Recovery of Nitrogen Pools and Processes in Degraded Riparian Zones in the Southern Appalachians

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Establishment of riparian buffers is an effective method for reducing nutrient input to streams. However, the underlying biogeochemical processes are not fully understood. The objective of this 4-yr study was to examine the effects of riparian zone restoration on soil N cycling mechanisms in a mountain pasture previously degraded by cattle. Soil inorganic N pools, fluxes, and transformation mechanisms were compared across the following experimental treatments: (i) a restored area with vegetation regrowth; (ii) a degraded riparian area with simulated effects of continued grazing by compaction, vegetation removal, and nutrient addition (+N); and (iii) a degraded riparian area with simulated compaction and vegetation removal only (-N). Soil solution NO$_3^-$ concentrations and fluxes of inorganic N in overland flow were >90% lower in the restored treatment relative to the degraded (+N) treatment. Soil solution NO$_3^-$ concentrations decreased more rapidly in the restored treatment relative to the degraded (-N) following cattle (*Bos taurus*) exclusion. Mineralization and nitrification rates in the restored treatment were similar to the degraded (-N) treatment and, on average, 75% lower than in the degraded (+N) treatment. Nitrogen trace gas fluxes indicated that restoration increased the relative importance of denitrification, relative to nitrification, as a pathway by which N is diverted from the receiving stream to the atmosphere. Changes in soil nutrient cycling mechanisms following restoration of the degraded riparian zone were primarily driven by cessation of N inputs. The recovery rate, however, was influenced by the rate of vegetation regrowth.

Nutrients from nonpoint sources have been identified as major contributors to water quality degradation in the United States (USEPA, 2007). Specifically, agricultural sources of N, including synthetic fertilizer and animal manure, are of primary concern. Chronic loading of excess N to aquatic ecosystems may lead to eutrophication and its associated impacts including loss of biodiversity, oxygen depletion, toxic algal blooms, and fish kills (Vitousek et al., 1997). Riparian buffers have been identified as an effective method for reducing terrestrial N input to streams (NRCS, 2003). In a recent review, Mayer et al. (2007) reported a mean N removal efficiency, surface and subsurface combined, of 67.5% for the 88 riparian zones studied. Nitrogen removal and transformation processes include trace gas production and emission, plant uptake, soil storage, and microbial immobilization (Lowrance et al., 1997; Walker et al., 2002; Mayer et al., 2007). While the effectiveness of riparian buffers as a water quality management tool is well established, the underlying biogeochemical mechanisms are not fully understood.

Net N budgets in undisturbed forested watersheds in western North Carolina indicate that efficient N cycling processes result in very little N loss to streamwater, typically <0.10 kg N (NO$_3^- +$ NH$_4^+$) ha$^{-1}$ yr$^{-1}$, relative to atmospheric inputs, which are on the order of 5.0 kg N (NO$_3^- +$ NH$_4^+$) ha$^{-1}$ yr$^{-1}$ (Swank and Vose, 1997; National Atmospheric Deposition Program, 2008; USEPA, 2008). However, streamwater N increases considerably when disturbances such as forest cutting (Swank, 1988), prescribed burning (Knoepp and Swank, 1993), species conversion (Swank and Vose, 1994), or herbivory disrupt the N cycle (Swank et al., 1981). These studies show that even subtle disturbances influence streamwater quality in southern Appalachia. Additional N inputs from agricultural sources are therefore likely to have major impacts on stream N concentrations and stream quality in general. One of the primary water quality stressors in western North Carolina is cattle grazing in riparian areas, which results in direct N input to streams, vegetation removal, soil compaction, reduced infiltration, and stream bank degradation (Bolstad and Swank, 1997). Hence, it is critical that we understand the effectiveness of riparian zone restoration for improving and preserving stream water quality in this region.
We examined soil N cycling pools and transformation mechanisms in a restored mountain pasture riparian zone previously impacted by cattle. We hypothesized that exclusion of cattle and vegetation regrowth would reverse soil compaction and that reductions in organic N inputs following cattle exclusion would influence inorganic N pools (soil solution and extractable N), fluxes (overland flow, trace gas emissions), and N transformation mechanisms (nitrification, mineralization, trace gas production), with a net effect of substantial increases in N retention in the restored riparian zone. The objectives were to: (i) quantify differences in N pools, fluxes, and transformation mechanisms in restored and degraded experimental treatments; (ii) assess the importance of simulated chemical versus physical effects of cattle grazing on treatment differences; and (iii) characterize the time scale of response following restoration.

