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Impacts of Fertilizer Additions on Water Quality of a Drained Pine Plantation in North Carolina. A Worst Case Scenario.

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Abstract. *Intensive plantation forestry will be increasingly important in the next 50 years to meet the high demand for domestic wood in the US. However, forestry management practices can substantially influence downstream water quality and ecology. In this study, the effect of fertilization on drainage water quality of a coastal pine plantation located in Carteret County, NC was studied. The pine plantation consists of three watersheds, two mature (31-year old) and a young (8-year old) stands (age at treatment). One of the mature stands was commercially thinned in 2002. The un-thinned mature stand was designated as a control and was not fertilized. The two other stands (young and thinned) were fertilized with diammonium phosphate, urea, and boron. Each treatment watershed received a different fertilizer rate. Both the flow rates and nutrient concentrations in water drained from each of the watersheds were measured. Nutrient concentrations and nutrient loadings were analyzed using a paired watershed approach and GLM statistical procedures. Three large storm events occurred soon after fertilization, a 5-year 24 hr, a 1 to 2-year, and a third event (46 mm in 46 hr) occurred six, 29 and 47 days after fertilization respectively. It was determined that peak nutrient concentrations soon after fertilization were much higher than the average concentrations, which were significantly ($\alpha = 0.05$) higher on both treatment watersheds soon after fertilization than during any other period during the study. The effect of fertilization on both the nutrient concentrations and loading rates was short lived and the levels were back to pre-fertilization levels as soon as three months after fertilization. Also, the average nutrient increase on the thinned stand was higher than on the young stand as a result of a higher fertilizer rate applied on the thinned stand one.*

Keywords. Drainage outflow, Nutrient Concentrations, Nutrient Loadings, Water Quality, Paired Watershed.

Introduction

Water pollution threatens public health both directly and indirectly (USEPA, 2002a). Poor water quality also threatens fish and shellfish habitat, negatively impacts commercial and recreational fisheries, causes the closure of harvestable shellfish beds, and could also have a negative impact on tourism (Bricker et al., 1999; Morand and Briand, 1996; Valiella et al., 1997; Lapointe and Bedford, 2007). The 2000 National Water Quality Inventory (NWQI) reports that nutrients are the leading pollutants in lakes and reservoirs, the fifth in rivers and streams and the eleventh in estuaries. The same report concludes that forestry activities contribute to approximately four-percent of the water quality problems in all surveyed rivers and streams, and 11% in impaired waters in the same systems. Intensive Management Practices (IMPs) (which include, harvesting, thinning, pruning, site preparation, bedding, fertilization, herbicide application, and artificial regeneration) have increased Southern timber yields as much as 65% over standard site preparation and planting and 100% over naturally regenerated forest (Weir and Greis, 2002). IMPs affect the hydrology and water quality of downstream ecosystems by altering water input (caused by a change in outflow in the affected area), and nutrient and sediment concentration, among others (Amatya et al., 2006; Grace et al., 2006). This study concentrates on the impacts of forestry practices, particularly fertilization, on nutrient concentration and loading in waters drained from a pine plantation in eastern North Carolina.

Several previous studies have focused on the physiological effects (tree growth and development, absorption and nutrient process, etc.) of fertilization on loblolly pine plantations (Sampson et al., 2006; Will et al., 2006; Cough et al., 2004; Murthy and Dougherty, 1997; Vose and Allen 1991) but not on the effects of fertilization on stream water nutrient concentrations.

Binkley et al. (1999) summarized information from studies of forest fertilization around the world and reported that in general, peak concentrations of nitrate-N (NO_3-N) in stream water increase after forest fertilization. Increases in average concentrations of NO_3-N are much lower than peak values, and the highest annual average NO_3-N ever reported was 4 mg N/L. Relatively high concentrations of stream-water NO_3-N tend to occur with repeated fertilization, use of ammonium nitrate (rather than urea), and fertilization of N-saturated hardwood forest. Ammonium-N (NH_4-N) concentrations may also show large peaks following fertilization (up to 15 mg N/L, but annual averages remain <0.5 mg N/L. Fertilization with phosphate can lead to increased peak concentrations >1 mg P/L, but annual averages remain <0.25 mg P/L.

Previous studies at this study site in eastern North Carolina determined the water quality impacts of drainage and related water and forest management practices. Smith (1994) determined that the concentration of nutrients using different water management treatments in these watersheds with 14 – 15 year old pine plantations were below the North Carolina water quality standards, and were in general lower than those in a receiving state highway ditch. Amatya et al. (1998) concluded that seasonal controlled drainage can be used to effectively reduce total drainage outflows and, thereby, total suspended solids (TSS) and nutrient exports from these drained forested watersheds. Amatya et al. (2003) determined that orifice-weir outlet drainage increased average annual concentration of TKN, and decreased TP and sediment concentration but did not have a significant effect on average concentrations of NO_3-N and TN compared to expected results for conventional drainage. Amatya et al. (2006a) concluded that fertilization applied after a commercial thinning of a control stand in 1989 did increase the nitrogen and TP levels, which were substantially reduced by six years after fertilizer application. In another study at this particular location Amatya et al. (2006b) argue that although harvesting of a 21 year old pine plantation resulted in substantial increases in both the nutrient concentrations and loadings (except for TP) the increases were short-lived (three years or less after harvest).

It is not quite clear from the aforementioned studies if the nutrient concentration and loadings of waters drained from these forested watersheds vary as a function of fertilization rate and amount of biomass as indicated by the stand age.

Study Objectives

The first objective of this study is to compare the concentrations and loading rates from two fertilized watersheds (stand ages were 8 and 31 years at fertilization) with an unfertilized (control) watershed (31 years at fertilization). The second objective is to evaluate and quantify the effects of fertilization on both nutrient concentrations and loading on the two fertilized watersheds. Fertilizer was applied at different rates on the treatment watersheds. We hypothesize that nutrient concentrations and loadings from the fertilized pine stands (as a function of fertilization and biomass) will be significantly higher than from the unfertilized pine stand (control) but they will be short lived. Similarly, we hypothesize that the stand with higher fertilization rate would have higher concentrations and loadings than the one with reduced rate.

