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.

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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 replications (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 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 NO_3^- and NH_4^+. After sample collection, 0.3 bar of tension was applied to the lysimeter in preparation for sample collection during the following week. Concentrations of NO_2^- and NO_3^- in lysimeter samples were determined by ion chromatography and NH_4^+ was determined by colorimetry as described below for KCl extractions.

Soil extractable NO_3^- and NH_4^+ 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 NH_4^+ and NO_3^- 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 (NH_4^+ plus NO_3^- production) and net nitrification (NO_3^- 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 (t_0) 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 NO_3^- and NH_4^+ concentrations were determined on a 5-g subsample as described above. After 28 d, the remaining cores were collected (t_1) 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 t_1 and t_0 NO_3^- and NH_4^+ 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 NO_2^-, NO_3^-, and NH_4^+. Samples were collected and analyzed for total volume and inorganic N concentrations after each runoff-producing rainfall. Collectors consisted of a Teflon container attached to a 10 cm (h) by 30 cm (w) stainless steel mouth buried to ground level at the lowest point of the outside edge of each plot adjacent to the stream (one collector per plot). Concentrations of NO_2^- and NO_3^- in monthly composite samples were determined by ion chromatography and NH_4^+ was determined by colorimetry.

Trace Gas Emissions

Ammonia (NH_3) and nitric oxide (NO) emissions from the soil surface were determined using a flow-through (Walker et al., 2002) chamber technique. Chambers consisted of a 18.5-L polytetrafluoroethylene lined, acrylic cylinder [32 cm (d) by 23 cm (h)], on a stainless steel collar driven into the soil approximately 25 cm. Soil collars were inserted at least 12 h before flux sampling. Chambers were flushed with dry zero grade air at a constant rate of 3.0 to 10.0 L min^{-1} and air was drawn from the chamber at 1 L min^{-1}; excess air was vented. The emission flux (J, ng N m^{-2} s^{-1}) was calculated as

$$J = C\left(\frac{Q}{A}\right) \quad [1]$$

where C is the gas concentration (ng m^{-3}) at the chamber outlet, Q is the zero air flow rate (m^3 s^{-1}), and A is the soil surface area (A = 0.0794 m^2) enclosed by the chamber. Chambers reached steady state within 30 min and fluxes were typically sampled for a period of 1 to 3 h. It should be noted that the use of zero air may lead to enhanced fluxes under some conditions (Hall et al., 2008). However, the purpose of the measurements in this study was to compare treatment differences and temporal variability as influenced by soil processes, which would not be affected by the use of zero air. Potential wall losses, which, conversely, may impart a low bias to the measured flux (Kaplan et al., 1988), were not considered. Care was taken to minimize moisture condensation in the chambers and data were discarded when condensation on chamber walls or tubing was observed. Concentrations of NO and NH_3 inside the chamber were determined using a Thermo Environmental Instruments Incorporated (TEI) Model 17C chemiluminescence NO_x/NH_3 analyzer (Walker et al., 2002).

Nitrous oxide (N_2O) emissions were determined using the same chamber configured in a closed-loop mode in which the emission flux was calculated as

$$J = \frac{dC}{dt}\left(\frac{V}{A}\right) \quad [2]$$

where dC/dt is the rate of N_2O increase in the chamber (ng N m^{-3} s^{-1}) and V is the internal volume of the chamber (m^{-3}). Fluxes were determined from the change in concentration observed over a period of 30 min to 1 h. The concentration of N_2O was determined using a TEI Model 46C gas filter correlation analyzer. Analyzers were multipoint calibrated before and after each measurement campaign by mass flow controlled dilution of certified NO, NH_3, and N_2O gas standards (Scott Specialty Gases, Plumsteadville, PA). Concentrations were output from the analyzers every 5 s and stored as 1 min averages along with soil temperature (0–10 cm) and soil volumetric water (0–15 cm) measured adjacent to flux chambers.