Materials and Methods

Site Description

The study site is located west of Franklin, NC, in the Blue Ridge Mountains. Cartoogechaye Creek flows south to north across the site, which is moderately steep pastureland used for livestock grazing and hay production. Soils in the riparian area of this site are primarily Rosman series (coarse-loamy, mixed, superactive, mesic Fluventic Humic Dystrudepts), which are moderately rapidly permeable and well-drained loams with a clay content of 16% (Zegre, 2003). The study watershed is approximately 5 ha and ranges in elevation from 646 m at the top ridge in the pasture to a low point of 628 m at Cartoogechaye Creek. On average, air temperature in the study area ranges from 4°C during winter to 24°C during the summer and annual rainfall totals approximately 130 cm (USDA, 1996).

In June 2000, a 10-m wide riparian buffer was established along the creek by fencing to exclude cattle. After fencing, physical and chemical impacts of continued cattle activity within the riparian zone were simulated by experimentally controlled compaction, grazing, and nutrient additions. The experiment was laid out as a randomized complete block design with four replicates (plots) of the following treatments: (i) a restored riparian area with natural re-vegetation and no grazing; (ii) a degraded (+N) riparian zone with simulated compaction, vegetation removal, and nutrient addition; and (iii) a degraded (-N) riparian zone simulated with vegetation removal, and nutrient addition; and (iii) a degraded (-N) riparian zone with simulated compaction and vegetation removal, but without nutrient addition. Treatments were randomly assigned to 3 m (w) by 9 m (l) plots oriented lengthwise parallel to the stream. We used the degraded (-N) treatment to separate solely physical (i.e., soil compaction + vegetation removal) vs. chemical and physical (i.e., nutrient addition + compaction + vegetation removal) impacts of cattle activity. Treatments were initiated in July 2000 and measurements are presented for the period July 2000–December 2003.

Degraded treatments (+N,-N) were compacted with a 114 kg lawn roller [61 cm (w) by 46 cm in (diam.)] four times per month. Grazing was simulated by mowing plots to a height of approximately 2.5 cm four times per month during the growing season (March through November) with a lawn mower equipped with a grass catcher. Livestock nutrient addition was simulated by adding sterilized cow manure at a rate of 132 kg N ha⁻¹ yr⁻¹ and liquid urea at a rate of 266 kg N ha⁻¹ yr⁻¹. These rates of N addition are based on an observed stocking density of 15 to 30 animals within the adjacent 5 ha unfertilized pasture and N excretion rates (0.1–0.55 kg N cow⁻¹ d⁻¹) reported by Jarvis et al. (1989) and Bussink (1994). Manure and urea were applied uniformly over the entire plot once per month.

Nitrogen Pools

Nitrogen in the soil solution was sampled with porous cup lysimeters. Two pairs of tension lysimeters were randomly placed within each plot at 30 and 90 cm depths, which was approximately the bottom of the A and B horizons, respectively. Samples were collected weekly and volume weighted monthly composites were analyzed for NO₃⁻ and NH₄⁺. After sample collection, 0.3 bar of tension was applied to the lysimeter in preparation for sample collection during the following week. Concentrations of NO₃⁻ and NO₄⁻ in lysimeter samples were determined by ion chromatography and NH₄⁺ was determined by colorimetry as described below for KCl extractions.

Soil extractable NO₃⁻ and NH₄⁺ were determined by quarterly core sampling (10 cm depth) at two random locations within each plot. Soils were sieved (<6 mm) and a 5-g subsample was added to 20 mL of 2 mol L⁻¹ KCl. Following centrifugation, concentrations of NH₄⁺ and NO₃⁻ in the KCl supernatant were determined on an autoanalyzer using alkaline phenol (USEPA, 1983a) and cadmium reduction (USEPA, 1983b) techniques, respectively. Percent soil moisture was determined on a 10- to 20-g subsample dried overnight at 105°C. Air-dried soil samples sieved to <2 mm were analyzed for total C and N.

Nitrogen Transformation Processes

Monthly net N mineralization (NH₄⁺ plus NO₃⁻ production) and net nitrification (NO₃⁻ production) were determined with the closed core in situ incubation method (Adams and Attiwill, 1986; Knoepp and Swank, 1995). Two pairs of intact soil cores [PVC, 4.3 cm (d) by 15 cm (l)] were collected from random locations along transects (0.5 m from the 9 m plot axis) in each plot at a depth of 10 cm, 25 cm apart. One core (t₀) from each pair was removed, returned to laboratory, and stored at 4°C until processed (within 24 h). Soil from each core was sieved to <6 mm, and NO₃⁻ and NH₄⁺ concentrations were determined on a 5-g subsample as described above. After 28 d, the remaining cores were collected (t₁) and processed as described above, and new sets of paired cores were placed in the field. Net mineralization and nitrification were determined as the difference between t₁ and t₀ NO₃⁻ and NH₄⁺ concentrations. Time zero soil cores were used to determine soil bulk density.

