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INSTITUTE OF FOOD AND AGRICULTURAL SCIENCES, UNIVERSITY OF FLORIDA
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Effectiveness of Silviculture Best Management Practices for Forest Fertilization in Pine Straw Production Using Polymer-Coated Urea fertilizer on excessively drained soils in the Suwannee Valley

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SUMMARY

A silvicultural fertilization Best Management Practices (BMPs) effectiveness monitoring project was installed in the fall of 2013 in an eight-year-old slash pine plantation in the Suwannee Valley of Florida. The primary objective of the project was to observe the environmental fate of polymer-coated urea (ESN) applied at 25, 50 or 125 pounds per acre N (28, 56, 140 kg N ha^{-1}). The medium rate is typical of annual nitrogen (N) fertilization in pine straw production. ESN was also compared to non-coated, conventional urea at the medium rate. Three sequential annual fertilizations in June of 2014, 2015 and 2016 compared these four fertilized treatments and a non-fertilized control, in plots with and without annual February pine straw harvesting. Pine straw harvesting (raking) began four months prior to the first fertilization. The fertilized treatments also received 11 lb $acre^{-1}$ (12 kg ha^{-1}) elemental phosphorus (P), 50 lb $acre^{-1}$ (56 kg ha^{-1}) potassium (K), and 8.2 lb $acre^{-1}$ (9 kg ha^{-1}) calcium (Ca) to ensure sufficiency. Three annual fertilizations using the highest examined ESN rate exceeded the Florida BMP maximum amount of N for a three-year period by 50 percent.

Pre-treatment baseline monitoring started in the fall of 2013 and post-treatment monitoring continued until June 2017. Monitoring included periodic measurements of NO_x-N, NH_4-N and total P concentrations in surficial groundwater (along with standard parameters), NO_x-N and NH_4-N concentration in soil solution, the host of soil nutrient concentrations at various depths, ammonia volatilization post-fertilization, dormant season pine foliar nutrient concentrations, quarterly amounts and nutrient concentrations for pine needlefall, annual harvested pine straw yield and nutrient concentrations, and annual dormant season pine growth response and disease incidence. Continuous measurements of rainfall, rain through-fall (through the pine canopy), various weather parameters, and soil moisture and temperature at various depths were collected on-site to help interpret the results.

Major Findings in Fulfillment of Project Goals:

A. Determine the environmental fate of supplied nutrients following three sequential annual fertilizations under a regime of annual pine straw raking.

In soil:

- Fertilization affected only soil nitrate-nitrite (NO_x-N) concentration, which was observed following the second and third fertilization, but concentrations were near the 0.74 mg kg^{-1}

MDL (maximum 1.02 mg kg^{-1}, observed at 0-15 cm depth) and were not dissimilar to pre-fertilization baseline values.

- Although mean comparisons among treatments were not significant, ANOVA slice tests indicated significant effects of fertilization on soil NO_x-N concentrations at 30-180 cm depth fractions at 10.5 months following each fertilization (maximum 2.61 mg kg^{-1}).

In soil solution:

- All fertilization treatments increased nitrate-nitrite (NO_x-N) and ammonium (NH_4-N) concentration in soil solution collected with suction-cup lysimeters at 30-cm depth, compared to the non-fertilized control and to pre-fertilization levels.
- Elevated NO_x-N concentrations were observed from one to 13 or 26 weeks after each fertilization, with peaks at four or eight weeks.
- Soil solution NO_x-N concentrations increased with increasing N application rate. The 98.4 mg L^{-1} maximum concentration, recorded four weeks after the third application of ESN at 140 kg N ha^{-1} in non-raked plots, was more than 200-fold greater than the concentration in the non-fertilized control at that sampling date. At the same time, the lowest ESN rate (28 kg N ha^{-1}) resulted in 39.3 mg L^{-1} NO_x-N, more than 80-fold greater than the control.
- The comparison between conventional urea and ESN applied at the same N rate was not conclusive. We observed the advantage of ESN application only after the first fertilization, when it resulted in a smaller and later peak in NO_x-N concentration (4.6 mg L^{-1} at eight weeks) than urea (10.0 mg L^{-1} at four weeks).
- The period of elevated NH_4-N concentration occurred between one and four weeks after the second and third fertilizations. In general, magnitude and duration of concentration increases corresponded with increasing N application rate. The peak concentrations of 16.0 and 11.6 mg L^{-1} were recorded two weeks after the second urea application in non-raked plots and one week after the third 140 kg N ha^{-1} ESN application in raked plots, respectively.
- Conventional urea resulted in greater NH_4-N increase than ESN applied at the same N rate, especially in the non-raked plots.
- Longer periods of elevated NO_x-N concentration and higher concentrations of NO_x-N and NH_4-N occurring sooner after the third fertilization, suggest a cumulative effect of the three consecutive fertilizations.

In surficial groundwater:

- Surficial groundwater NO_x-N and NH_4-N concentrations in quarterly samples collected from well monitoring of the fertilized area did not increase through the 36-month monitoring period following the first of the three annual fertilizations, when compared to pre-fertilization baseline levels.
- Measures of groundwater NO_x-N and NH_4-N did not exceed the Practical Quantitation Limit (PQL), 0.5 mg L^{-1}, except for NH_4-N at one pre-fertilization sampling date. NO_x-N concentration was below Method Detection Limit (MDL) of 0.148 mg L^{-1}, except for two

sampling dates, three weeks before the first fertilization and 6 months after the second fertilization (0.42 and 0.17 mg L^{-1}, respectively).