Methodology

The study site is located on a loblolly pine (*Pinus taeda* L.) plantation owned and managed by Weyerhaeuser Company in Carteret County, North Carolina (34°48' Latitude 76°42' Longitude) (Figure 1). The research site consists of three artificially drained experimental watersheds, (D1, D2, and D3) which are 24.72 hectares (ha), 23.62 ha, and 26.75 ha respectively. Topography of the site is characterized by flat, shallow water table soils (McCarthy et al., 1991). The soil is a hydric series, Deloss fine sandy loam (fine-loamy mixed,) Thermic Typic Umbraquult. Each of the three experimental watersheds is drained by four 1.4 to 1.8 m deep and 2.0 m wide at the surface lateral ditches spaced 100 m apart (Figure 1).

The three artificial watersheds were planted in 1974 at a density of 2100 trees ha^{-1} with trees separated 1.74 m apart and rows separated 2.74 m apart. Watershed D1 has served as the control treatment throughout various studies conducted on the site since 1988 (McCarthy et al., 1991; Amatya et al., 1996; 1998; 2000; 2003; 2006a; 2006b). D1 is now a 33-year old mature pine plantation that underwent pre-commercial thinning in 1981 (thinned to 988 trees ha^{-1}) and commercial thinning in the later part of the growing season in 1988 (thinned to 370 trees ha^{-1}).

Watershed D2 was harvested in July 1995 and planted back in February 1997 with 30 to 46 cm tall seedlings 1.52 m apart in rows separated 3.66 m apart giving a density of 2100 seedlings ha^{-1}. The survival rate on this stand was 93% and it is now a ten-year old plantation. Watershed D3 is currently a 33-year old pine plantation that received the same thinning treatment in 1988 as watershed D1. Additionally, watershed D3 was commercially thinned (about 50% of the biomass removed) in July 2002 to a density of about 185 trees ha^{-1}. After monitoring for eight years since plantation for regeneration on D2 and for three years since thinning on D3, watersheds D2 and D3 were fertilized on September 8, 2005 to study the effects of fertilization on water quality drained from these pine stands of different ages.

Readers are referred to McCarthy (1990), and Amatya (1993), and Amatya et al. (1996) for a more detailed description of the site.

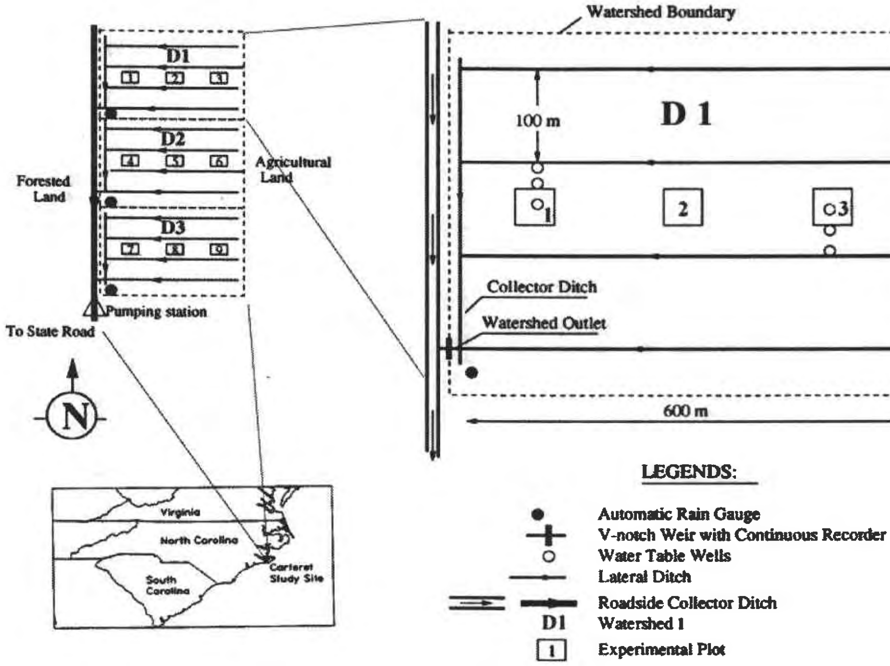

Figure 1. Location and layout of three experimental watersheds at Carteret site, NC. (After Amatya et al., 2000).

Following Weyerhaeuser procedure for this type of plantation site, tree age, and levels of available nutrients in the soil, fertilization was aerially applied on both D2 and D3 (Figure 2) while making efforts to avoid the areas covered by the lateral ditches (ephemeral streams) that are 100 meters apart. Two aerial passes were made over the central 70-m of the field, leaving about 15 meters from the edge of the lateral ditch on either side, and thus the 15-m strip at the ditch edge may function as an unfertilized stream side management zone (SMZ), a type of BMP adopted in upland forests.

The watersheds were aerially fertilized on September 08, 2005 with nitrogen (N), phosphorus (P) and boron (B). The fertilization rate was 303 kg ha^{-1} for the young stand (D2) and 454 kg ha^{-1} for the old thinned stand (D3). The analysis was 38/9/0 N/P/K per 45.5 kg, thus the stands received 115 kg ha^{-1} N/27 kg ha^{-1} P/0 K on D2 and 172 kg ha^{-1} N/41 kg ha^{-1} P/0 K on D3. Phosphorus was applied as diammonium phosphate (DAP) and N as urea (after accounting for N in DAP). Boron, a micronutrient considered deficient on some Coastal Plain sites, was added to the fertilization mix as a coating on the urea.

Two methods of water sampling (composite using automatic water samplers SIGMA-900 and grab sampling) were used. All collected samples were preserved frozen in the storage until they were transported to the laboratory at North Carolina State University in Raleigh, NC. Laboratory analyses of NO_3-N-N, NH_4-N-N, total Kjeldahl nitrogen (TKN), and total phosphorus (TP) were colorimetric and done according to U.S. Environmental Protection Agency methods (USEPA, 1979).