Nitrogen Fluxes

Overland Flow

Surface fluxes of N in overland flow were determined by analyzing precipitation runoff for NO₃⁻, NO₂⁻, and NH₄⁺. Samples were collected and analyzed for total volume and in-
Fluxes of \( \text{NH}_3 \), \( \text{NO} \), and \( \text{N}_2\text{O} \) were measured during eight sampling campaigns, typically lasting from 7 to 10 d, between October 2000 and December 2003. During each campaign, fluxes were measured in three plots within each of the restored, degraded (-N), and degraded (+N) treatments. Within each plot, fluxes were measured in two randomly chosen locations, at least 1 m from the nearest lysimeter. At the end of each experiment, three soil cores (10 cm depth) were taken from each flux ring, composited, and analyzed for total C, total N, and extractable \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) according to the procedures described above. Soil pH was determined on a 5-g subsample of fresh soil added to 10 mL of 0.01 mol L\(^{-1}\) CaCl\(_2\). Additional information concerning the flux measurement method can be found in Walker et al. (2002).

### Statistical Analysis

Treatment differences were tested using standard multiple comparison procedures (Proc GLM; SAS Institute, 2003). When the assumptions of normality and variance homogeneity were violated, the nonparametric Dunn’s test was used, as implemented by Juneau (2007) using SAS. Time series analysis of lysimeter \( \text{NO}_3^- \) chemistry was also performed to examine temporal trends, using a combination of least squares and locally weighted regression procedures. Log-transformed \( \text{NO}_3^- \) values were first modeled using linear regression with maximum likelihood estimation (Proc Autoreg; SAS Institute, 2003). An autoregressive error structure was used to correct for serial correlation of residuals. Residuals from the parametric regression model were analyzed for temporal trend using locally weighted regression (Proc LOESS; SAS Institute, 2003, Cleveland, 1979). The LOESS smoother was selected by an automatic fitting procedure in which the generalized cross-validation (GCV) mean square error (MSE) is minimized (SAS Institute, 2003). Relationships between N trace gas fluxes and soil parameters were examined using linear regression (Proc Reg; SAS Institute, 2003).

### Results and Discussion

#### Nitrogen Pools

Lysimeter \( \text{NO}_3^- \) concentrations were much higher in the degraded (+N) plots than the degraded (-N) and restored plots at both depths (30 and 90 cm) during all years (Fig. 1). On average, concentrations in the restored treatment were 99 and 97% lower than concentrations in the degraded (+N) treatment at 30 and 90 cm depths, respectively. At the 30 cm depth, concentrations in the degraded (-N) plots were generally higher than the restored plots, likely reflecting greater fine root biomass and plant uptake in the restored plot. We did not measure vegetation biomass in this study; however, in other studies in comparably degraded riparian zones, vegetation biomass is typically fourfold greater (i.e., 400 vs. 100 g m\(^{-2}\)) for restored vs. degraded, respectively) within 2 yr of post-cattle exclusion (Vose et al., 2005). Soil solution \( \text{NO}_3^- \) concentrations in undisturbed forested riparian zones in western North Carolina are typically of the order of 0.01 mg L\(^{-1}\) (Yeakley et al., 2003); comparable to soil solution \( \text{NO}_3^- \) concentrations in restored plots at 30 cm depth (Fig. 1).
A similar pattern of much higher \( \text{NH}_4^+ \) concentrations in the degraded (+N) treatment was also observed. Concentrations of \( \text{NH}_4^+ \) in the restored treatment were, on average, 99 and 88\% lower than concentrations in the degraded (+N) treatment at 30 and 90 cm depths, respectively. Ammonium concentrations were generally much lower than \( \text{NO}_3^- \), which likely reflects a combination of rapid depletion of the soil solution \( \text{NH}_4^+ \) pool and lower mobility of \( \text{NH}_4^+ \) relative to \( \text{NO}_3^- \).

Soil solution \( \text{NO}_3^- \) concentrations at 30 cm in the degraded (-N) plots showed an apparent decreasing trend over time (Fig. 1). One objective of this analysis was to determine the rate at which N pools equilibrated following treatment initiation. To assess trends, we first examined temporal variability in concentrations using the linear regression approach described above. The majority of variability in log-transformed monthly \( \text{NO}_3^- \) concentrations at 30 cm was explained by seasonality and first order autocorrelation, yielding a regression model of the form:

\[
Y_i = a_0 + \beta_1 Y_{i-1} + \beta_2 \cos\left(\frac{2\pi i}{12}\right) + \beta_3 \sin\left(\frac{2\pi i}{12}\right) + e_i
\]

where \( N \) represents the number of months in the time series, \( Y_i \) is natural log-transformed \( \text{NO}_3^- \) concentration for the \( i \)th month, \( a_0 \) is the intercept, \( Y_{i-1} \) represents the first order autoregressive term, with corresponding regression coefficient \( \beta_1 \), and \( e_i \) is the error term (residual). The sine and cosine terms in model (3) represent the seasonal component of the variation in \( \text{NO}_3^- \) concentration.

