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Chapter 5

Spatial Variations in Stream Nitrate Concentrations in a Region Containing a Nitrogen Saturated Watershed

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ABSTRACT

Streams on 27 forested watersheds in northcentral West Virginia were sampled during summer baseflow to determine the local spatial variation in stream nitrate concentrations. Factors associated with the observed stream nitrate variation were identified. A study of stream nitrate concentrations at upper, middle, and lower locations on eight watersheds was also conducted to assess the importance of longitudinal variations in stream nitrate. Baseflow stream NO_3-N concentrations ranged from 1.08 to 0.18 mg L^{-1}, with Fernow watershed 4, a stream noted for high nitrogen export, exhibiting a near median concentration of 0.63 mg L^{-1} of NO_3-N. Stream nitrate concentrations were positively correlated with stream specific electrical conductance (SEC) and pH. These positive correlations were probably linked to greater soil fertility and higher soil pH. Soil fertility and soil pH both directly affect soil nitrogen cycling rates, which largely control nitrate leaching to streams. Stream nitrate concentrations did not show any consistent longitudinal variation across the eight watersheds.

INTRODUCTION

Northern temperate forests have long been considered nitrogen limited ecosystems, yielding low concentrations of nitrogen in stream flow. This theory has recently been challenged by researchers who observed increasing levels of nitrogen export from forested headwater streams (Aber et al., 1989; Driscoll et al., 1989, Johnson and Lindberg, 1992; Murdoch and Stoddard, 1992; Stoddard, 1994), implying that a state of nitrogen saturation has been reached in these watersheds. Nitrogen saturation refers to a condition within forested ecosystems in which nitrogen is supplied in excess of the microbial and vegetative demand (Aber et al., 1989; Stoddard, 1994). Inorganic nitrogen is supplied to a forest by atmospheric deposition of nitrogen, nitrogen fixation by bacteria and fungi, and microbial transformations of nitrogen (organic N to ammonium to nitrate). Excess nitrogen is readily leached to stream water in the form of nitrate, given the lack of adsorption of the nitrate anion within the soil matrix. Watershed 4 at the Fernow Experimental Forest has been cited as the best example of a nitrogen saturated watershed in the northeastern United States (Peterjohn et al., 1996; Fenn et al., 1998).

The Fernow Experimental Forest is located in northcentral West Virginia, an area that receives high amounts of wet atmospheric nitrate deposition (5.05 kg ha^{-1} yr^{-1} of NO_3-N) (P. Edwards-written comm.). Watershed 4 at Fernow is a control watershed that has been exporting high rates of nitrate (mean of 5.12 kg ha^{-1} yr^{-1} of NO_3-N) for an extended period of time (past two decades) (Adams et al., 1993). With inputs of nitrate (5.05 kg ha^{-1} yr^{-1}) equal to outputs of nitrate (5.12 kg ha^{-1} yr^{-1}), watershed 4 is exhibiting symptoms of nitrogen saturation. The nitrate concentrations on watershed 4 now show little seasonal variation, another symptom of nitrogen saturation

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(Peterjohn et al., 1996). Fernow also contains two other control catchments: watersheds 10 and 13. Watershed 13 (3.98 kg ha^{-1} yr^{-1}) and watershed 10 (1.22 kg ha^{-1} yr^{-1}) export lesser amounts of nitrate than watershed 4 (P. Edwards-written comm.). Both watersheds are in close proximity to watershed 4, and it can be assumed that they receive similar amounts of atmospheric deposition. All three of the control watersheds contain deciduous vegetation with stand ages between 60 and 90 years old.

The primary objective of the study was to examine the spatial variability of stream nitrate concentrations in an area that contains a nitrogen-saturated watershed (Fernow 4). Assessing the local variability in stream nitrate concentrations may help us understand the great regional variability that exists in stream nitrate from forested watersheds. A secondary objective of the study was to determine whether any longitudinal patterns in nitrate concentrations existed within stream reaches on small headwater catchments from the same area. This is important in determining where grab samples should be taken to obtain representative nitrate concentrations across watersheds. Any longitudinal patterns in stream nitrate concentrations may indicate that in-stream cycling of nitrogen is occurring within the stream reaches.