- NO_x-N groundwater concentrations stayed substantially below the EPA-established Maximum Contaminant Level Goal (MCLG) for nitrate or nitrite nitrogen of 10 or 1 mg L^{-1}, respectively
- Concentration of groundwater total phosphorus (Pt) fluctuated between 5.7 and 34.0 µg L^{-1}, irrespective of fertilization treatment, and a year after the second fertilization was below the pre-fertilization baseline.

Uptake by pine foliage:

- Fertilization affected pine foliar concentrations of total Kjeldahl nitrogen (TKN), K and Ca (supplied nutrients).
- Comparing treatment TKN concertation averaged across three post-fertilization years, there was a significant positive ESN rate response. All ESN treatments had greater foliar TKN than the non-treated control, and 140 kg N ha^{-1} ESN resulted in significantly greater foliar TKN than any other treatment.
- Comparing the average response for three post fertilization years, foliar TKN concentration was greater (7%) for the 56 kg N ha^{-1} ESN treatment than for the same N rate supplied as conventional urea.
- The lack of fertilization response in foliar total phosphorus (Pt) concentration may be explained by adequate inherent soil Mehlich 3-extractable P (32-55 mg kg^{-1} at 0-15 cm depth), soil pH below 5.5 (fostering P precipitation by Al and Fe in soil), and low inherent P mobility in the soil.
- Foliar K concentration was generally higher for fertilized treatments compared to the non-fertilized control and declined with increasing N fertilization rate, which may be due to corresponding mass increases.
- Foliar Ca concentration was effected only after the first fertilization, and was greater following ESN at 140 kg N ha^{-1} or conventional urea at 56 kg N ha^{-1} than observed for the non-fertilized control (Ca concentration increases of 20 or 18%, respectively).

In pine needlefall:

- Fertilization positively affected concentration and content of total Kjeldahl nitrogen (TKN), K and Ca (supplied nutrients) in pine needlefall and, to a lesser degree, Mg content.
- Treatment effects on the nutrient contents in the needlefall were the result of combined effects on the needlefall DM and nutrient concentrations.
- A positive needlefall TKN concentration response to ESN rate was observed after the first fertilization and increased with consecutive fertilizations, suggesting a cumulative effect.
- ESN rates of 56 or 140 kg N ha^{-1} resulted in higher TKN concentrations than non-fertilized control every year, but the greatest difference (40%) was observed after the

third ESN application at 140 kg N ha^{-1}. Conventional urea application at 56 kg N ha^{-1} increased the TKN 3-year concentration average.

- Needlefall TKN content response to fertilization was similar to that of TKN concentration, except that the significant effects began after the second rather than first fertilization.
- Needlefall TKN concentration or content were not affected by fertilizer formulation (ESN versus conventional urea) when applied at the same N rate of 56 kg ha^{-1}.
- In general, needlefall total P (Pt) concentration was lower for fertilized treatments than for the non-fertilized control, but the difference was significant only after the second fertilization when highest ESN rate resulted in 20% lower Pt concentration than the control. A similar tendency was observed for needlefall Pt content, but fertilization effect was not significant in any year.
- Both needlefall K concentration and K content were higher in all fertilized treatments than in non-fertilized control. There were no differences among the fertilized treatments as they all received the same rate of K.
- Needlefall Ca concentration and content generally increased with ESN rate from 28 to 140 kg N ha^{-1}, even though Ca application rate was the same for all ESN treatments. Both concentration and content were higher for ESN applications at 140 kg N ha^{-1} than for the non-fertilized control.
- Fertilizer form significantly affected needlefall Ca concentration, and not Ca content, but both measures were generally higher following fertilization with conventional urea compared to ESN applied at the same N rate.
- Needlefall Mg concentration was not affected by fertilization, but Mg content was higher for ESN at 140 kg N ha^{-1} than for the non-fertilized control, after the second and third application.
- TKN, Pt, and K concentrations in the needlefall were generally lower than in the foliage, but the treatment effects were similar for both types of tissue.
- Mg needlefall and foliar concentrations were similar.
- Ca concentration in the needlefall was higher than in the foliage, possibly because this nutrient is least mobile in the plant and was not retrieved from foliage before senescence.

Nutrient removals by pine straw raking:

- Increased pine straw yields with fertilization were accompanied by greater removals of TKN, K, Ca and Mg.
- The high ESN rate resulted in the greatest cumulative nutrient removal, and increased removals relative to the control by 49% for TKN, 85% for K and 32% for Mg. The high ESN rate resulted in greater Ca removals than other fertilized treatments, but was not different from the non-treated control.
- Computing mass balance as a function of cumulative fertilization inputs and removals, the non-fertilized control had a deficit of -48.7 kg TKN, -4.2 kg Pt, -5.9 kg K, -73.9 kg Ca and -9.7 kg Mg per hectare.

- Annual applications of 28 kg N ha^{-1} as ESN more than compensated for N removals in annual pine straw harvesting.
- Fertilized treatments had Ca deficits ranging from -33.8 to -64.6 kg ha^{-1} (27.4 kg ha^{-1} Ca was supplied in all, except conventional urea), and Mg deficits from -9 to -12.8 kg ha^{-1}.

Volatile losses of ammonia:

- The 140 kg N ha^{-1} ESN and 56 kg N ha^{-1} urea treatments volatilized significantly higher amounts of NH_3 (6.71 mg L^{-1} and 6.09 mg L^{-1}, respectively) than the control (0.30 mg L^{-1}) one week after fertilization, which was 22.6 and 20.5 times greater than the control, respectively.
- The 140 kg N ha^{-1} ESN treatment yielded significantly higher amounts of volatilized NH_3 for weeks 2 thru 7 when compared to all the other treatments.
- NH_3 volatilization for the 28 kg N ha^{-1} ESN treatment was not significantly different than the control over all weeks.
- NH_3 volatile losses were significantly lower on raked plots when compared to non-raked plots over the first four weeks after fertilization.