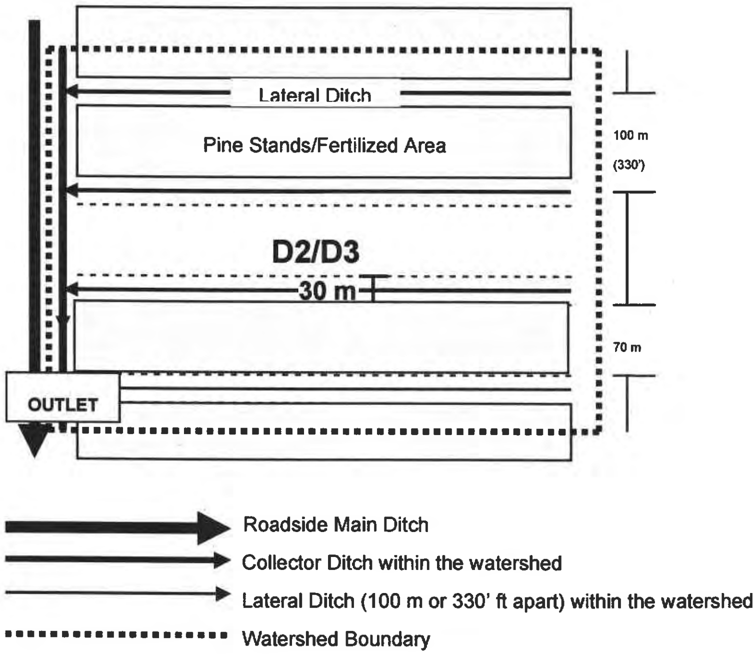

Figure 2. Schematic of the fertilized area on the treatment watersheds.

Intensive composite sampling using automatic samplers and grab sampling were conducted on all three watersheds for three storm events occurring immediately after fertilization on the treatment watersheds in 2005. These storms were Hurricane Ophelia (September 16 – 22) and two other independent events in October (Oct 7 – 13 and Oct 25 – 31). After initial collection of all sample bottles during each event, it was later decided to composite the samples even more by choosing the critical ones based on sampling points on the storm hydrograph for the event to optimize costs, time and data analysis. Another reason was due to high weir submergence at some outlets during these events. Constant maximum flow rate value and an insignificant change on nutrient concentrations were assumed in these cases.

Data analysis

To study the effects of fertilization on these watersheds data for both hydrology and water quality were analyzed in detail. These data included rainfall, water table, stage height, and weather, besides nutrient concentrations and flow rates. Flow was estimated using standard weir equations for 120° V-notch weir and stage (head) measured above V-notch bottom upstream of it.

Secondly, nutrient concentration and loading data analysis for determining the effects of fertilization on the treatment watersheds was conducted using the paired watershed approach suggested by USEPA (1993) for NPS water quality studies at this site (Amatya et al., 1998; 2000; 2003). As a first step, all nutrient concentrations below the detection limit were assumed to be at detection limit (0.1 mg/L for NH_4-N, NO_3-N, TKN; and 0.01 mg/L for TP).

General linear models (GLM) (USEPA, 1993) were used to analyze the effect of fertilization on the water draining from the pine plantations between the control and the treatment watersheds. One of the assumptions in GLM procedures is the normality of the residuals. After examining both type of plots (with log and non-log values), it was decided to run the GLMs on the log transformed data because it was visually determined from the Draftman Plots that the assumption of normality of the residuals is not greatly violated when the data were log transformed. All tests were run at a significance level of α=0.05.

Comparisons for nutrient concentration and nutrient loading were made between four different periods (*Calibration, Pre-fertilization, Rain Events, Post Rain Events*) (Table 1) for each nutrient (NH_4-N, NO_3-N, TP, and TKN) between the treatment watersheds (D2 and D3) and the control watershed (D1).

Table 1. Comparisons made between different time periods to analyze the effects of fertilization on nutrient concentration and loading draining from the study watersheds.

PERIOD	Pre-Fertilization Jan 2004 - Aug 2005	Rain Events Sep - Oct 2005	Post Rain Events Nov 2005 - Mar 2007
Calibration May 1989 - May 1990	X	X	X
Pre-Fertilization Jan 2004 - Aug 2005		X	X
Rain Events Sep - Oct 2005			X

The stands on D1, D2 and D3 were of different ages and possibly different biomass from January 2004 to August 2005 due to previous harvesting of D2 during July 1995 and commercial thinning of D3 in June 2002. Regardless of this, the *Pre-fertilization* period was considered as a second calibration period because the watersheds presented a similar hydrologic behavior as the one they had during *Calibration* (Amatya 2006b).

GLM Analysis

The response and explanatory variables were transformed using the natural logarithm transformation. Let Y represent the measured concentration of a nutrient on one of the watersheds that received a treatment (either D2 or D3) and let X represent the measured level of the same nutrient during the same time period on the control watershed D1. Linear models of the following type were constructed:

$$ln(Y) = \beta_0 + \beta_1 \times ln(X) + \beta_2 \times Tr + \beta_3 \times ln(X) \times Tr \qquad (1)$$

where Tr will be a binary variable (0 or 1) depending on whether or not the measurements were taken during the treatment time period. The full model F-test tested the null hypothesis that $\beta j = 0$ *for all* $j = 1, 2, 3$ (Figure 3a) versus the alternative that at least one of these coefficients was nonzero (Figures 3b, c, d, e and f). Since the variable *Tr* was binary, the full model yielded two distinct linear regression models, one for each time period. When $Tr = 0$ the linear model became

$$ln(Y) = \beta_0 + \beta_1 \times ln(X)$$

and when $Tr = 1$ the linear model became

$$ln(Y) = (\beta_0 + \beta_2) + (\beta_1 + \beta_3) \times ln(X).$$

The models were fitted sequentially and the sequential sums of squares and the corresponding F-tests indicated if the next coefficient was statistically significant (α = 0.05) with the previous coefficients already in the model. For example, the first F-test for the coefficients was used to test the hypothesis that the coefficient $\beta_1 = 0$. If this hypothesis was rejected, then the model $ln(Y) = \beta_0 + \beta_1 \times ln(X)$ (Figure 3b) provided an improvement over the model $ln(Y) = \beta_0$ (Figure 3a). The subsequent F-test was used to determine if $\beta_2 = 0$. If this hypothesis was rejected then the 'parallel line' model $ln(Y) = \beta_0 + \beta_1 \times ln(X) + \beta_2 \times Tr$ (Figure 3c, d) provided an improvement over the 'single line' model $ln(Y) = \beta_0 + \beta_1 \times ln(X)$. Finally, the 'separate slopes and intercepts' model was tested by the third F-test to determine if the full model (1) (Figure 3e, f) was an improvement over the parallel lines model. The Type III sums of squares tests were used to determine if any of the terms provided a significant improvement in the model with the other two coefficients already fit to the model.