A seasonal pattern of maximum concentrations in the late fall and early winter and minimum concentrations in the late spring and early summer explained the majority of the temporal variability in all treatments. Though initially included in the regression model, monthly precipitation amount did not influence lysimeter \( \text{NO}_3^- \) concentrations. The observed seasonality of \( \text{NO}_3^- \) concentrations likely reflects a pattern of increased root uptake following emergence of new vegetation in the spring and lower rates of uptake following senescence in the late fall.

Residuals from the parametric regression model (3) were examined for temporal trends using nonparametric locally weighted (LOESS) regression (Fig. 2). Residuals in the degraded (+N) treatment showed an increasing trend over the first 15 mo after treatment initiation before leveling off. The length of this equilibration period is likely related to the rate and frequency of N application. A decreasing trend was observed in the degraded (-N) treatment residuals over the same period, consistent with depletion of the \( \text{NO}_3^- \) pool and reduced nitrification rates following cattle exclusion. A slight decreasing trend was observed in the restored plot residuals over the same period. From this analysis and the average results shown in Fig. 1, it appears that chemical conditions in the restored area responded rapidly following cessation of nutrient input. Significant differences in the 30 and 90 cm \( \text{NO}_3^- \) concentrations between the restored and degraded (-N) plots were observed during the first 6 mo following treatment initiation. Depletion of \( \text{NO}_3^- \) in the degraded (-N) treatment proceeded more slowly, likely due to more efficient uptake by vegetation in the restored plot as a result of greater fine root biomass.

The more rapid decrease in lysimeter \( \text{NO}_3^- \) in the restored treatment relative to the degraded (-N) treatment suggests that the rate of recovery following cattle exclusion is influenced by the rate of reversal of the physical effects of grazing, which include vegetation removal and compaction and their interactions. On average, bulk density was lowest in the restored treatments (Table 1) due to a slight increase in bulk density over time in the degraded plots, which were similar to the adjacent grazed pasture (1.2 ± 0.15 g cm\(^{-3}\); Zegre, 2003) at the end of the study. Bulk density
in the restored treatment remained relatively constant throughout the study (Table 1). This lack of response to restoration is consistent with other studies (see Greenwood and McKenzie [2001] and Drewry [2006]), in which the natural recovery of soil physical characteristics following cessation of cattle grazing proceeded over the course of several years. It is therefore more likely that the more rapid decrease in lysimeter NO$_3^-$ in the restored treatment relative to the degraded (-N) treatment is the result of vegetation regrowth, rather than a compaction effect. Furthermore, it appears that soil compaction had a more limited capacity for improvement following restoration than soil chemical conditions.

While similar temporal patterns were observed for lysimeter NO$_3^-$ and NH$_4^+$ in the degraded (+N) plots, trends in NH$_4^+$ were not apparent in the restored and degraded (-N) treatments. Given that the majority of applied N is in the reduced form, much lower concentrations of soil solution NH$_4^+$ relative to NO$_3^-$ in the degraded (+N) plots clearly indicates that the soil solution NH$_4^+$ pool is depleted rapidly, most likely through a combination of nitrification and root uptake. Thus, NH$_4^+$ concentrations may be expected to decrease rapidly from an already low level following exclusion of cattle from the riparian area, which is consistent with the absence of detectable trends in the restored and degraded (-N) plots (Fig. 1).

Extractable NO$_3^-$ from the 0 to 10 cm depth also showed higher concentrations in the N amended plots during all years (Table 1). Concentrations in the restored and degraded (-N) plots were not significantly different ($P > 0.1$) during any period. The NH$_4^+$ concentrations were significantly higher in the degraded (+N) plot during the first year but concentrations were similar across treatments throughout the rest of the study (Table 1). This pattern of higher concentrations of extractable NO$_3^-$ relative to NH$_4^+$ and the similarity of NH$_4^+$ concentrations across treatments is consistent with rapid depletion of the soil NH$_4^+$ pool.