B. Compare leaching potential and nutrient budgets for fertilization in raked versus non-raked stands.

Leaching potential:

- Raking did not have a significant effect on soil nutrients except that aluminum concertation at 30-60 cm depth was greater in non-raked than in raked plots.
- In general, soil solution NO_x-N concentration was greater in raked plots after urea application, but in non-raked plots after ESN application.
- Effects of pine straw raking were not consistent, but generally soil solution NH_4-N concentrations were greater for non-raked than raked treatments.

Nutrient budgets:

- Harvested pine straw TKN concentration was increased after two annual fertilizations with the high ESN rate, and after three fertilizations all fertilized treatments increased TKN and K concentration relative to the non-fertilized control by up to 29% and 73%, respectively.
- We did not observe a consistent effect of annual pine straw harvesting on any foliar nutrient after four years. However, after the first raking foliar Ca and Mg were approximately 8% greater in raked than non-raked plots, which may be explained by increased mineralization rates with raking disturbance and subsequent uptake by pines.
- NH_3 volatile losses were significantly lower on raked plots when compared to non-raked plots over the first four weeks following fertilization.

C. Determine tree growth and pine straw yield responses following a wide range of N fertilization rates to guide cost-effective fertilization practices.

Tree growth responses:

- The effect of annual raking was not significant on any pine response variable, nor was there any interaction between fertilization and raking treatments.
- When nitrogen was supplied as ESN pine mortality increased with increasing N rate, and at the highest rate, 140 kg N ha^{-1}, the number of pines per hectare and pine survival were significantly less than observed in the non-fertilized control.
- Conventional urea applied at the standard 56 kg N ha^{-1} rate did not differ from the non-treated control in pines per hectare or pine survival.
- Annual fertilization with the standard 56 kg N ha^{-1} rate using ESN reduced average height and height of dominant and codominant trees relative to the non-fertilized control; whereas, fertilization with conventional urea at 56 kg N ha^{-1} did not differ from the control.

Pine straw yield:

- Harvested pine straw yield began to show a response following the second fertilization, at the third raking. At the forth raking bale count and dry weight was greater for the high ESN rate than any other treatment, except dry weight following fertilization with conventional urea. At the fourth raking the high ESN rate increased bale count by 35% and dry mass by 30% over the non-treated control.

D. Provide pertinent information in support of Extension training and education programs for fertilization practices in pine straw production.

– Please see "EDUCATION" summary on next page

BMPS:

Florida silvicultural BMPs specify that over a three year period applied fertilizers should not exceed 280 kg N ha^{-1} (250 lb N $acre^{-1}$ N) or 90 kg elemental P ha^{-1} (80 lb P $acre^{-1}$). Three annual applications of the highest polymer coated urea (ESN) rate tested provided 420 kg N ha^{-1}, 150% of the maximum BMP limit. All fertilizer treatments provided 37 kg elemental P ha^{-1} (33 lb P $acre^{-1}$) over three annual applications, 41% of the BMP maximum. In soil, fertilization elevated only NO_x-N concentration, 10.5 months following the second and third fertilizations, at 30 to 180 cm depth. The maximum concentration, observed with the high ESN rate after the second fertilization, was 2.61 mg kg^{-1} at 120 to 180 cm depth.

All fertilization treatments increased soil solution NO_x-N and NH_4-N concentrations sampled by suction-cup lysimeters at 30 cm depth, compared to the non-fertilized control and pre-fertilization baseline levels. Elevated NO_x-N concentrations were observed from one to 13 or 26 weeks after each fertilization, with peaks at four or eight weeks. Soil solution NO_x-N concentrations increased with increasing N application rate. The 98.4 mg L^{-1} maximum concentration, recorded four weeks after the third application of ESN at 140 kg N ha^{-1} in non-raked plots, was more than 200-fold greater than the concentration in the non-fertilized control at that sampling date. At the same time, the lowest ESN rate (28 kg N ha^{-1}) resulted in 39.3 mg L^{-1} NO_x-N, more than 80-fold greater than the control. The period of elevated NH_4-N concentration occurred between one and four weeks after the second and third fertilizations. In general, the magnitude and duration of NH_4-N concentration increases corresponded with increasing N application rate. The peak concentrations of 16.0 and 11.6 mg L^{-1} were recorded two weeks after the second urea application in non-raked plots and one week after the third 140 kg N ha^{-1} ESN application in raked plots, respectively. Conventional urea resulted in greater NH_4-N increase than ESN applied at the same N rate, especially in the non-raked plots. Longer periods of elevated NO_x-N concentration, and higher concentrations of NO_x-N and NH_4-N occurring sooner after the third fertilization, suggest a cumulative effect of the three consecutive fertilizations.

Despite elevated concentrations in soil solution following fertilization, surficial groundwater NO_x-N and NH_4-N concentrations in quarterly samples collected from well monitoring of the fertilized area did not increase through the 36-month post-fertilization monitoring period, when compared to pre-fertilization baseline levels.