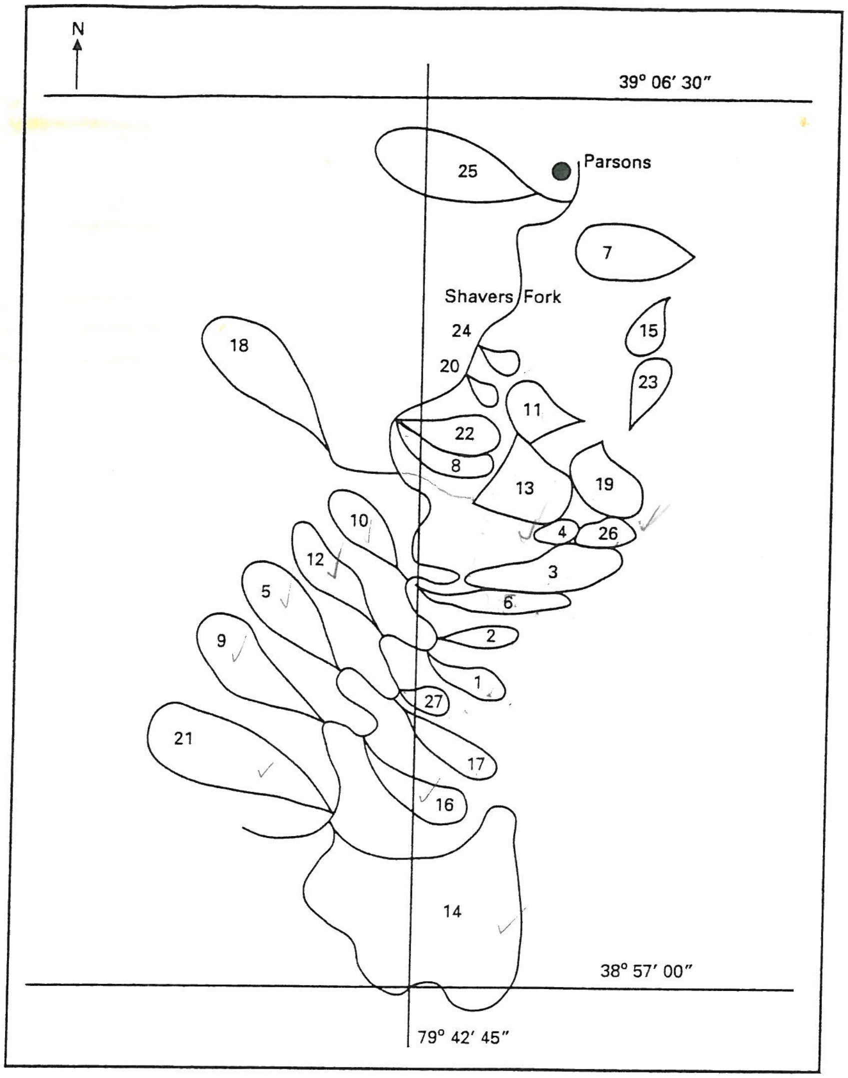
METHODS

Study watersheds were located within close proximity (within 10 km) to the Fernow Experimental Forest in order to keep environmental and geological conditions as uniform as possible (Figure 1). The watersheds selected for the study were all 100% forested and contained mature or nearly mature stands. Watersheds were located on the west and east side of Shavers Fork river (Figure 1).

A stream water grab sample was taken on June 17, 1997 between 9:00 a.m and 6:00 p.m. near the mouth of each watershed during baseflow conditions and immediately put on ice for transport to the Water Analysis Laboratory at the Environmental Resources Research Institute, Penn State. Samples were analyzed for dissolved nitrate and ammonium using the cadmium reduction and the automated phenate method, respectively (American Public Health Association, 1995). Stream pH and specific electrical conductance were also taken at each watershed using calibrated, portable meters (pHTestr 3 and TDSTestr, both by Oakton Inc.).

The 27 watersheds chosen for sampling were delineated on topographic maps (Parsons, Bowden, Elkins, and Montrose, WV 7.5 minute quadrangles) and their bedrock geology types were determined with the use of quadrangle geology maps (Reger, 1923; Reger, 1931). The geomorphic parameters, relief ratio and average basin slope were calculated for each watershed using topographic maps. 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.

Streams with the four highest and four lowest nitrate concentrations from the first round of sampling were chosen for the longitudinal study. The streams at baseflow were sampled at a low, mid, and high point along the length of the stream on July 30, 1997 during daylight hours. The high point was located at the extreme headwaters of the watersheds just below where the stream emerged on the day of sampling, and the low point was located near the mouth of the watershed. Grab samples were again taken for nitrate and ammonium analysis, and pH and specific electrical conductance were measured in the field.