Nitrogen Transformation Processes and Fluxes

Mineralization and Nitrification Rates

Mineralization and nitrification rates were similar in the restored and degraded (-N) treatments throughout the course of the study (Table 1). Rates were much higher in the degraded (+N) treatments, with statistically significant differences from the other plots observed after the first year. Measurements taken at the site by Tian et al. (2004) in 2001 and 2002 showed significantly greater populations of denitrifiers, NH$_4^+$ oxidizers, and NO$_2^-$ oxidizers in the degraded (+N) plots relative to the restored and degraded (-N) plots. The higher mineralization and nitrification rates observed in the degraded (+N) plots are consistent with larger N pools and the treatment differences in microbial community structure observed by Tian et al. (2004). The similarity of net monthly mineralization and nitrification in the restored and degraded (-N) plots suggests that these processes were not significantly affected by the physical effects of vegetation removal and compaction. Rather, the much higher
rural landscapes, and is often caused by nutrient inputs from riparian zones, such as from agricultural activities and urban development. The effect of riparian zones on nutrient cycling is significant because they often act as filters for overland flow, reducing nutrient loss to adjacent water bodies. A study conducted by Lowrance et al. (1997) demonstrated that riparian zones can reduce overland flow nutrient and sediment loads to adjacent streams.

### Overland Flow

Numerous studies have demonstrated the effectiveness of riparian buffers for reducing overland flow nutrient and sediment inputs to adjacent streams (see Lowrance et al., 1997). Over the course of our study, the cumulative (total) volume of overland flow exiting the restored treatment was 3.0 and 7.0% less than the degraded (+N) treatment, compared to 36 samples from each of the degraded treatments. While the differences between the restored and degraded plots clearly demonstrate the effect of restoration, monthly differences in volume between the degraded treatments often exceeded 100%, illustrating the strong influence of microtopography on overland flow patterns. Median monthly composite samples were collected in the restored treatment, compared to 36 samples from each of the degraded treatments. The average monthly flux of N in overland flow exiting the restored treatment, calculated as the product of N concentration and volume, was only 4% of the flux from the degraded (+N) treatment, including months in which no runoff was collected from the restored treatment. Restoration significantly reduced the flux of N in overland flow to the adjacent stream, primarily due to reductions in volume rather than N concentrations.

### Nitrogen Trace Gas Emissions

Riparian zone restoration may alter soil N trace gas production and emission in several ways. Numerous studies have shown a positive correlation between soil NOx emissions and available soil N (see Davidson and Verchot (2000) and references therein). Reduced N input following cattle exclusion and associated changes to mineralization and nitrification rates, as well as increased plant uptake, should correspond to reduced inorganic N pools and N transformation rates and therefore lower N trace gas fluxes. Changes in microbial activity and community structure may alter patterns of nitrification and denitrification, and therefore the rates of NO and N2O production.

Before analysis, fluxes were averaged by plot level replicate (i.e., individual collar locations) and matched with corresponding soil chemistry samples, average soil temperature and average soil volumetric moisture. The final flux data set included 116 NO and NH3 observations and 86 N2O observations. Fluxes of all species were significantly higher in the degraded (+N) treatment, which contained the highest concentrations of extractable soil NH4+ and NO3− (Table 2). Emissions of N2O and NH3 were similar in the restored and degraded (-N) treatments, and much higher in the degraded (+N) treatment. This pattern of treatment differences is consistent with the observed pattern of highest mineralization and nitrification rates and largest soil inorganic N pools in the degraded (+N) treatment and similar rates and pools in the degraded (-N) and restored treatments (Tables 1 and 2). These results suggest that fluxes of N2O and NH3 were primarily driven by the availability of N for microbial processing and less influenced by vegetation removal or soil compaction.

Nitric oxide emissions were also highest in the degraded (+N) treatment. However, NO emissions from the restored treatment were significantly lower than in the degraded (-N) treatment, which may be related to compaction or vegetation regrowth. Assuming soil NO emissions are representative of net production rates, treatment differences are related to the balance between gross production and consumption. Consumptive processes may include denitrification, oxidation to NO2− or NO3−, and microbial assimilation, all of which can be expected to increase with residence time in the soil profile (Remde and Conrad, 1991; Firestone and Davidson, 1989; Rudolph et al., 1996). However, lower bulk density in the restored treatment (Table 2) should correspond to shorter residence times. Thus, lower NO fluxes likely resulted from lower

### Nitrogen Trace Gas Emissions

<table>
<thead>
<tr>
<th>Year</th>
<th>NOx−</th>
<th>NH4+</th>
<th>Mineralization</th>
<th>Nitrification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>6.7 (5.6)a</td>
<td>1.3 (0.9)b</td>
<td>1.1 (0.7)b</td>
<td>18.9 (21.5)a</td>
</tr>
<tr>
<td>2001</td>
<td>10.3 (13.1)a</td>
<td>0.6 (0.5)b</td>
<td>1.2 (1.2)b</td>
<td>5.8 (4.4)a</td>
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<tr>
<td>2002</td>
<td>15.6 (10.3)a</td>
<td>1.2 (1.2)b</td>
<td>2.7 (2.1)b</td>
<td>3.5 (3.1)a</td>
</tr>
<tr>
<td>2003</td>
<td>4.9 (3.0)a</td>
<td>2.0 (0.8)a</td>
<td>2.0 (0.8)a</td>
<td>3.5 (2.8)a</td>
</tr>
</tbody>
</table>