Increased pine straw yields with fertilization were accompanied by greater removals of TKN, K, Ca and Mg. The high ESN rate resulted in the greatest cumulative nutrient removal, and increased removals relative to the control by 49% for TKN, 85% for K and 32% for Mg. The high ESN rate resulted in greater Ca removals than other fertilized treatments, but was not different from the non-treated control. Computing mass balance as a function of cumulative fertilization inputs and removals, the non-treated control had a deficit of -48.7 kg TKN, -4.2 kg Pt, -5.9 K, -73.9 Ca and -9.7 Mg per hectare. Annual applications of 28 kg N ha^{-1} as ESN more than compensated for N removals in annual pine straw harvesting. Fertilized treatments had Ca deficits ranging from -33.8 to -64.6 kg ha^{-1} (27.4 kg ha^{-1} Ca was supplied in all), and Mg deficits from -9 to -12.8 kg ha^{-1}.

Together with results from previous monitoring projects in our program, models are being developed to quantify nutrient budgets and potential leaching losses in southern pine plantations using diammonium phosphate (DAP), urea, and polymer coated urea N fertilizer materials. Our research will provide a scientific basis for verification or improvement of current silvicultural BMPs to protect water quality in Florida and the region. Current guidelines do not address controlled release materials or repeated annual fertilizations, which some growers employ.

EDUCATION:

In addition to providing guidance to the Florida Forest Service supporting BMP revisions, we have an active University Extension outreach program to growers, which has been supported by the current DEP Nonpoint Source grant award and two prior 319 grants. From 2010 through 2017 this program included 22 workshops with 3,166 total contact hours. Of the 475 participants evaluated, 97% indicated that they learned something new, 70% said they intended to change management practices as a result of the information they obtained, and 53% said they learned something that would reduce their cost or increase profitability. When asked to list specific changes in behavior or economic status as the result of something they learned, common responses included:

- Change in pine straw management regime to protect soil and water resources (will adopt less frequent pine straw raking, fertilize to replace removed nutrients, limit the raking period to five years, etc.)
- Change in pine straw management practices to increase profitability (will consider discounted returns for both pine straw and timber values in deciding optimal rotation length, consider projected internal rate of return when deciding on investment inputs such as fertilization, manage competing vegetation to improve straw yields and quality, change planting density to improve overall profitability, etc.)
- Will use soil tests or foliar nutrient status to guide fertilization recommendations

- Will follow silvicultural fertilization BMPs to safeguard water quality

Presentations at Research Conferences and Extension Workshops Supported by the Current Section 319 Award[1]:

*Whann, A. and P.J. Minogue. 2016. Fate of applied nitrogen from urea and polymer coated urea in silvicultural fertilization. Fifth University of Florida Water Institute Symposium. February 16-17, 2016. Gainesville, FL. (selected)

Osiecka, Anna. 2013. Pine Straw Program. Alternative Income from Your Forest Expo. January 16, 2013. Bear Creek Educational Forest, Gadsden County, FL. (Invited)

Published Proceedings Abstracts:

Cristan, R., P.J. Minogue, and A. Osiecka. 2018. Effect of harvesting pine straw on ammonia volatilization following polymer-coated and non-coated urea fertilizer applications on a North Florida slash pine plantation. Water Institute Proceedings, University of Florida. February 6-7, 2018. Gainesville, FL. (selected)

Osiecka, A., P.J. Minogue, and R. Cristan. 2018. Effects of fertilization and pine straw removal from slash pine plantations on the concentration of ammonium and nitrate-nitrite nitrogen in soil solution. Water Institute Proceedings, University of Florida. February 6-7, 2018. Gainesville, FL. (selected)

Cristan, R., P.J. Minogue, and A. Osiecka. 2017. Effect of pine straw raking on ammonia volatilization following nitrogen fertilization of slash pine. Proceedings Society of American Foresters National Convention, November 15-18, 2017. Albuquerque, NM. (In press)

Refereed Extension and Journal Papers:

*Chevasco, E.D., P.J. Minogue, C.L. Mackowiak, and N.B. Comerford. 2016. Fertilization and pine straw raking in slash pine plantations: P removals and effects on total and mobile soil, foliage and litter P pools. Forest Ecology and Management 376:310-320.

Osiecka, A., P.J. Minogue and E.D. Dickens. 2015. Guide to Fertilization for Pine Straw Production on Coastal Plain Sites. University of Florida Cooperative Extension Service Circular. 17 p. http://edis.ifas.ufl.edu/fr378

Popular Publications (non-refereed):

Dickens, E.D., D.J. Moorhead, P.J. Minogue, R. Franklin. 2016. Fertilization in Longleaf Pine Stands. Longleaf Leader, Longleaf Alliance, Vol. IX:18-20.

Published Thesis, Master of Science:

*Whann, A. 2016. Fate of applied nitrogen from urea and polymer coated urea in silvicultural fertilization. Thesis submitted to University of Florida Graduate School in partial fulfillment of the Master of Science degree. August 2016. Gainesville, Florida. 70 pp. (see abstract in appendix)

Please see Section 8.0, Educational Tasks, for planned publications

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[1] * denotes graduate student

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1.0 INTRODUCTION

1.1 Fertilization for Pine Straw Production

Pine straw producers in North Florida typically apply repeated applications of mineral fertilizers, with diammonium phosphate, ammonium nitrate, and urea being most common (Minogue et al. 2007a). Nutrient use efficiencies for fertilization of southern pines are typically about 50% (Fox et al. 2007a). Nitrogen and phosphorus removals from pine straw raking are largely a function of the harvestable area, site productivity, and stand conditions. Studies in the Georgia Piedmont showed removals for a single raking varied widely, ranging from 5-60 lb N and 0.5-5 lb P per acre (Morris et al. 1992). Morris et al. (1992) provide specific fertilization recommendations for Piedmont old field or cutover sites, different stand ages, raking frequencies, and various site types, but they do not recommend fertilization for sandhill sites characterized by soils with surface horizons greater than 40 inches deep without fine textured subsoils. Specific guidelines for sandy Coastal Plain soils and use of slow release fertilizers are lacking in the literature.