Watershed

1. *Edwards Run
2. *DeWalle Run
3. Canoe Run
4. Sugarcamp Run
5. Flatbush Run
6. Rock Camp Run
7. John B. Hollow
8. *Williard Run
9. Boar Run
10. Laurel Run I
11. Fernow 4
12. Nail Run
13. Stonelick Run
14. Little Black Fork
15. Fernow 13
16. Wamsley Run
17. Two Lick Run
18. Panther Fork
19. Elklick Run
20. *Sharpe Run
21. Clifton Run
22. *McGuire Run
23. Fernow 10
24. Porterwood Run
25. Sugarcamp Run II
26. Elklick Run II
27. *Swistock Run

*Previously unnamed streams.

Figure 1. Locations of the 27 study watersheds in northcentral West Virginia (p. 37, West Virginia Atlas and Gazetteer, DeLorme, 1997).

RESULTS AND DISCUSSION

The 27 forested watersheds exhibited a wide distribution of NO_3-N concentrations (0.178 to 1.085 mg L^{-1}) at a local scale (Table 1). The range of NO_3-N concentrations approaches the range of NO_3-N export (0.041 to 5.15 $kg^{-1}ha^{-1}yr^{-1}$) that DeWalle and Pionke (1996) observed at a regional scale in their review of forested watersheds in the Chesapeake Bay region. Fernow 4 (0.629 mg L^{-1} NO_3-N) was in the middle of the distribution of nitrate concentrations. If Fernow 4 is considered to be the best example of a nitrogen-saturated watershed in the northeast United States, nitrogen saturation could be a widespread phenomenon in the local area and perhaps the mid-Appalachian region. (The authors realize the potential shortcomings of using nitrate concentrations as a surrogate for nitrate export when inferring nitrogen saturation status, but it was not in the scope of the study to measure stream flow on the 27 watersheds.)

Ammonium concentrations were near or below the detection limit for all of the study watersheds. Generally, dissolved ammonium is not a significant component of nitrogen export in forested streams (DeWalle and Pionke, 1996). Most of the dissolved ammonium in soil solution is either converted to nitrate by nitrifying bacteria, taken up by vegetation or bacteria, or physically bound to the cation exchange sites in the soil.

Stream nitrate concentrations were positively correlated with stream specific electrical conductance (SEC) ($r=0.571$, $p<0.001$). Stream SEC from undisturbed watersheds (no past mining activity) in this region is normally related to soil fertility, with more fertile forested watersheds having greater stream SEC. Therefore, greater stream nitrate concentrations may be linked to greater soil fertility. This could be due to greater microbial nitrification rates in watersheds with better soil fertility. Nitrate concentrations also exhibited a positive correlation with stream pH ($r=0.380$, $p<0.05$). To the extent that stream pH is indicative of soil pH, this result is supported by the finding that at lower soil pH, bacterial nitrification is depressed (Alexander, 1977; Paul and Clark, 1996).

It is difficult to determine what causes the significant localized variation in nitrate concentrations among the forested watersheds. A variety of factors could be coupled to cause this variation, including soil nitrogen cycling rates, which in turn can be affected by soil fertility and acidity. The underlying geology of the watersheds determines the soil chemical characteristics and thus can affect the internal nitrogen cycling. All of the watersheds contain some non-acidic bedrock (Catskill, Chemung, Pocono, Mauch Chunk, or Greenbrier) (Table 2), which does not help explain the observed differences in stream nitrate concentrations. Of the non-acidic bedrock types, Greenbrier limestone normally produces the most fertile and least acidic soils. The three watersheds with the highest nitrate concentrations (Edwards Run, DeWalle Run, and Canoe Run) all contained Greenbrier limestone, but watersheds with mid and low nitrate concentrations (Little Black Fork, Wamsley Run, Two Lick Run, Elklick Run II) also contained the Greenbrier formation.

Table 1. Water chemistry for the 27 study watersheds.

Watershed	*NO_3-N (mg L^{-1})*	*NH_4-N (mg L^{-1})*	*pH*	*Specific Electrical Conductance µS/cm*
Edwards Run	1.085	<0.005	7.88	110
DeWalle Run	1.033	0.075	8.04	110
Canoe Run	0.821	0.044	7.69	80
Sugarcamp Run	0.791	0.033	6.83	30
Flatbush Run	0.777	0.028	6.78	20
Rock Camp Run	0.722	0.060	7.86	70
John B. Hollow	0.716	0.027	6.71	20
Williard Run	0.694	0.035	6.61	30
Boar Run	0.680	0.027	7.08	30
Laurel Run I	0.643	<0.005	6.96	30
Fernow 4	0.629	<0.005	6.34	10
Nail Run	0.629	0.031	7.12	20
Stonelick Run	0.616	0.032	6.96	20
Little Black Fork	0.576	<0.005	7.68	50
Fernow 13	0.532	0.032	6.60	20
Wamsley Run	0.525	0.029	7.51	60
Two Lick Run	0.514	0.032	7.70	70
Panther Fork	0.446	0.027	7.12	30
Elklick Run	0.444	<0.005	7.44	50
Sharpe Run	0.436	0.052	6.92	20
Clifton Run	0.369	0.046	7.22	30
McGuire Run	0.339	<0.005	6.71	30
Fernow 10	0.294	<0.005	6.24	20
Porterwood Run	0.255	0.030	7.24	30
Sugarcamp Run II	0.225	0.030	7.19	30
Elklick Run II	0.187	<0.005	7.42	40
Swistock Run	0.178	0.031	6.26	10

