.

## **Statistical Methods**

The SAS statistical package, Version 7 for Windows (SAS Institute Inc., Cary, NC), was used to analyze the data sets. Prior to performing any analysis of variance procedures (ANOVA) or t-tests, the data sets were analyzed to determine if the error terms were normally distributed and homogeneous (assumptions underlying ANOVA). Normal probability plots and Shapiro-Wilk test statistics confirmed that all the data sets were normally distributed. Bartlett's tests showed error variances for the various ANOVA models to be relatively homogeneous. Given the normal distribution of data and the homogeneity of error variance, no data transformations were required.

T-tests, assuming equal variances, were used to determine if mean summer and fall nitrate concentrations were significantly different at a=0.05. One-way ANOVA models were developed to test if summer and fall mean stream nitrate-N concentrations, SEC, and pH were significantly different between the two geology categories [(1) Catskill/Chemung/Pocono shale and sandstone and (2) Mauch Chunk shale/Greenbrier limestone). The two geology categories were assigned quantitative dummy variables (CCP=1, MCG=2) in linear regression models of summer and fall stream nitrate versus geology category. Pearson correlation coefficients were determined for measured summer and fall stream chemistry variables (NO<sub>3</sub>, SEC, pH) and the watershed physiographic parameters (average basin slope, relief ratio, and area). Significant correlation coefficients were noted for p values < 0.05.

# **RESULTS AND DISCUSSION**

# **Stream Nitrate-N Concentrations**

Stream nitrate concentrations were measured in the summer and fall on 27 forested watersheds in close proximity to Fernow 4, a watershed that exports relatively high amounts of nitrate (5.1 kg NO<sub>3</sub>-N ha<sup>-1</sup> yr<sup>-1</sup>) (Adams and others 1993). The 27 watersheds exhibited a wide distribution of NO<sub>3</sub>-N concentrations (0.005 to 1.54 mg L<sup>-1</sup>) at the local scale of the study (fig. 2). The range of NO<sub>3</sub>-N concentrations approaches the range of NO<sub>3</sub>-N export (0.04 to 5.15 kg ha<sup>-1</sup>yr<sup>-1</sup>) DeWalle and Pionke (1996) observed at a regional scale in their review of forested watersheds in the Chesapeake Bay region.

Our measured stream nitrate-N concentrations on Fernow 4 (0.63 and 0.56 mg  $L^{-1}$  NO<sub>3</sub>-N) were close to the mean (0.72 ± 0.10 mg  $L^{-1}$  NO<sub>3</sub>-N)

and within the range  $(0.50 \text{ to } 1.00 \text{ mg } \text{L}^{-1} \text{ NO}_3\text{-N})$ of nitrate-N concentrations measured at the U.S. Forest Service gauging station during 1997 and 1998 (P. Edwards written communication). Fernow 4's stream nitrate-N concentrations were approximately in the middle of the distribution of nitrate concentrations among the 27 watersheds (fig. 2). There were 10 watersheds in both the summer and fall sampling periods that had greater stream nitrate concentrations than Fernow 4. Given that Fernow 4 has been cited as the best example of a nitrogen saturated watershed in the northeastern United States (Stoddard 1994, Peterjohn and others 1996, Fenn and others 1998), the study results indicate that nitrogen saturation could be relatively widespread among forested watersheds in the local study area.

Mean dormant (late October) season nitrate-N concentrations  $(0.59 \pm 0.16 \text{ mg L}^{-1})$  were not significantly different from growing season (mid-June) nitrate concentrations  $(0.56 \pm 0.09)$ mg L<sup>-1</sup>). The late fall sampling was assumed to represent dormant season concentrations because the sampling occurred after leaf fall and stream temperatures (5.2 to 10.8°C) were already declining toward dormant season levels. Many of the watersheds, including Fernow 4, had elevated stream nitrate concentrations during both the dormant season and growing season (fig. 2). The elevated (>  $0.5 \text{ mg NO}_3\text{-}N \text{ L}^{-1}$ ) growing season nitrate concentrations indicate that these watersheds are at stage 2 of nitrogen saturation, where the capacity of the microbes and vegetation to retain nitrogen during the growing season has been exceeded (Aber and others 1989, Stoddard 1994). In non-saturated systems, nitrate leaching rates are expected to be lower in the growing season compared to the dormant season because of greater nitrogen demands by microbes and vegetation in the growing season.