Table 1. Yearly summary of extractable soil NOx− and NH4+ concentrations, bulk density (sieved <6 mm), and mineralization and nitrification rates. Treatment means are compared for statistical significance within years. Values carrying the same letter are not significantly different (P > 0.1). Standard deviation is given parenthesis.
gross production rates. This is supported by a lower ratio of NO flux to soil NH$_4^+$ in the restored plot, which suggests that a smaller fraction of the N (i.e., NH$_4^+$) available for nitrification was emitted as NO. Treatment differences in the ratio of N$_2$O to soil NO$_3^-$ were not significantly different ($P > 0.1$).

Ammonia emissions were also highest in the fertilized plots, coincident with the highest treatment mean soil extractable NH$_4^+$ concentrations. The ratio of NH$_4^+$ flux to soil NH$_4^+$ was also significantly higher ($P < 0.1$) in the degraded (+N) treatment, suggesting that more of the available NH$_4^+$ was emitted relative to the restored and degraded (-N) treatments. This is consistent with the observed ratio of soil NH$_4^+$ to H$^+$ concentrations, which was highest in the degraded (+N) treatment. The higher mean pH (lower H$^+$ concentration) observed in the degraded (+N) treatment, caused by chronic urea fertilization, in combination with high NH$_4^+$ concentrations produces a larger soil NH$_3$ compensation point (Dawson, 1977; Nemitz et al., 2001) relative to the restored and degraded (-N) treatments. Thus, lower NH$_3$ emissions in the restored treatment are due to a combination of more acidic soil conditions and lower available NH$_4^+$.

To examine potential relationships between trace gas flux and treatment differences in microbial communities, we compared treatment mean fluxes to nitrifier (NH$_4^+$ and NO$_2^-$ oxidizers) and denitrifier populations measured by Tian et al. (2004) during 2001 and 2002 (Fig. 3). Nitric oxide emission, which is primarily a product of aerobic nitrification (Anderson and Levine, 1986), was positively correlated ($P < 0.001$) with the population of NH$_4^+$ oxidizers, (Fig. 3, Plot A). The ratio of NO to N$_2$O emissions also varied across treatments (Table 2). Assuming N$_2$O is primarily a product of anaerobic denitrification (Russow et al., 2000), the ratio of NO to N$_2$O emissions may be used to quantify the relative importance of nitrification and denitrification to soil NOx production (Skiba et al., 1997). As illustrated in Fig. 4, the NO/N$_2$O ratio is a strong function of soil volumetric water content. At higher water contents, reduced oxygen availability limits nitrification and promotes anaerobic denitrification, resulting in lower NO/N$_2$O ratios. Figure 4 also illustrates that treatment differences in the NO/N$_2$O ratio were more pronounced at lower water contents, which benefit nitrification. The pattern of larger treatment differences at low water contents was consistent with the observed positive correlation between the NO/N$_2$O ratio and the ratio of NH$_4^+$ oxidizers to denitrifiers (Fig. 3., Plot D). The average ratio of nitrite oxidizers

<table>
<thead>
<tr>
<th>Treatment</th>
<th>NH$_4^+$ (mg N kg soil$^{-1}$)</th>
<th>NO$_3^-$ (mg N kg soil$^{-1}$)</th>
<th>pH</th>
<th>NO flux (kg N m$^{-2}$ yr$^{-1}$)</th>
<th>N$_2$O flux (kg N m$^{-2}$ yr$^{-1}$)</th>
<th>NH$_3$ flux (kg N m$^{-2}$ yr$^{-1}$)</th>
<th>NO/NH$_4^+$</th>
<th>N$_2$O/NO$_3^-$</th>
<th>NH$_3$/NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Restored</td>
<td>2.5 (1.4)a</td>
<td>1.7 (1.4)a</td>
<td>5.05 (0.16)a</td>
<td>5.05 (0.16)a</td>
<td>5.05 (0.16)a</td>
<td>0.3 (0.2)a</td>
<td>0.2 (0.2)a</td>
<td>0.2 (0.2)a</td>
<td>0.5 (0.8)a</td>
</tr>
<tr>
<td>Degraded (-N)</td>
<td>2.0 (1.6)a</td>
<td>1.8 (3.8)a</td>
<td>4.99 (0.17)a</td>
<td>9.0 (0.9)a</td>
<td>9.0 (1.4)a</td>
<td>0.7 (0.8)b</td>
<td>0.5 (0.5)b</td>
<td>0.5 (0.5)b</td>
<td>0.6 (1.0)a</td>
</tr>
<tr>
<td>Degraded (+N)</td>
<td>6.0 (9.8)b</td>
<td>10.4 (18.2)b</td>
<td>5.25 (0.28)b</td>
<td>4.3 (6.6)b</td>
<td>10.4 (25.5)b</td>
<td>5.1 (11.2)c</td>
<td>1.5 (2.4)c</td>
<td>1.0 (1.0)a</td>
<td>1.9 (4.3)b</td>
</tr>
</tbody>
</table>