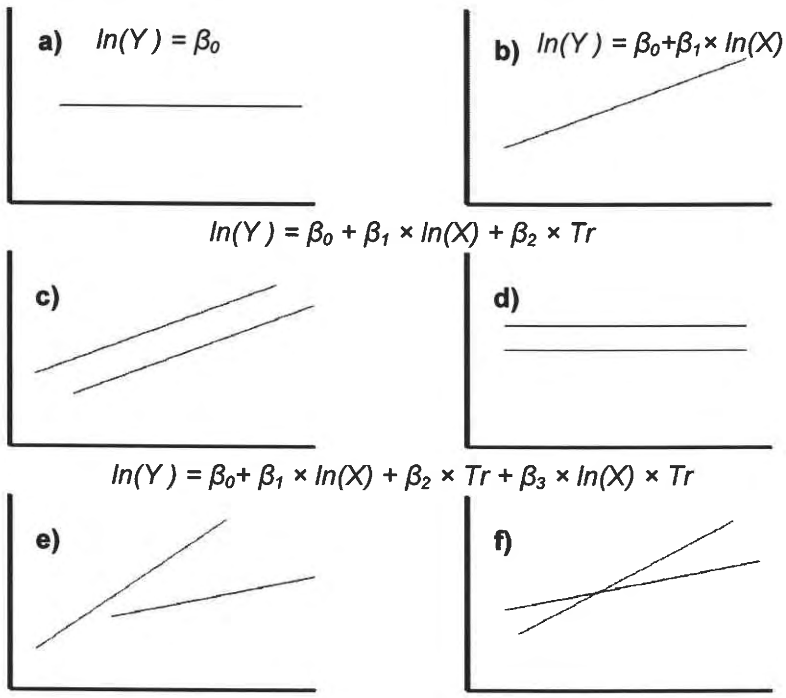

Figure 3. Different model scenarios, a) Model is not significant and does not have any predicting power over the data, $\beta j = 0$ for all j = 1, 2, 3; b) 'Single line model' is significant, $\beta_1 \neq 0$; c) 'Parallel line model' and 'single line model are significant, β_1 and $\beta_2 \neq 0$; d) only 'Parallel line model' is significant $\beta_2 \neq 0$; e) 'Separate slopes and intercepts model' is significant, $\beta_3 \neq 0$ (lines do not cross); f) 'Separate slopes and intercepts model' is significant, $\beta_3 \neq 0$ (lines cross). The model's fit is sequential and a significant difference of one coefficient from zero means that that model gives more predictive power over the data with the previous model(s) already fitted.

Note that because of the logarithmic transformation of the variables, the original relationship between X and Y must be 'decoded'. For example, the relationship $ln(Y) = \beta_0 + \beta_1 \times ln(X)$ can be expressed as $Y = e^{\beta 0}X^{\beta 1}$. For the 'parallel lines' model with $Tr = 0$ this yields $Y = e^{\beta 0}X^{\beta 1}$ and with $Tr = 1$ it becomes $Y = e^{\beta 0+\beta 2} X^{\beta 1}$. For example if $\beta_2 = ln(k)$ then, under the condition $Tr = 1$ the mean value of Y is estimated to be k times the mean value of Y under $Tr = 0$. For the separate slopes and intercepts models the original relationship between Y and X under $Tr = 0$ becomes $Y = e^{\beta 0}X^{\beta 1}$ and under $Tr = 1$ becomes $Y = e^{\beta 0+\beta 2} X^{\beta 1+\beta 3}$. Here the relationship between Y and X for the two treatment levels changes in both the exponent on X and by a multiplicative constant.

To accurately quantify the actual effects of fertilization on nutrient concentration and loading, expected values under no fertilization were calculated from ratios developed between the treatment and control watersheds during Calibration. For each nutrient, expected concentration and loading (had the treatment watersheds not been fertilized) during the treatment period is calculated using the following formulas:

$$D2\ exp. = (D2(cal)/D1(cal)) \times D1\ meas.$$

$$D3\ exp. = (D3(cal)/D1(cal)) \times D1\ meas.$$

These expected values were then compared to the measured values during the treatment periods to determine if there was a significant increase in nutrient concentration or loading after fertilization. This analysis provides the actual amount or percentage increase, if any, in nutrient concentration and loading for the Rain Events when combined to the GLM Procedures that were used to evaluate the statistical significance of the models and, the difference in both slopes and/or intercepts of regression for calibration and treatment periods.

Nutrient Loading was analyzed using the same methods used to analyzed nutrient concentration.

Results

Nutrient Concentration

Peak nutrient concentrations during *Rain Events* were much higher than mean concentrations. Intra-watershed comparison shows that fertilization increased the average nutrient concentration on water draining from the treatment watersheds (D2 and D3), as evidenced by the higher average nutrient concentration during *Rain Events* compared to all other analyzed periods (Figure 4).

Table 2 shows the expected and the measured concentrations during the *Rain events* when nutrient concentrations were considerably higher. In this table we can observe that, except for NH_4-N on D2, which is 52% lower than the expected concentration, and TP on D3 which presents the same concentration as the expected values, all other measured nutrient concentrations are higher than the expected value under no fertilization. Increase in average nutrient concentrations (reported in mg L^{-1}) after fertilization were found to be larger on watershed D3 (thinned) than on watershed D2 (regenerated) (Table 3).

During 2006, gross evatpotranspiration (ET) on D2 was 1073 mm. During the same year gross ET on D3 was 1146 mm. The mature watershed (D3) total ET is 73 mm higher than D2 which is equivalent to seven-percent higher ET. During 2007 (January – March), gross ET on D2 was 213 mm, while it was 275 mm on D3. The gross ET difference between the treatment watersheds during 2007 was 62 mm which is equivalent to 30% higher ET on D3 than on D2. These comparisons were made only on 2006 and 2007 when weir submergence occurred only once for a brief period, and did Higher ET rates on D3 than on D2 suggest that it is likely that nutrient uptake rates from D3 are higher than D2not influence the calculation of outflow rates.