1.2 Potential Concerns with Pine Straw Removal

Pine straw serves many important purposes in the forest stand and there are concerns that its removal can have detrimental effects on tree growth and stand health. Mineralization of pine straw is part of normal nutrient cycling in pine stands (Switzer and Nelson 1972, Gholz et al. 1985, Jorgensen and Wells 1986). Nutrients can be replaced by fertilization, but pine straw also has an important effect on soil moisture, improving water infiltration and reducing evaporative water loss in much the same way as it does when used in ornamental applications as mulch (Duryea 2003). Decomposing pine needles add to soil organic matter thus improving nutrient availability and soil water holding capacity. Removing pine straw can increase tree water stress on dry sites (McLeod et al. 1979, Ginter et al. 1979) and can also increase soil bulk density (Haywood et. al 1998). In the Florida Sand Ridge region there are large areas of deep sand, excessively drained soils with little soil profile development (CRIFF group G), where silvicultural practices should strive to maintain soil organic matter, thus providing better soil moisture availability and tree nutrition (Jokela and Long, 2000). Pine litter also protects the soil from erosion, improves water infiltration (Pote et al. 2004) and insulates against rapid temperature changes. Because of these important benefits of pine litter in the forest, it is recommended that pine straw should not be removed more than five times during the stand's life (Duryea 2003).

1.3 Impacts of Forest Fertilization on Water Quality

Many published reviews have examined the impacts of forest fertilization on water quality (Tamm et al. 1974, Fredriksen et al. 1975, Norris et al. 1991, Bisson et al. 1992, Binkley and Brown 1993, Shephard et al. 1994, Binkley et al. 1999, Anderson 2002, Fulton and West 2002, Aust and Blinn 2004, Michael 2004, Grace et al. 2005). All of these reviews have reached a similar conclusion that standard forest fertilization practices, usually occurring one to three times in a 30 to 50 year rotation, are not detrimental to water quality. However, many pine straw producers are fertilizing annually without adequate guidance regarding appropriate fertilizer rates or precision in application. In their recent review, Binkley et al. (1999) emphasized the need for further studies examining effects of repeated applications and larger scale studies, as we are conducting. Most studies have focused on only two forms of N, nitrate and ammonium. Very little is known about other forms on N, such as dissolved organic N, which is the predominant form of nitrogen in streams of conifer forests of the southeast. Our study assesses TKN as well as NO_X and NH_4 to quantify nitrogen in organic complexes.

Because soils in Florida have low P-fixing capacity, the fate of applied phosphorus is of special concern. Only one study (Harris et al. 1980) in the US has reported the effects of phosphorus fertilization on soil solution chemistry in forests. This is a significant gap in the literature which is being addressed in our study. Also, the effect of phosphorus fertilization is often delayed. Riekerk (1989) reported the maximum concentration of P was observed in streams in a significantly wet year four years after fertilization, suggesting that short-term studies may not be sufficient to determine leaching losses. Our study quantifies P leaching following annual fertilization through quantification of total phosphorus and plant available P using Mehlich III extraction.

Pines grown on the sandy, excessively drained sites of the Sand Ridge do not respond well to fertilization (Fisher and Garbett, 1980) and nutrient leaching to groundwater, which can be only 10 m from the surface, is a real concern (German 1997). On an excessively drained, deep sandy site in the Florida Sand Ridge the flux of nitrate-nitrite movement observed using lysimeters at a four foot depth was observed only 12 weeks following spring DAP fertilization (Minogue et al. 2007, Minogue et al. 2013). Our study determines nutrient dynamics and leaching potential in an eight year old slash pine stand on a location representing the extreme high leaching potential in north Florida.

Coated slow release fertilizers, including sulfur coated urea (SCU) and various polymer coated urea (PCU) fertilizers reduce volatile losses, but also provide slow release of N, thus extending the period for plant uptake and reducing potential leaching losses as well. Polymer coated urea has been utilized in forest management, and its cost may be justified by high pine straw product values, which typically range between $100 and $200 per acre. Polymer coated urea is comprised of a soluble urea nitrogen source core, which is coated with one of several polymer materials including linseed oil, polyethylene, polypropylene, or various other organic polymers. Nitrogen is released through the polymer coating by diffusion, and the release rate increases strongly with increasing temperature. The rate of nitrogen release can be manipulated by coating thickness and composition. Polymer coated urea products are a newer technology than sulfur coated urea and generally are more expensive. However, they contain higher amounts of N (typically 44% vs. 34% N) and provide superior long-term fertilization, significantly reducing the amounts of N needed as compared to conventional mineral fertilizers.