Fluxes of NH_3, NO, and N_2O 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 NO_3^- and 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 0.01mol 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 NO_3^- chemistry was also performed to examine temporal trends, using a combination of least squares and locally weighted regression procedures. Log-transformed 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 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 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 NO_3^- concentrations in restored plots at 30 cm depth (Fig. 1).

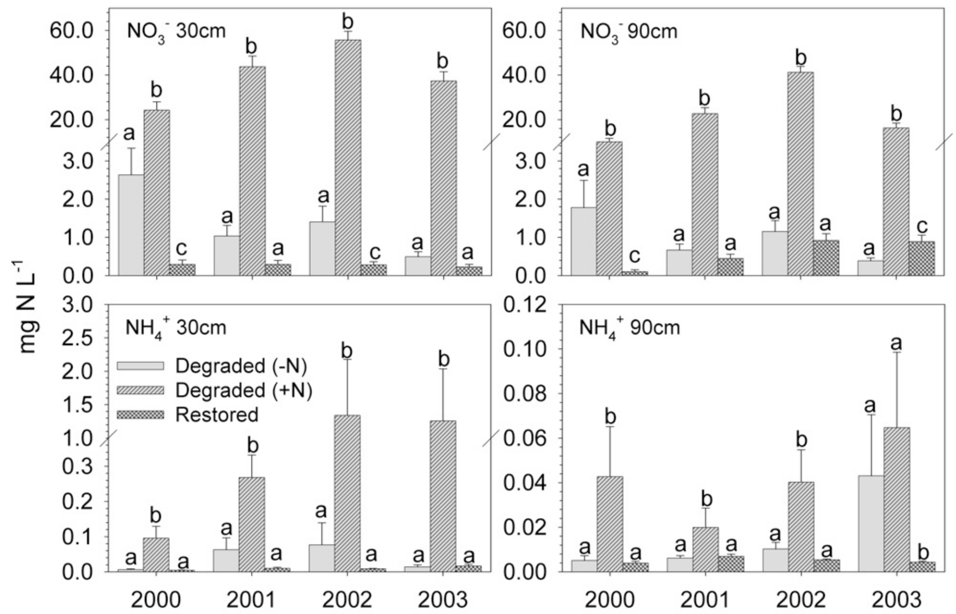

Fig. 1. Yearly treatment summary of lysimeter NO_3^- and NH_4^+ concentrations at 30 and 90 cm depths. Treatment means are compared for statistical significance within years. Bars carrying the same letter are not significantly different (*P* > 0.1).

A similar pattern of much higher NH_4^+ concentrations in the degraded (+N) treatment was also observed. Concentrations of 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 NO_3^-, which likely reflects a combination of rapid depletion of the soil solution NH_4^+ pool and lower mobility of NH_4^+ relative to NO_3^-.

Soil solution 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 NO_3^- concentrations at 30 cm was explained by seasonality and first order autocorrelation, yielding a regression model of the form:

$$Y_i = a_o + \beta_1 Y_{i-1} + \beta_2 \cos(2\pi i/12) + \beta_3 \sin(2\pi i/12) + e_i \qquad [3]$$

i = 1,..... N.

where N represents the number of months in the time series, Y_i is natural log-transformed NO_3^- concentration for the ith month, a_0 is the intercept, Y_{i-1} represents the first order autoregressive term, with corresponding regression coefficient β_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 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 NO_3^- concentrations. The observed seasonality of 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 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 NO_3^- concentrations between the restored and degraded (-N) plots were observed during the first 6 mo following treatment initiation. Depletion of 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 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