Higher ET rates on D3 than on D2 suggest that it is likely that nutrient uptake rates from D3 are higher than D2; therefore, rather than a difference in nutrient uptake rates we attribute the higher nutrient concentrations on D3 to the higher fertilizer rate on this watershed.

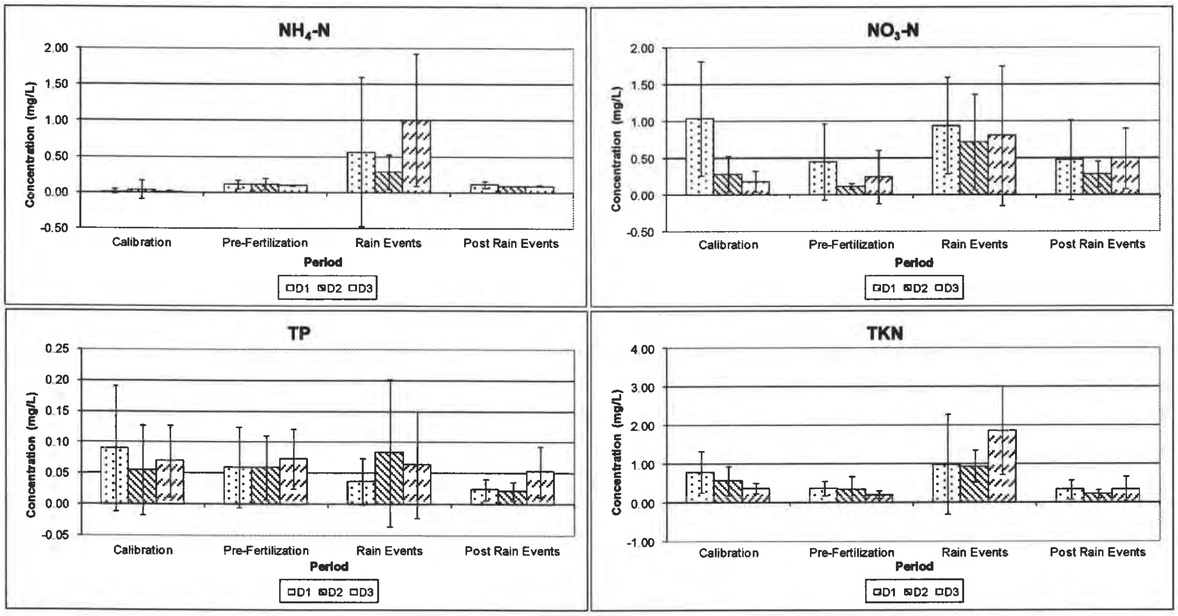

Figure 4. Average nutrient concentrations during the analyzed periods.

Table 2. Comparison between expected nutrient concentrations under no treatment (fertilization) and the measured nutrient concentrations after fertilizer was applied.

Period	Nutrient	WS	Measured (mg/L)	Expected (mg/L)	Percent increase/decrease (%)
Rain Events	NH_4-N	D2	0.29	0.61	-52
		D3	1.02	0.36	183
	NO_3-N	D2	0.71	0.6	19
		D3	0.80	0.23	246
	TP	D2	0.08	0.05	67
		D3	0.06	0.06	6
	TKN	D2	0.94	0.66	43
		D3	1.87	0.4	368

Average nutrient concentrations during each of the four periods analyzed were normalized by flow (Table 3) to obtain flow weighted concentrations. It is important to normalize average nutrient concentrations by flow because there would probably be more samples or data during a wet year or period than during dry periods. For this reason it would not be appropriate to compare raw mean concentration between treatment periods without normalizing by flow.

Nutrient concentration normalized by flow also shows a substantial increase in nutrient concentration right after fertilization. This effect is not present as early as three months after fertilization (Table 3).

During the *Rain Events* period, average nutrient concentration increased several fold for all nutrients, except for total phosphorus (TP) which in some cases decreased slightly. TP was the nutrient which responded the least after fertilization with a ratio response of as much as six-times higher than normalized average nutrient concentration during *Rain Events*. NH_4-N was the nutrient which responded the most with as much as 70 times increase for the *Rain Events* when compared to the other periods. This was generally expected due to the relatively rapid hydrolysis of urea in forest soils to form NH_4. The low response of TP is attributed to the ability of P as phosphate to be held by soils through both electrostatic and non-electrostatic mechanisms; P usually does not leach in most soils (Sparks 2003).

Table 3. Flow-weighted average nutrient concentration in each watershed during all analyzed periods.

PERIOD	WS	Duration yr	FLOW m^3	Avg. Nutrient Conc. (mg/L)			
				NH_4-N	NO_3-N	TP	TKN
CALIBRATION	D1	1.35	217984	0.03	0.82	0.06	0.93
	D2	1.35	194488	0.03	0.26	0.05	0.59
	D3	1.25	187887	0.01	0.16	0.07	0.33
PRE-FERTILIZATION	D1	1.59	182939	0.10	0.63	0.04	0.37
	D2	1.60	175310	0.11	0.11	0.06	0.25
	D3	1.59	172517	0.10	0.26	0.09	0.19
RAIN EVENTS	D1	0.24	827352	0.49	1.01	0.03	0.95
	D2	0.23	761410	0.44	1.15	0.05	1.03
	D3	0.23	807203	0.82	1.39	0.10	1.49
POST RAIN EVENTS	D1	1.41	993298	0.13	0.80	0.03	0.34
	D2	1.41	100926	0.10	0.24	0.03	0.20
	D3	1.41	79105	0.10	0.56	0.02	0.25

*Note: Some periods vary in length as data might have been collected at different times and/or intervals at times.

As stated earlier watershed D3 received 1.5 times more fertilizer per hectare than watershed D2. The average normalized (flow weighted) nutrient concentration for D2 during the *Rain Events* were 0.44, 1.15, 0.05, and 1.03 mg L^{-1} for NH_4-N, NO_3-N, TP, and TKN, respectively. For watershed D3 the flow weighted nutrient concentrations during the same period were 0.82, 1.39, 0.10, and 1.49 mg L^{-1} for NH_4-N, NO_3-N, TP, and TKN, respectively. The increase nutrient concentration on watershed D3 compared to watershed D2 is not linearly correlated with the fertilizer rate applied. As mentioned previously, watershed D3 received 1.5 times more fertilizer per hectare than watershed D2, but the average nutrient response rates on watershed D3 were 1.9, 1.2, 2.0, and 1.4 times higher than watershed D2 for NH_4-N, NO_3-N, TP, and TKN, respectively.