Approximately one-half (14 of 27) of the watersheds had greater stream nitrate-N concentrations in the summer compared to the fall (fig. 2). This was not expected, given the significant vegetative uptake and microbial immobilization of nitrogen during the growing season. Perhaps there was significant N fixation rates occurring on some of these watersheds during the growing season, which resulted in greater nitrate leaching. Watersheds with greater summer stream concentrations were not of a particular geology type or geographically clustered in one area of the study region. Of the 18 study watersheds containing actively managed timber stands, 10 of them had higher stream nitrate concentrations in the summer. Thus, the presence of timber management does not help explain why certain watersheds have higher stream nitrate concentrations in the summer.

Repeated sampling of a large number of watersheds allows the assessment of whether a onetime baseflow survey is an adequate representation of relative stream nitrate concentrations. Specifically, this can be assessed by ranking summer and fall stream nitrate concentrations and examining if stream nitrate ranks change over time. Using a non-parametric sign test with an S table (Noether 1991), the median change in rank was found to be 3 with a 95 percent confidence interval of 1 to 5 (fig. 3). Thus, the 27 streams exhibited relatively little change in rank, which indicates that one-time baseflow sampling can serve as an adequate index to stream nitrate concentrations.



Figure 2.—Fall stream nitrate-N concentrations for the 27 study watersheds.



Figure 3.—Change in stream nitrate-N ranks between summer and fall among the 27 forested watersheds.

# Explaining the Variability in Stream Nitrate-N Concentrations

### Geology

Forested watersheds containing predominantly Mauch Chunk shale/Greenbrier limestone (MCG) bedrock (n=8) were found to have significantly greater mean summer stream nitrate concentrations than watersheds containing predominantly Catskill/Chemung/Pocono shale and sandstone (CCP) bedrock (table 1). Geology dummy variables (CCP=1, MCG=2) explained 18 percent of the variation in summer stream nitrate-N concentrations.

The observed stream nitrate differences among watersheds with different bedrock types agree with Ponce and others (1979) findings on tributaries of the Little Black Fork Creek, WV, which was one of the 27 study watersheds. Ponce and others (1979) reported that stream base cations, pH, and SEC differed among tributaries with different bedrock types. Ponce and others (1979) measured stream nitrate-N, but they did not analyze it as a variable that could differ by bedrock type. Nevertheless, Ponce and others (1979) raw data showed that stream nitrate-N did vary among three geology types contained in our study (Greenbrier, Mauch Chunk, and Catskill). Stream nitrate-N concentrations were relatively high on tributaries draining Greenbrier (1.31 mg L<sup>-1</sup>) and Mauch Chunk (1.02 mg L<sup>-1</sup>) bedrock types. The Catskill bedrock type yielded waters with significantly lower mean nitrate-N concentrations (0.69 mg L<sup>-1</sup>), which agrees with our findings.

Even though there were mean differences between the two geology categories (MCG and CCP), there was significant variability in stream nitrate-N concentrations within each category. Fernow 4, 10, and 13 all contained 100 percent Catskill shale and sandstone bedrock yet Fernow 4 and 13 had significantly higher stream nitrate-N concentrations than Fernow 10. Thus, geology did not help explain stream nitrate concentration differences among the three Fernow watersheds.

The mechanism by which geology affects stream nitrate can only be speculated upon. Geology probably has an indirect control on nitrate leaching through its relationship with soil chemistry. Low soil pH and calcium have been noted to limit soil microbial activity and growth rates, respectively (Alexander 1977, Norris and others 1991, Smith 1995, Paul and Clark 1996).

The two represented geology categories likely have significantly different soil Ca and pH, based on the stream SEC and pH measurements and earlier findings by Auchmoody (1972). Mean summer and fall stream SEC levels were significantly higher among watersheds containing MCG bedrock (shale/limestone) compared to CCP bedrock (shale/sandstone) (table 1). Stream SEC generally is correlated well with Ca leaching rates, which are normally higher in watersheds with greater soil Ca pools. Further evidence for a geology/soil calcium link in our study is provided by Auchmoody (1972), who sampled forest soils from different geology types within Randolph and Tucker Counties, WV (our study location).

	NO <sub>3</sub> -N (mg L <sup>-1</sup> )		рН		SEC (μS cm <sup>-1</sup> )	
Basin geology	Summer	Fall	Summer	Fall	Summer	Fall
Catskill/Chemung/Pocono Mauch Chunk/Greenbrier	0.50 a <sup>1</sup> 0 72 b	0.52 a 0 75 a	6.86 a 7 72 b	6.98 a 7 59 b	24.7 a 75 0 b	24.2 a 70 0 b
<sup>1</sup> Parameter means with different letters in a column are significantly different at $\alpha$ =0.05.						