Some of the watersheds contain Pottsville and Allegheny bedrock, which are considered to be acidic bedrock types. Those watersheds containing Pottsville and Allegheny (Elklick Run, Elklick Run II, Rock Run, DeWalle Run, Edwards Run, Two Lick Run, Wamsley Run, Little Black Fork) exhibited the same range of nitrate concentrations as the entire 27 watersheds. Most of the watersheds containing Pottsville and Allegheny bedrock had higher nitrate concentrations, which would be opposite of what is expected. One would expect low nitrate concentrations from acidic watersheds because high soil acidity has been shown to depress microbial nitrification. None of the watersheds contained more than 20-30% Pottsville/Allegheny, so acidic bedrock effects could have been masked by the predominant non-acidic bedrock geology.

Nitrate concentrations did not exhibit any statistically significant ($\alpha=0.05$) relationships with the geomorphic parameters of average basin slope ($r=0.340$, $p<0.081$) and basin relief ratio ($r=-0.290$, $p<0.142$). However, the relationship between nitrate and average basin slope is significant enough to warrant analysis. 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.

Nitrate leaching to streams can also be affected by stand age and past land disturbances (farming, fire). Younger stands usually have more vigorous growth and assimilate greater quantities of nutrients into their woody biomass than older stands. Stand ages on each watershed were not measured, but from field observations the 27 stands could be assumed to be in the range of 60 to 100 years old. Therefore, there were no striking differences in stand age among the study watersheds. Past land disturbances such as farming and fire can also affect nitrate leaching to streams by affecting soil nitrogen pools. Severe fire can volatilize nitrogen in the organic layer and upper mineral horizons, depleting soil nitrogen pools (Raison, 1979). 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 could still be in an aggrading phase, which would limit nitrate leaching to streams. Past land disturbances were not assessed in this study but could play a role in causing the observed variability in nitrate concentrations from the study watersheds, which is a part of on-going research.

Table 2. Geology and geomorphic parameters for the 27 study watersheds.

Watershed	*Basin Slope (degrees)*	*Relief Ratio (km/km)*	*Geology Types (listed from low to high elevation in watershed)*
Edwards Run	22.89	0.238	<5% Chemung, 25% Catskill, 15% Pocono, 15% Greenbrier, 25% Mauch Chunk, 15% Pottsville
DeWalle Run	27.18	0.275	<5% Chemung, 25% Catskill, 15% Pocono, 15% Greenbrier, 25% Mauch Chunk, 15% Pottsville
Canoe Run	24.08	0.205	20% Chemung, 25% Catskill, 10% Pocono, 15% Greenbrier, 20-30% Mauch Chunk
Sugarcamp Run	19.07	0.075	100% Chemung
Flatbush Run	20.89	0.219	100% Chemung
Rock Run	26.43	0.289	<5% Chemung, 25% Catskill, 15% Pocono, 15% Greenbrier, 25% Mauch Chunk, <10%Pottsville
John B. Hollow	21.79	0.168	100% Catskill
Williard Run	35.64	0.362	80-90% Chemung, <10% Catskill
Boar Run	18.83	0.147	100% Chemung
Laurel Run	15.20	0.129	100% Chemung
Fernow 4	12.50	0.153	100% Catskill
Nail Run	17.76	0.103	100% Chemung
Stonelick Run	17.50	0.161	40% Catskill, 60% Chemung
Little Black Fork	20.76	0.106	30% Catskill, 10% Pocono, 10% Greenbrier, 20% Mauch Chunk, 20-30% Pottsville
Fernow 13	17.99	0.216	100% Catskill
Wamsley Run	18.48	0.288	>5% Chemung, 15% Catskill, 15% Pocono, 15% Greenbrier, 15% Mauch Chunk, 20-30% Pottsville
Two Lick Run	17.37	0.215	10% Chemung, 15% Catskill, 15% Pocono, 15% Greenbrier, 30% Mauch Chunk, 15%-20% Pottsville
Panther Fork	22.35	0.105	100% Chemung
Elklick Run	16.24	0.210	40%-50% Catskill & Pocono, Mauch Chunk, 20% Pottsville/Allegheny
Sharpe Run	24.86	0.533	95% Catskill, <5% Chemung (lower slopes)
Clifton Run	20.48	0.052	95% Chemung, 5% alluvium (in center valley)
McGuire Run	25.28	0.371	80-90% Chemung, 10% Catskill
Fernow 10	16.38	0.180	100% Catskill
Porterwood Run	28.05	0.736	95% Catskill, 5% Chemung (lower slopes)
Sugarcamp Run II	17.79	0.270	100% Chemung
Elklick Run II	15.90	0.457	20% Catskill, 50%-60% Pocono, Greenbrier, Mauch Chunk, 20-30% Pottsville/Allegheny
Swistock Run	9.69	0.154	50% Chemung, 50% Catskill