Similarly, *Post Rain Events* flow weighted nutrient concentrations for watershed D2 were 0.10, 0.24, 0.03, and 0.20 mg L^{-1} for NH_4-N, NO_3-N, TP, and TKN, respectively, compared to 0.10, 0.56, 0.02, and 0.25 mg L^{-1} for the same nutrients from the thinned watershed D3.

The peak nutrient concentrations during the *Rain Events* for NH_4-N, NO_3-N, TP, and TKN, on watershed D2 were 0.84, 2.2, 0.46, and 1.9 mg L^{-1}, respectively. On watershed D3 the peak concentrations of NH_4-N, NO_3-N, TP, and TKN for the same period were 4.7, 4.2, 0.44, and 6.2 mg L^{-1}, respectively. The peak concentration rates on watershed D3 were 5.6, 1.9, 0.96, and 3.3 times higher than watershed D2 for NH_4-N, NO_3-N, TP, and TKN, respectively. This indicates that peak concentration rates are not linearly correlated to the difference on fertilizer application rate.

During the *Post Rain Events* period the nutrient concentration peaks were not as high as during the *Rain Events* periods. Nutrient concentration peaks in watershed D2 during the *Post Rain Events* were 0.1, 0.66, 0.6, and 0.44 mg L^{-1} for NH_4-N, NO_3-N, TP, and TKN respectively. For watershed D3 during the same period the peak concentrations were 0.11, 1.6, 0.11, and 1.4 mg L^{-1} for NH_4-N, NO_3-N, TP, and TKN, respectively.

We reject our initial assumption that *Calibration* and *Pre-fertilization* are not different. As shown previously, some of the relationships comparing these two periods among the watersheds are significantly different. Watersheds D2 and D3 were fertilized three months before the start of nutrient concentration measurements in 1989, and although the treatment watersheds have not been disturbed after thinning in 2002, the different management practices applied through time in these watersheds might account for the difference in nutrient levels.

We found that the calculated nutrient concentrations (Table 4) of NH_4-N, NO_3-N, and TKN during the *Rain Events* were significantly higher from pre-treatment calculated concentrations on both treatment watersheds. Except for NO_3-N all the concentrations were back to pre-treatment levels as early as three months after fertilization.

An increase on NO_3-N, NH_4-N and TKN is observed in the control watershed after fertilization. After careful data and recorded field notes analysis it was ruled out that this increase was the result of fertilizer drift during fertilization (Nettles, Personal Communication), or the effect of nitrification. Levels of NO_3-N and TKN have been historically higher in the control watershed (D1) than in the treatment watersheds (D2, and D3), therefore high levels of these nutrients in the control watershed should not be considered an anomaly.

Table 4. Calculated average nutrient concentration (mg/L) on the treatment watersheds (D2 and D3) from the measured average nutrient concentration on the control watershed (D1) using the linear equations developed by the GLM models.

PERIOD	NUTRIENT	D1 measured average nutrient concentration	D2 calculated average nutrient concentration	D3 calculated average nutrient concentration
Pre-fertilization	NH_4-N	0.12	0.11	0.10
	NO_3-N	0.44	0.11	0.16
	TP	0.06	0.05	0.06
	TKN	0.37	0.25	0.20
Rain Events	NH_4-N	0.57	0.24	0.44
	NO_3-N	0.93	0.65	1.15
	TP	0.04	0.05	0.04
	TKN	0.98	0.85	1.44
Post Rain Events	NH_4-N	0.12	0.10	0.10
	NO_3-N	0.47	0.29	0.36
	TP	0.02	0.02	0.03
	TKN	0.34	0.22	0.29

Nutrient Loading

Nutrient loadings were determined for all three watersheds for the same four periods as for the nutrient concentration section.

Unlike nutrient concentration, the average of nutrient loading (kg/ha) is not consistently higher during the *Rain Events* period than during the other analyzed periods. Peak loading values are not consistently higher either during the *Rain Events* period right after fertilization.

Because the analyzed periods were all of different length in time, nutrient loading rates were normalized by the time (Table 5). This allowed compare all periods among each other and determine the effect of fertilization on nutrient loading. Total drainage outflow (in cubic meters) per watershed during each period is presented in Table 5 along with the total mass of nutrients leaving each watershed (kg/ha/yr). Table 5 shows substantial increases in nutrient loading from the treatment watersheds (D2 and D3) for the *Rain Events* period compared to other periods and to the control watershed (D1). Although the nutrient loading is reported in kg/ha/yr, it is important to remember that none of the analyzed periods were exactly one year long and the values were reported in this manner to normalize the data and make an accurate comparison.

Table 5. Outflow volume in cubic meters (Flow, cu m) and total nutrient load (kg/ha/yr) per watershed during the study period.

PERIOD	WS	Time yr	Flow cu m	NH_4-N kg/ha/yr	NO_3-N kg/ha/yr	TP kg/ha/yr	TKN kg/ha/yr
CALIBRATION	D1	1.35	217984	0.17	5.34	0.38	6.15
	D2	1.35	194488	0.16	1.58	0.31	3.63
	D3	1.25	183887	0.06	0.88	0.37	1.79
PRE-FERTILIZATION	D1	1.59	182939	0.48	2.94	0.17	1.70
	D2	1.60	175310	0.51	0.53	0.26	1.17
	D3	1.59	172517	0.41	1.06	0.36	0.79
RAIN EVENTS	D1	0.24	82735	6.72	13.97	0.41	13.09
	D2	0.23	76141	6.12	16.05	0.69	14.38
	D3	0.23	80720	10.90	18.53	1.29	19.87
POST RAIN EVENTS	D1	1.41	99330	0.36	2.28	0.08	0.98
	D2	1.41	100927	0.30	0.74	0.08	0.60
	D3	1.41	79105	0.21	1.18	0.03	0.51

Expected nutrient loading is presented in Table 6. A comparison between Table 5 and 6 shows that during the *Rain Events* nutrient loading was between two (TKN) to eight (NO_3-N) times higher than expected. The exception to this pattern was NH_4-N on D2 which was ten-percent lower than the expected value.