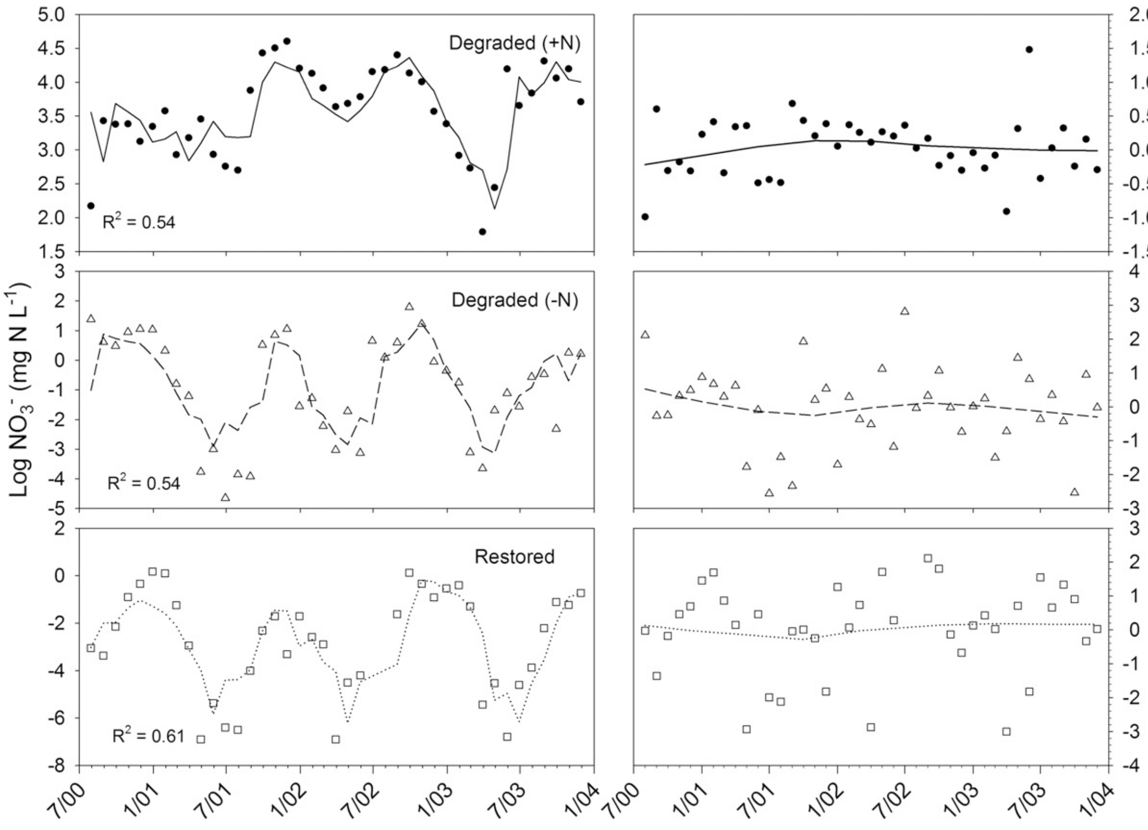

Fig. 2. Results of linear and locally weighted regression modeling of log-transformed 30 cm lysimeter NO_3^- concentrations by treatment.

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

Table 1. Yearly summary of extractable soil NO_3^- and NH_4^+ 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.