Auchmoody (1972) found that forest soils derived from both Greenbrier and Mauch Chunk bedrock had significantly greater calcium concentrations than soils derived from Catskill and Chemung bedrock. Watersheds with MCG bedrock had significantly higher mean summer and fall stream pH than watersheds with CCP bedrock (table 1). The MCG bedrock watersheds likely have higher mean soil pH values than the CCP watersheds, since relative differences in stream pH are generally correlated with differences in soil pH. Differences in soil pH and Ca levels may be causing the observed differences in stream nitrate concentrations among watersheds with MCG and CCP bedrock.

### **Physiographic Parameters**

Summer and fall stream nitrate concentrations were not significantly ( $\alpha = 0.05$ ) correlated with the physiographic parameters average basin slope, watershed relief ratio, and watershed area. Average basin slope did exhibit a weak correlation with summer (r = 0.341, p = 0.081) and fall (r = 0.329, p = 0.093) stream nitrate-N concentrations. Nitrate concentrations could be greater on steeper sloped watersheds because recharge water has shorter residence times. Thus, there is less opportunity for microbes and vegetation to assimilate the nitrate in the infiltrating water. Steeper sloped watersheds generally have more narrow riparian zones, which results in a lower percentage of anoxic soils. In these watersheds there would be less opportunity for denitrification, yielding higher nitrate concentrations. Average basin slope means were not significantly different between the two geology categories (MCG and CCP), indicating that geology effects did not confound the correlation of average basin slope with stream nitrate concentrations.

### **Past Land Disturbances**

Nitrate leaching to streams can be affected by past land disturbances (logging, fire, farming) (Fenn and others 1998). Eighteen of the twentyseven study watersheds were at least partially logged within the last 30 years, based on records from the Monongahela National Forest, WV (L. White, personal communication) and the Fernow Experimental Forest, WV (P. Edwards, personal communication). Four of the watersheds were partially cut as recently as 1993, 4 years prior to stream sampling. Clearcutting experiments on forested watersheds showed short term increases in stream nitrate concentrations (1 to 4 years), with nitrate export returning to pre-cutting levels by the third or fourth year due to nitrogen uptake by regrowing vegetation (Patric 1980, Hornbeck and others 1987, Lynch and Corbett 1991, Dahlgren and Driscoll 1994, Pardo and others 1995). Based on these findings, even the most recent partial cutting (4 years prior to sampling) on the study watersheds should not have impacted stream nitrate concentrations.

Previous fires also can affect nitrate leaching to streams by impacting soil nitrogen pools. Severe fire can volatilize nitrogen in the organic layer and upper mineral horizons, depleting longterm soil nitrogen pools (Raison 1979). There was no record of severe fire on any of the study watersheds. However, the effects of fire cannot be ruled out given the high frequency of slashrelated fires after the initial logging of mid-Appalachian forests in the late 1800s to early 1900s.

Farming can either build-up or deplete soil N pools depending on the amount of fertilization that occurred. If soil nitrogen pools were severely depleted by past land disturbance, the pools still could be in an aggrading phase that would limit nitrate leaching to streams. The existence of past farming was not assessed on any of the study watersheds. However, it is likely that some of the watersheds were historically cultivated. In the early 1900s, many of the steep mid-Appalachian forested slopes were cleared and farmed until yields declined and they were left to revert to forest land (Lima and others 1977).

### CONCLUSIONS

Fernow 4, a watershed cited to be nitrogen saturated, was representative of the local forested watersheds in terms of baseflow stream nitrate concentrations. Fernow 4 was just above the median stream nitrate concentration of the 27 watersheds sampled, indicating that nitrogen saturation may be a prevalent condition among local forested watersheds. The majority of the watersheds had elevated stream nitrate concentrations both in the fall and summer, symptoms of nitrogen saturation.

Differences in bedrock geology explained 18 percent of the variation in summer stream nitrate concentrations. Watersheds containing primarily Mauch Chunk shale/Greenbrier limestone had significantly greater summer stream nitrate concentrations than watersheds containing Catskill/Chemung/Pocono shale and sandstone. Geology likely had an indirect effect on stream nitrate concentrations, based upon its relationship with soil chemistry. Differences in soil pH and Ca concentrations among the two geology categories could be causing the observed differences in stream nitrate leaching, given their documented effects on microbial nitrate production. Stream nitrate-N differences between Fernow watersheds 4, 10, and 13, which all contain Catskill bedrock, suggest that other factors such as past land use history (e.g., fire, farming, and logging) may also play a role in explaining stream nitrate variation at a local scale.

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