(Reger 1923, 1931)

The longitudinal nitrate survey on 8 watersheds was conducted after the 27-watershed survey. In five of the eight watersheds sampled, the low elevation site (mouth) had higher nitrate concentrations than the high elevation site (source) (Figure 2). In other words, nitrate was sequentially added as the stream flowed through the catchment. This could be caused by differences in bedrock and subsequent differences in soil fertility between the upper and lower sections of the watersheds. Expected differences in bedrock acidity and fertility between the upper and lower sections are evident in only two (Edwards and DeWalle Runs) of the five watersheds that have an increasing nitrate trend. These watersheds contain acidic Pottsville/Allegheny bedrock in the upper sections and non-acidic bedrock in the lower sections.

In streams with lower nitrate concentrations at mouth than source, photoautotrophic uptake of nitrate could be occurring within the stream channel or denitrification could be occurring within the hyporheic zone. Burns (1998) suggests that these processes were both important in explaining the net loss of nitrate from the headwaters toward the mouth of the Neversink River. Lower nitrate concentrations in the downstream direction could also be caused by dilution of the stream water nitrate by groundwater and tributary inputs with lower nitrate concentrations than the main stream. The lack of a consistent longitudinal pattern in stream nitrate concentrations suggests that more watersheds should be surveyed to determine an appropriate sampling location. Until a consistent longitudinal pattern is discovered, sampling could occur at any uniform point across watersheds.

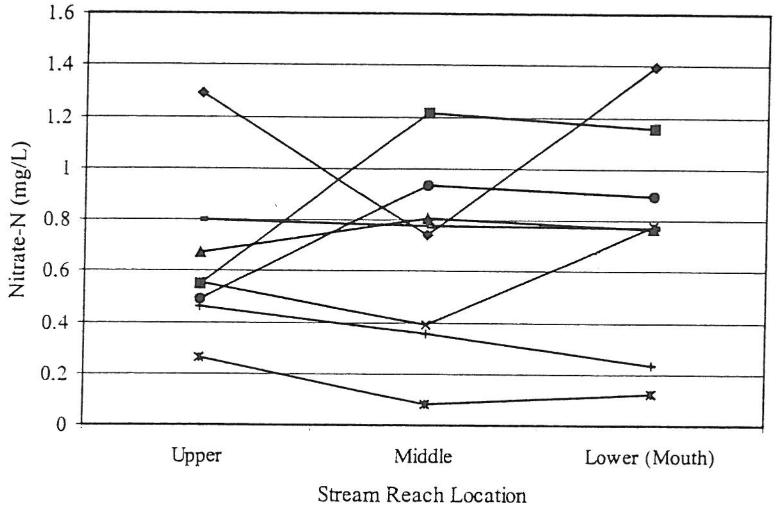


Figure 2. Nitrate variability along eight stream reaches.

CONCLUSIONS

Fernow watershed 4 was found to be representative of the local forested watersheds in terms of stream nitrate concentrations. It was just above the median stream nitrate concentration for 27 watersheds sampled. Since Fernow 4 is often cited as the best example of a nitrogen saturated watershed, this finding has important implications in terms of the amount of nitrogen saturation that is present in the local area and throughout the mid-Appalachians. The observed local variability in stream nitrate concentrations, where geologic and environmental conditions were relatively constant, helps us to understand why there is significant regional variability in nitrate export from forested watersheds. Stream nitrate concentrations were positively correlated with stream SEC and pH, suggesting that controls (soil fertility and acidity) on soil microbial activity may be important in explaining the observed variability in stream nitrate. There were no consistent patterns in the longitudinal survey of stream nitrate concentrations on eight reaches, which suggests that any uniform sampling location across watersheds is appropriate until a more consistent longitudinal pattern is established.

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