1.4 Florida Silvicultural Fertilization BMP's

Existing silvicultural fertilization BMP’s include several specific criteria and recommend "developing a nutrient management plan based on soil, water, plant and organic material sample analysis based on desired timber yields to supply nutrient inputs efficiently; so that the benefit of fertilization is captured by target vegetation and the adverse effects to water resources are minimized " (Anonymous 2003). The current BMP guidelines stipulate certain maximum amounts:

Forestry fertilization BMP’s for elemental N:

- No more than 1000 lb $acre^{-1}$ (1121 kg ha^{-1}) over any 20-year period.
- No more than 250 lb acre-1 (280 kg ha^{-1}) for any 3-year period
- No more than 80 lb $acre^{-1}$ (90 kg ha^{-1}) during the first 2-years of newly established plantations

Forestry fertilization BMP's for elemental P:

- No more than 250 lb $acre^{-1}$ (280 kg ha^{-1}) over any 20-year period
- No more than 80 lb $acre^{-1}$ (90 kg ha^{-1}) for any 3-year period

1.5 Project Location and Site Description

This project utilized an eight year old slash pine plantation (31.8 acres) on private ownership in Suwannee County, FL (approximately 3 miles S-SE of Live Oak, FL) (Table I1 and Figure I1). The soil at the study site is described as Bonneau-Blanton-Padlock complex (Ultisols) with inclusions of Alpin and Chipley (Entisols) (USDA-NRCS 2017). According to soil texture analyses, the top 30-cm layer was characterized as sand throughout the study area and was composed of 89.6 to 97.6% sand, 0.4 to 4.4% clay and 0 to 6.4% silt, with very little difference between 0 to 15 and 15 to 30-cm layers. These soils occur over unconfined Floridian Aquifers in the Suwannee Valley Region and Florida Sand Ridge; representing a worst case scenario with respect to leaching potential and groundwater contamination. This work examined the effectiveness of current silviculture fertilization BMPs to provide needed information for nutrient management in pine straw production, so that the benefit of fertilization is captured by tree crops and the adverse effects on water resources are minimized.

Table I1. Information regarding the Live Oak study site.

Geographic location	Suwannee County, FL
Latitude and Longitude	N 30° 14.003, W 83° 01.047
Impacted watershed name	Lower Suwannee County, FL
HUC	31102050102
WBID	3422B
Affected waterbody	Lower Suwannee River Basin
Impairment	Dissolved oxygen and nutrients; N and P concentrations
Land owner	Mr. Tommye Collins

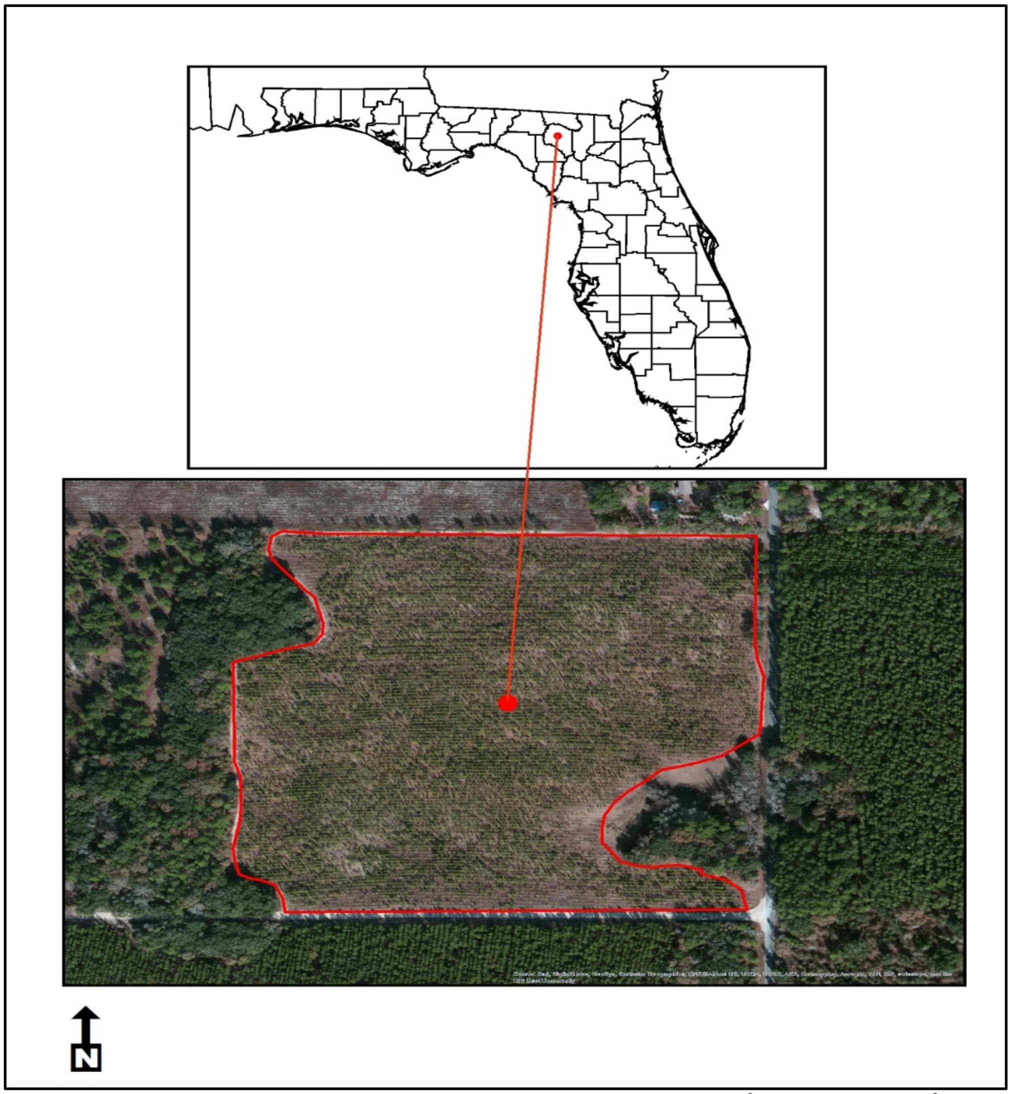

Figure I1. Site location in Suwannee County, Florida. (N 30⁰ 13.931 W 83⁰ 00.922)