An intra-watershed comparison shows that fertilization increased the nutrient loading on water draining from the treatment watersheds. This is evidenced by using Table 6 to calculate the ratio of nutrient loading increase during the *Rain Events* when compared to all other periods. Nutrient loading increased several fold for all nutrients during the *Rain Events* period when compared to *Calibration, Pre-fertilization,* and *Post-Rain Events*. NH_4-N was the nutrient which responded the most with an increase as high 170 times more nutrient loading during the *Rain Events*. TP was the nutrient which responded the least after fertilization with a ratio response as low as two times more nutrient loading during the *Rain Events*. As with the average concentration, the low response of TP loading is attributed to the ability of Phosphorus (P) as phosphate to be held by soils through both electrostatic and non-electrostatic mechanisms, P usually does not leach in most soils (Sparks 2003). Figure 5 illustrates the cumulative loading during each analyzed period (Figure 5a (NH_4-N), Figure 5b (NO_3-N), Figure 5c (TP), and Figure 5d (TKN)).

Table 6. Expected total nutrient loading compared to measured nutrient loading in the treatment watersheds after *Calibration*. Expected outflow volume in cubic meters (Flow, cu m) is also presented.

PERIOD	WS	Flow cu m	NH_4-N kg/ha/yr		NO_3-N kg/ha/yr		TP kg/ha/yr		TKN kg/ha/yr	
			Exp.	Meas.	Exp.	Meas.	Exp.	Meas.	Exp.	Meas.
PRE-FERTILIZATION	D2	163220	0.46	0.51	0.87	0.53	0.14	0.26	1.01	1.17
	D3	154324	0.18	0.41	0.48	1.06	0.17	0.36	0.50	0.79
RAIN EVENTS	D2	73817	6.42	6.12	4.13	16.05	0.34	0.69	7.73	14.38
	D3	69794	2.54	10.90	2.29	18.53	0.40	1.29	3.81	19.87
POST RAIN EVENTS	D2	88623	0.34	0.30	0.68	0.74	0.07	0.08	0.58	0.60
	D3	83793	0.14	0.21	0.37	1.18	0.08	0.03	0.28	0.51

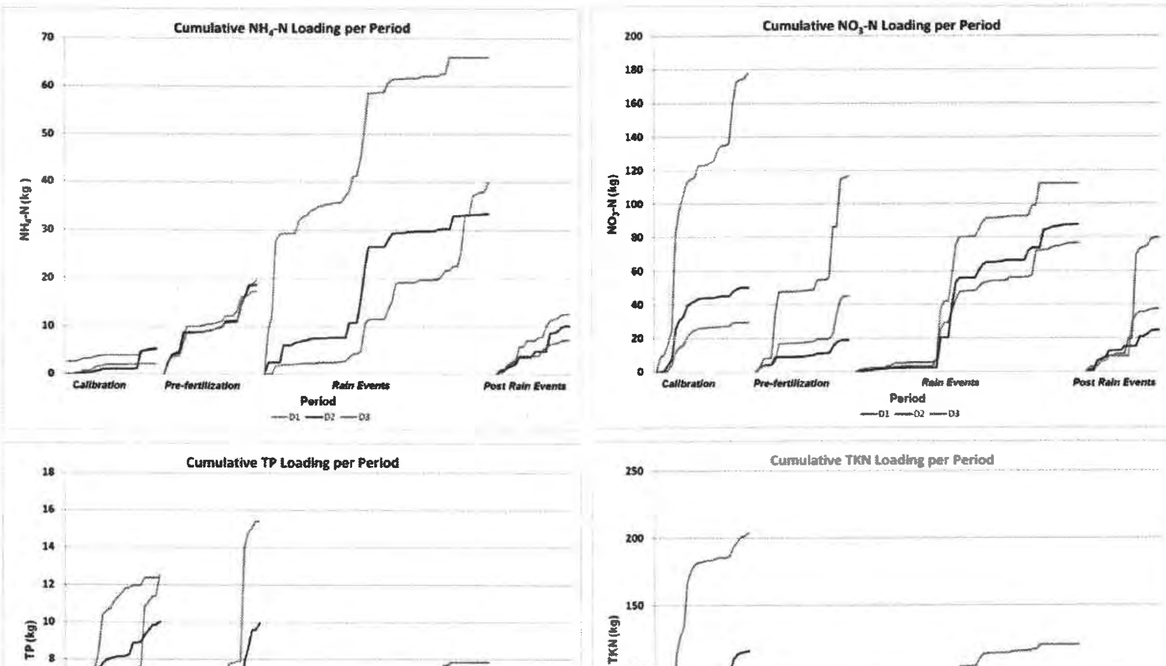

Figure 5. Cumulative nutrient loading measured on a weekly to by-weekly basis on watersheds D1, D2, and D3 during the analyzed periods a) NH_4-N, b) NO_3-N, c) TP, and d) TKN.

A change in cumulative loading patterns is observed in all nutrients except TP during the *Rain Events* period (Figure 5). NH_4-N cumulative loading (Figure 5a) was substantially larger on the control watershed than on both treatment watersheds during *Calibration* and *Pre-fertilization* periods. This pattern is reversed during the *Rain Events* period with both treatment watersheds having larger cumulative nutrient loadings than the control watershed, except for the recently planted watershed (D2) at the end of the period (Figure 5b). Pre-fertilization patterns are observed again during the *Post Rain Events* period. The same pattern is observed on NO_3-N and TKN cumulative loading except for the fact that both treatment watersheds have higher loading than the control watershed at all times (Figures 5c, and 5d). Pre-fertilization patterns are also observed during the *Post Rain Events* period. These results indicate that the increase in nutrient loading on the treatment watersheds was caused by fertilization.

In order to evaluate if the effects of fertilization on nutrient loading were significant, a detailed statistical analysis was conducted again using GLM Procedure. Since the measured loading data during the analyzed periods are not normal, loading data were transformed like nutrient concentration data and the same analyses were performed.