Table 2. Treatment summary of soil extractable NH$_4^+$ and NO$_3^-$ (mg N kg soil$^{-1}$), soil pH, and trace gas fluxes (kg N ha$^{-1}$ yr$^{-1}$). Values represent means over the entire study with corresponding standard deviation in parenthesis. Means carrying the same letter across treatments are not significantly different ($P > 0.1$). Soil chemistry samples correspond to trace gas flux measurements and were taken independently of the results in Table 1.

Fig. 3. Comparison of treatment mean trace gas fluxes and microbial [log (X + 1)] populations: (A) N$_2$O flux vs. denitrifier population, (B) NO flux vs. NO$_2^-$ oxidizer population, (C) NO flux vs. NH$_4^+$ oxidizer population, (D) NO/N$_2$O flux ratio vs. nitrifier/denitrifier population ratio. Microbial populations were sampled by Tian et al. (2004). Treatments are identified as R (restored), –N (degraded), and +N (degraded + nutrients).
to denitrifiers did not vary across treatments (Tian et al., 2004) (Fig. 3, Plot D). Cumulatively, our results indicate that restoration significantly altered the relative importance of nitrification versus denitrification as pathways for N trace gas production. Cattle exclusion and revegetation yielded larger reductions in populations of nitrifying bacteria than denitrifiers, with a subsequent greater reduction in the production of NO relative to N$_2$O. Thus, restoration reduced the relative importance of nitrification as a mechanism of soil N trace gas production.

The simulated grazing treatments were implemented to minimize spatial and temporal variation in physical and chemical impacts typical of mid-size cattle operations in the southern Appalachians and thus, maximize our ability to detect potential changes in N cycling pools and processes. We acknowledge that the simulated grazing (compaction, vegetation removal, and nutrient addition) does not replicate the spatial heterogeneity of N excretion or compaction from cattle. The N treatments in this study were based on annual amounts that would realistically be distributed across the grazed area in patches, thus our approach can be viewed as spreading the equivalent N over a larger area. Nitrogen pools beneath cattle inputs can be much larger than in our N amended treatment and higher N mineralization and nitrification rates, as well as N trace gas emissions, would therefore be expected. Furthermore, the temporal variability of N pools and processes observed in the N amended treatments would be confounded by variability in stocking density (seasonal and annual) and diet (seasonal). In general, for a given N application, we likely would have observed greater rates of N cycling recovery on restored plots compared to actual N inputs. Hence, our results are likely conservative estimates of soil N cycling responses following restoration.

Future work should examine changes in the most responsive parameters (e.g., soil solution NO$_3^-$ concentrations, mineralization, nitrification, and nitrifying bacteria) in realistic N “hot spots” to obtain improved estimates of N cycling pools and processes following restoration. Such studies should also examine subsurface flow and N processing at deeper soil horizons, which may be more important under actual grazing conditions.

Conclusions

By comparing restored riparian areas, previously degraded by cattle, to areas in which continued chemical and physical effects of grazing were simulated, we conclude that the restored riparian area was highly efficient at reducing above and belowground fluxes of inorganic N to the adjacent stream. While overall treatment differences in N pools and N transformation processes were primarily driven by chemical effects (i.e., nutrient inputs), changes in N pools over time following cattle exclusion suggested that the rate of recovery was influenced to some extent by the rate and extent of vegetation regrowth. The physical characteristics of the riparian soil had a more limited capacity for improvement, relative to chemical characteristics, following restoration. With respect to N transformation processes, restoration reduced mineralization and nitrification rates as well as N trace gas emissions. Nitric oxide emissions were influenced more strongly by restoration than N$_2$O, consistent with a more significant reduction in NH$_4^+$ oxidizing bacteria relative to denitrifiers. Subsequently, restoration increased the importance of denitrification, relative to nitrification, as a pathway by which N was diverted from the receiving stream to the atmosphere.