2.0 PROJECT GOALS

The scope of this research project included applied and basic questions regarding: (1) the fate of applied N and P for a wide range of polymer-coated urea (ESN) controlled release fertilization rates (plus standard TSP) as compared to conventional urea plus DAP fertilization; (2) forest stand level nutrient budgets; and (3) effects of pine straw removal on nutrient cycling, tree growth, straw harvest yields, and soil chemical and physical properties. The primary objective was to assess the effectiveness of current silviculture fertilization BMP's to reduce nonpoint source pollution, as is consistent with EPA's "iterative process" for long-term BMP improvement. Specific objectives included:

1. Determine the environmental fate of N and P following three sequential annual fertilizations using a wide range of ESN application rates: 28, 56, 140 kg N per hectare (25, 50, 125 lb N per acre), plus standard 28 kg ha^{-1} (25 lb $acre^{-1}$) P_2O_5 from TSP, as compared to a non-fertilized control and conventional urea + DAP treatment, providing 56 kg ha^{-1} (50 lb $acre^{-1}$) N and 28 kg ha^{-1} (25 lb^{-1}) P_2O_5.
2. Compare leaching potential and nutrient budgets for fertilization in raked versus non-raked stands to refine forest fertilization BMP's and provide new information regarding the efficient use of fertilizers in pine straw production in the Suwannee Valley.
3. Determine tree growth and pine straw yield responses following a wide range of N fertilization rates to guide cost-effective fertilization practices for sandy soils of the Suwannee Valley, where the potential for leaching of applied nutrients is significant.
4. Provide pertinent information in support of Extension training and education programs for fertilization practices in pine straw production.

3.0 METHODS

3.1 Experimental design

The experiment was a factorial design with treatments randomly assigned in three complete blocks, testing the main effects of two pine straw raking levels (raked or non-raked), five levels of fertilization and the interaction of fertilization and raking (Table M1). The treatments were blocked according to treatment plot mean baseline pine tree height measures prior to treatment. Annual fertilization treatments included: a non-fertilized control, three rates of polymer-coated urea (ESN® Smart Nitrogen) supplying 28, 56 or 140 kg elemental N ha^{-1} (25, 50 or 125 lb N $acre^{-1}$), and one rate of a standard operational non-coated urea, supplying 56 kg N ha^{-1}, equal to the middle ESN rate. Triple superphosphate (TSP) was blended with the ESN treatments and diammonium phosphate (DAP) was blended with the standard urea fertilizer at appropriate rates to maintain P supply constant for all fertilized treatments at 12 kg elemental P ha^{-1} annually (10.7 lb P $acre^{-1}$). Muriate of potash (KCl) was included with all fertilizer treatments at 56 kg ha^{-1} to avoid K deficiency.

Table M1. Raking and nitrogen fertilization treatments with polymer-coated urea (ESN) and non-coated urea (Urea).

Treatment #	Raking Treatment	Fertilization Treatment	Annual fertilizer rate						Elemental nutrient							
									Annual rate				Supplied with three fertilizations			
			N		Other[1]				N	P	K	Ca	N	P	K	Ca
			(kg ha^{-1})													
1	Non-raked	Control (non-fertilized)	-			-			0	0	0	0	0	0	0	0
2	Non-raked	ESN 28 (low rate)	ESN	64	TSP	61	KCl	112	28	12	56	9	84	37	168	28
3	Non-raked	ESN 56 (medium rate)	ESN	127	TSP	61	KCl	112	56	12	56	9	168	37	168	28
4	Non-raked	ESN 140 (high rate)	ESN	318	TSP	61	KCl	112	140	12	56	9	420	37	168	28
5	Non-raked	Urea 50	Urea	98	DAP	61	KCl	112	56	12	56	0	168	37	168	0
6	Raked	Control (non-fertilized)	-			-		-	0	0	0	0	0	0	0	0
7	Raked	ESN 28 (low rate)	ESN	64	TSP	61	KCl	112	28	12	56	9	84	37	168	28
8	Raked	ESN 56 (medium rate)	ESN	127	TSP	61	KCl	112	56	12	56	9	168	37	168	28
9	Raked	ESN 140 (high rate)	ESN	318	TSP	61	KCl	112	140	12	56	9	420	37	168	28
10	Raked	Urea 50	Urea	98	DAP	61	KCl	112	56	12	56	0	168	37	168	0

[1]Additional P and K fertilization applied at the same elemental rate to all treatments (except for the Control) to avoid deficiency. Elemental P rate 12 kg P ha^{-1} equals 28 kg P_2O_5 ha^{-1}