		2000	2001	2002	2003
		mg N kg^{-1}			
NO_3^-	Degraded (+N)	6.7 (5.6)a	10.3 (13.1)a	15.6 (10.3)a	4.9 (3.0)a
	Degraded (-N)	1.3 (0.9)b	0.6 (0.5)b	1.2 (1.1)b	0.8 (0.4)b
	Restored	1.1 (0.7)b	1.2 (1.2)b	2.7 (2.1)b	2.2 (1.8)b
NH_4^+	Degraded (+N)	18.9 (21.5)a	5.8 (4.4)a	3.5 (3.1)a	3.9 (2.8)a
	Degraded (-N)	2.6 (0.8)b	2.4 (1.2)a	2.0 (0.8)a	2.2 (1.2)a
	Restored	2.3 (1.7)b	3.3 (3.0)a	2.0 (0.8)a	3.1 (1.7)a
		g cm^{-3}			
Bulk density	Degraded (+N)	1.01 (0.09)a	1.09 (0.11)a	1.15 (0.13)a	1.14 (0.18)a
	Degraded (-N)	0.98 (0.09)a	1.1 (0.11)a	1.13 (0.17)a	1.18 (0.16)a
	Restored	0.94 (0.05)a	0.97 (0.05)a	0.98 (0.15)a	0.97 (0.17)b
		mg N kg^{-1} 28 d^{-1}			
Mineralization	Degraded (+N)	11.8 (31.5)a	29.3 (22.7)a	58.7 (28.7)a	38.9 (15.3)a
	Degraded (-N)	4.9 (5.6)a	7.8 (5.6)b	15.1 (19.5)b	12.2 (7.2)b
	Restored	4.0 (2.5)a	5.9 (6.4)b	12.4 (6.6)b	10.8 (8.3)b
Nitrification	Degraded (+N)	17.1 (18.4)a	23.5 (14.0)a	60.0 (27.0)a	41.2 (16.9)a
	Degraded (-N)	6.7 (6.3)a	6.1 (4.8)b	15.1 (19.1)b	12.0 (6.9)b
	Restored	4.5 (3.8)a	6.0 (5.1)b	12.0 (6.1)b	10.5 (7.4)b

rates observed in the degraded treatments were driven by nutrient additions.

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% of the degraded (-N) and degraded (+N) treatments, respectively. Only 8 monthly composite samples were collected in the restored 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 inorganic N (NO_2^-+ NO_3^- + NH_4^+) concentrations in overland flow were 13.6, 2.9, and 4.7 mg L^{-1} in the degraded (+N), degraded (-N), and restored treatments, respectively. 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 N_2O 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 NH_3 observations and 86 N_2O observations. Fluxes of all species were significantly higher in the degraded (+N) treatment, which contained the highest concentrations of extractable soil NH_4^+ and NO_3^- (Table 2). Emissions of N_2O and NH_3 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 N_2O and NH_3 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 NO_2^- or NO_3^-, 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 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_2O 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_3 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_2O emissions also varied across treatments (Table 2). Assuming N_2O is primarily a product of anaerobic denitrification (Russow et al., 2000), the ratio of NO to N_2O 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_2O 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_2O ratios. Figure 4 also illustrates that treatment differences in the NO/N_2O 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_2O ratio and the ratio of NH_4^+ oxidizers to denitrifiers (Fig. 3., Plot D). The average ratio of nitrite oxidizers

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.

		Restored	Degraded (-N)	Degraded (+N)
Soil chemistry	NH_4^+	2.5 (1.4)a	2.0 (1.6)a	6.0 (9.8)b
	NO_3^-	1.7 (1.4)a	1.8 (3.8)a	10.4 (18.2)b
	pH	5.05 (0.16)a	4.99 (0.17)a	5.25 (0.28)b
Fluxes	NO	0.3 (0.4)a	0.7 (0.8)b	5.1 (11.2)c
	N_2O	1.0 (1.0)a	0.8 (0.6)a	4.3 (6.6)b
	NH_3	0.9 (0.9)a	0.9 (1.4)a	10.4 (25.5)b
Flux/Soil N	NO/NH_4^+	0.2 (0.2)a	0.5 (0.5)b	1.5 (2.4)c
	N_2O/NO_3^-	1.3 (2.1)a	1.7 (1.9)a	1.0 (1.0)a
	NH_3/NH_4^+	0.5 (0.8)a	0.6 (1.0)a	1.9 (4.3)b