We acknowledge that the simulated grazing (compaction, vegetation removal, and nutrient addition) does not ideally replicate the spatial nature of N excretion from grazing cattle and compaction from animal hoofs. Therefore, the results of our study should be applied cautiously to actual cattle operations.

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References


Drewry, J.J. 2006. Natural recovery of soil physical properties from treading...
damage of pastoral soils in the New Zealand and Australia: A review.


Firestone, M.K., and E.A. Davidson. 1989. Microbiological basis of NO and
N₂O production and consumption in soil. p. 7–21. In M.O. Andreea and
D.S. Schimel (ed.) Exchange of trace gases between terrestrial ecosystems

Agric. 41:1231–1250.


management on nitrogen losses from grazed swards through ammonia
volatilization: The relationship to excratal N returns from cattle. J. Agric.

117–150. In A. Dmitrienko et al. (ed.) Pharmaceutical statistics using

NO and deposition of O₃ in a topical forest system. J. Geophys. Res.
93:1389–1395.

southern Appalachian pine hardwood stands: Nitrogen responses in soil,

assays in control and burned forested sites. Soil Sci. Soc. Am. J.
59:1750–1754.

Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P. M. Groffman,
J. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield,
riparian forest buffers systems in Chesapeake Bay watersheds. Environ.
Manage. 21:687–712.

36:1172–1180.

Firestone, M.K., and E.A. Davidson. 1989. Microbiological basis of NO and
N₂O production and consumption in soil. p. 7–21. In M.O. Andreea and
D.S. Schimel (ed.) Exchange of trace gases between terrestrial ecosystems

Agric. 41:1231–1250.


management on nitrogen losses from grazed swards through ammonia
volatilization: The relationship to excratal N returns from cattle. J. Agric.

117–150. In A. Dmitrienko et al. (ed.) Pharmaceutical statistics using

NO and deposition of O₃ in a topical forest system. J. Geophys. Res.
93:1389–1395.

southern Appalachian pine hardwood stands: Nitrogen responses in soil,

assays in control and burned forested sites. Soil Sci. Soc. Am. J.
59:1750–1754.

Lowrance, R., L.S. Altier, J.D. Newbold, R.R. Schnabel, P. M. Groffman,
J. Denver, D.L. Correll, J.W. Gilliam, J.L. Robinson, R.B. Brinsfield,
riparian forest buffers systems in Chesapeake Bay watersheds. Environ.
Manage. 21:687–712.

36:1172–1180.

State Water Survey, Champaign, IL.

Natural Resources Conservation Service. 2003. National handbook of
conservation practices. USDA, Washington, DC.

Nemitz, E., C. Milford, and M.A. Sutton. 2001. A two-layer canopy
compensation point model for describing bi-directional biosphere-


Rudolph, J., F. Rothfuss, and R. Conrad. 1996. Flux between soil and
atmosphere, vertical concentration profiles in soil, and turnover of
nitric oxide: I. Measurements on a model soil core. J. Atmos. Chem.

NO and N₂O in soils by the coupled processes of nitrification and
denitrification: Results of kinetic ¹⁵N tracer investigations. Chemosphere-


agricultural soils in temperate and tropical climates: Sources, controls

W.T. Swank and D.A. Crossley, Jr (ed.) Forest hydrology and ecology at

forested watersheds in the southeastern United States of America. Global

the effectiveness of riparian zone restoration in the southern Appalachians by assessing soil microbial populations. Appl.
Soil Ecol. 26:63–68.

USDAG. 1996. Soil survey of Macon County, North Carolina. USDA, Natural
Resources Conservation Service, Wadesboro, NC.

Determination of nitrogen as ammonia. Method 350.1. Environmental
Monitoring and Support Lab., Office of Research and Development,
USEPA, Cincinnati, OH.

Determination of nitrate/nitrate by automated cadmium reduction.
Method 353.2. Environ. Monitoring and Support Lab., Office of Res.
and Development, USEPA, Cincinnati, OH.

Reporting Cycle. EPA/841/R-07/001. Office of Water, Washington, DC.

Protection Agency, Washington, DC.

Vitousek, P.M., J. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, S.W. Schindler,

Restoration effects on N cycling pools and processes. p. 77–94. In J.A.
Stanturf and P. Madsen (ed.) Restoration of boreal and temperate forests.
CRC Press, Boca Raton, FL.

trace gas emissions from a riparian ecosystem in southern Appalachia.

Yeakley, J.A., D.C. Coleman, B.L. Haines, B.D. Kloeppel, J.L. Meyer, W.T.
dynamics following upland riparian vegetation disturbance. Ecosystems

of subsurface flow on nitrate and ammonium transport. Masters thesis.
Virginia Polytechnic Inst. and State Univ., Blacksburg, VA.