The normalized nutrient loadings reported in kg/ha/yr (Table 5) for D2 during the *Rain Events* was 6.12, 16.05, 0.69, and 14.38 kg/ha/yr for NH_4-N, NO_3-N, TP, and TKN, respectively. For watershed D3 the normalized nutrient loadings during the same period were 10.90, 18.53, 1.29, and 19.87 kg/ha/yr for NH_4-N, NO_3-N, TP, and TKN, respectively. We assume that the difference in nutrient loading between the two treatment watersheds is due to the higher nutrient concentrations measured in the water draining from D3 rather than a significant difference in flow between these two watersheds. Due to weir submergence that caused inaccuracy in outflow calculation, a direct outflow comparison could not be made during the *Rain Events* to unquestionably determine if the nutrient loading difference was due to a change in nutrient concentration in the water or total outflow from the treatment watersheds.

Similarly, *Post Rain Events* nutrient loadings for watershed D2 were 0.30, 0.74, 0.08 and 0.60 kg/ha/yr for NH_4-N, NO_3-N, TP, and TKN, respectively, compared 0.21, 1.18, 0.03, and 0.51 for the same nutrients from the thinned watershed D3. Nutrient loading during *Post Rain Events* are below or near the levels during *Pre-fertilization* which indicates that the increase in nutrient loading was short lived as initially hypothesized and was back to pre-treatment levels as early as three months after fertilization.

With the exception of NH_4-N on D2, all observed nutrient loadings are substantially higher than the expected amounts (Table 5 and Table 6). This is also an indication that fertilization is the cause of the nutrient increase in the water draining from the treatment pine stands.

Finally, we reject our initial assumption that *Calibration* and *Pre-fertilization* are not different. As shown previously, some of the relationships comparing these two periods among the watersheds are significantly different (refer to water quality section for explanation).

Summary and Conclusions

Three large storm events occurred soon after fertilization. A 5-year 24 hr rain event (208 mm) just six days after fertilization, a 1-2-year event (197 mm) 29 days after fertilization, and a third event 47 days after fertilization (46 mm in 46 hr). These rain events provided the opportunity to analyze a worst case type scenario after fertilization, as the trees did not have time to absorb the fertilizer nutrients. We believe this resulted in maximum nutrient concentration and loading in waters drained from the fertilized watersheds.

After analyzing the data, we rejected the initial assumption that Calibration and Pre-fertilization periods are not different. This might be the result of having two different nutrient detection limits in these two periods. The detection limits for all nutrients during the Calibration period were substantially lower than during Pre-fertilization. Different laboratory equipment than the one currently used might have been used during the Calibration period (1989 – 1990). This could be the cause of the different detection limits between Calibration and Pre-fertilization.

Atmospheric deposition is not considered to be a major input of nutrients into the water draining out of these watersheds as ammonia (NH_4-N) and nitrate (NO_3-N) levels do not respond to the fluctuations in atmospheric deposition of nutrients in the area.

NH_4-N, NO_3-N, and total Kjeldahl nitrogen (TKN) concentration and loading increased significantly as a result of fertilization in the treatment watersheds. Except for NO_3-N concentration, which was significantly higher than pretreatment levels during the Post Rain Events period on both treatment watersheds, these increases were short lived and were only detected in the period from September 15 to October 31, 2005 (*Rain Events*). Both nutrient concentrations and loadings were higher on the mature thinned watershed (D3) than on the young watershed (D2). This is attributed to the higher fertilizer rate applied on D3 (1.5 times more than D2) rather than a difference in uptake rates in these watersheds. The nutrient level responses on D3 compared to D2 were not equivalent to the difference in fertilizer application rate between the watersheds. Measured nutrient concentrations and peak loading rates were substantially higher than the average measured values during the treatment period (*Rain Events*).

Total phosphorus (TP) concentration increased only slightly and was significantly higher during the Rain Events than during all other periods on D2. The net increase in average concentration was as high as 0.02 mg/L on D2 and 0.08 mg/L on D3.

Results from this study coincide with those of Binkley et al. (1999) in which nutrient concentration and peak loading rates after fertilization were much higher than the average values. Also, nutrient concentrations during the *Rain Events* were slightly higher than the ones reported by Chescheir et al. (2003) for 75% of study sites in Eastern North Carolina. During the *Post Rain Events* period, all nutrients, except for NO3-N, were below the reported values for 50% of the study sites in the same area. TP export from the treatment watersheds during the Rain Events and thereafter was lower than the annual TP export from all forested sites (0.36 kg/ha/yr) reported by Chescheir et al. (2003). Dissolved inorganic nitrogen (DIN) (NH_4-N, NO_3-N) export during the Rain Events was substantially higher than the value (6.5 kg/ha/yr) for 75% of the study sites reported by the same authors. Export levels were below the DIN value during the Post Rain Events period. It is important to remember that the Rain Events period was only 0.24 yr long and that the annual export values presented during this period are an extrapolation.

Nitrogen as nitrate (NO_3-N) concentration was always below the EPA drinking water standard of 10 (mg N)/L (USEPA, 2001), even during the *Rain Events* period, when the maximum average (0.80 mg NO_3-N/L D3) and peak (4.20 mg NO_3-N /L D3) nutrient concentration values in the treatment watersheds were the highest. To keep the level of ammonia below toxic levels [0.02 – 0.04 mg N/L as ammonia (pH 6.5 – 7.5, temperature 5° – 25°C)], the EPA set a maximum acute concentration of ammonium (NH_4-N) at 21 – 27 (mg N)/L (USEPA, 1996). During this study NH_4-N concentration was always below this range, even during the Rain Events period when the maximum average (1.02 mg NH_4-N/L) and peak (4.70 mg NH_4-N/L) nutrient concentration values in the treatment watersheds were the highest.

A drawback from this study is that although it provides a great opportunity to analyze maximum nutrient concentration and loadings, we believe it might not be an effective study to analyze the long term effects of fertilizer application. This is because we believe that the three major rain events soon after fertilization removed all excess nutrients and did not allow for the system to store nutrients in the soil and release them slowly into the drainage waters. A second drawback from this study is that due to weir submergence that caused some inaccuracy in outflow calculations, a direct outflow comparison could not be made during the *Rain Events* to unquestionably determine if the nutrient loading difference was due to a change in nutrient concentration in the water or total outflow from the treatment watersheds.

Nevertheless, it is remarkable that although nutrient concentrations and loading were at maximum levels, nitrogen levels were still below EPA standard for drinking water. We believe that this is the result of site specific fertilizer formulation and that this is an effective method that should continue to be used as a best management practice.

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