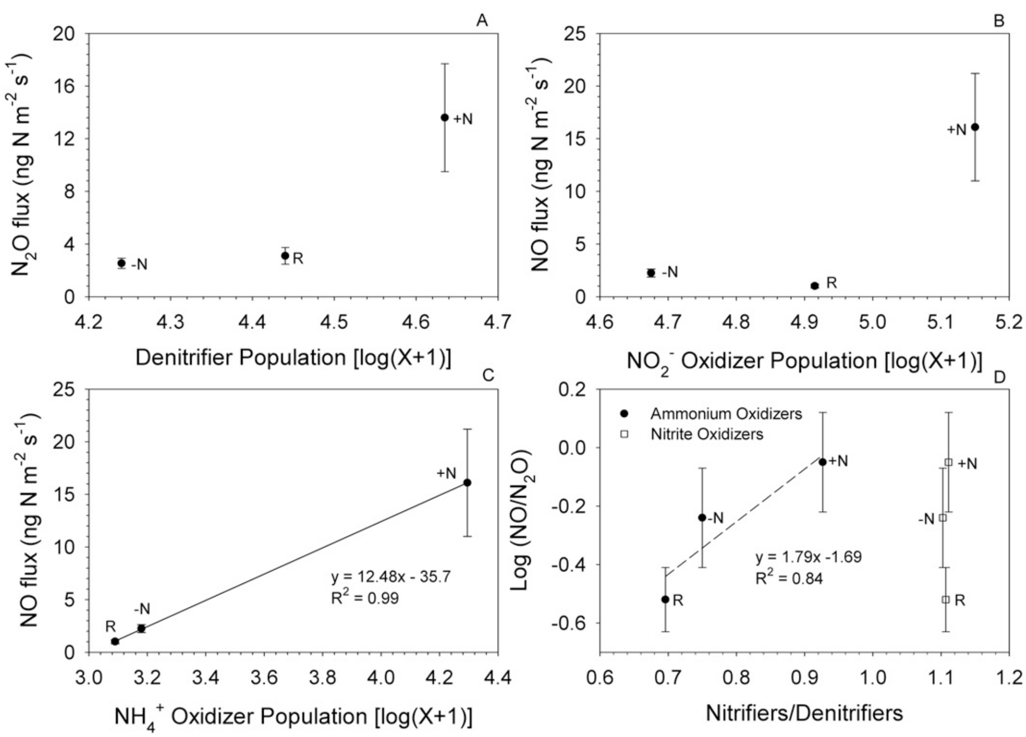

Fig. 3. Comparison of treatment mean trace gas fluxes and microbial [log (X + 1)] populations: (A) N_2O flux vs. denitrifier population, (B) NO flux vs. NO_2^- oxidizer population, (C) NO flux vs. NH_4^+ oxidizer population, (D) NO/N_2O flux ratio vs. nitrifer/denitrifier population ratio. Microbial populations were sampled by Tian et al. (2004). Treatments are identified as R (restored), –N (degraded), and +N (degraded + nutrients).

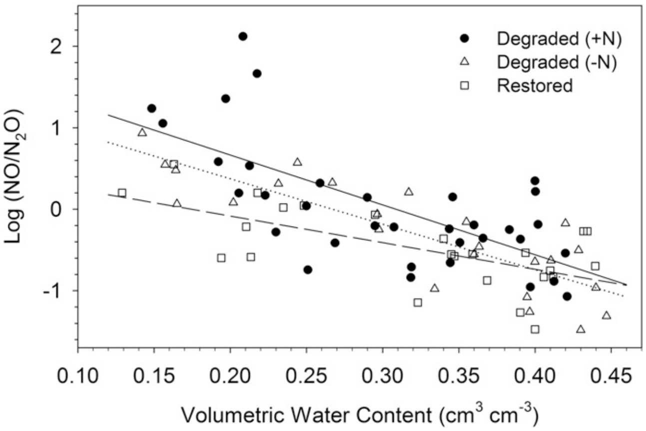

Fig. 4. Log transformed ratio of NO to N_2O fluxes vs. soil volumetric water content along with regression lines. Solid, dotted, and dashed lines correspond to degraded (+N) (y = −6.12x − 1.89, R^2 = 0.46), degraded (−N) (y = −5.58x + 1.49, R^2 = 0.41), and restored (y = −3.27x − 0.57, R^2 = 0.41) treatments, respectively.

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_2O. 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_2O, 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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