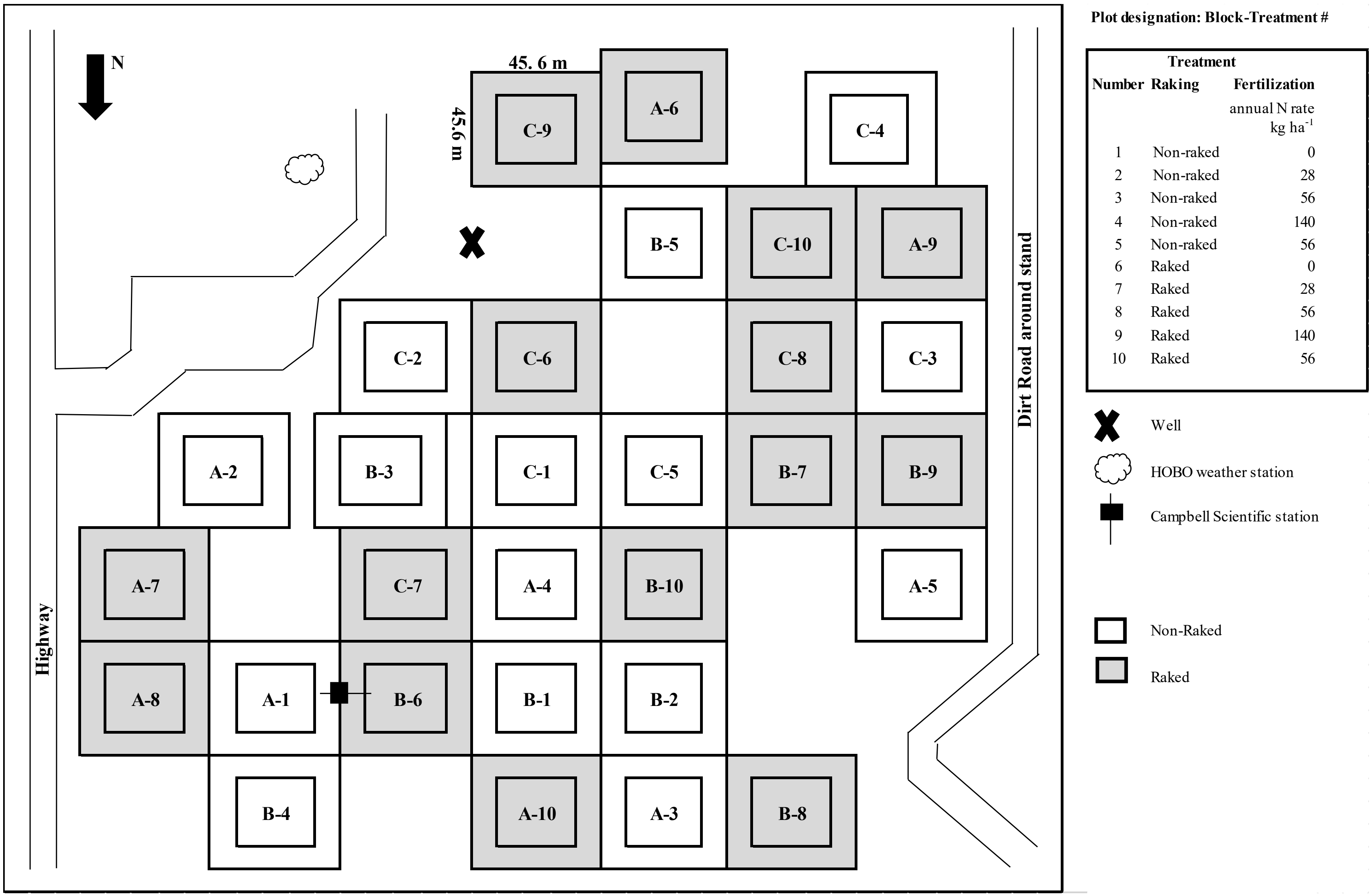

Figure M1. A factorial design tested five levels of fertilization in raked versus non-raked plots, comprising ten treatments (1-10), which were randomized within three blocks (A-C). The 30 treatment plots were 45.6 by 45.6 m, with a concentric 15.2 by 15.2-m measurement plot. Pine straw was raked annually from 15 treatment plots (in gray). A well, a weather station and a Campbell Scientific station were located on the site.

3.2 Treatment Application

Each of the 10 treatments was applied to three 45.6 by 45.6-m (150 by 150-ft) treatment plots (Figure M1). Pine straw harvesting (raking) occurred in February of 2014, 2015, 2016 and 2017. Pine straw from each entire raked treatment plot was raked and baled manually by a commercial crew. Fertilization treatments were applied by the University of Florida associates in mid-June of 2014, 2015, and 2016. Fertilizer blends (Table M1) were pre-weighted for small sections of measurement plots and uniformly hand-applied on the same day in all treatments. During measurement plots fertilization, 1 by 1 m areas around lysimeters were covered by plastic sheets and subsequently fertilized with fertilizer blends pre-measured for 1 m^2 areas to increase precision of application rates. For the application to the ammonia chamber areas, each component of each fertilizer blend was weighted separately on the analytical scale to ensure the exact amount and proportion of nutrients applied to a small area under each chamber: 90 cm^2 in case of open-chambers (bottle method) and 519 cm^2 in case of semi-open chambers (bucket method). The components were then mixed in the same proportions as the fertilizer blends and uniformly applied to the areas under the chambers. The treatment plots outside the measurement plots were hand-fertilized in sections with volumetrically measured amounts of fertilizer blends.

3.3 Sample Handling and Custody

All sampling and measurements were conducted within 15.2 by 15.2-ft measurement plots (Figure M2) centered in treatment plots to ensure a minimum 30.5 m buffer between each two measurement plots.

3.3.1 Environmental monitoring: Groundwater

Florida DEP personnel installed a monitoring well on site as specified in DEP SOP PCS-006 Design, Installation, and Placement of Monitoring Wells. Groundwater samples were collected directly into labeled 20-mL vials using a peristaltic pump. Two 20-mL vials labeled by date and unique sample number were used to collect a sufficient volume for analyses for each of two replicate groundwater samples to be analyzed for nitrate-nitrite N (NO_x-N), ammonium N (NH_4-N), and total P (Pt) concentration. Samples were preserved with H_2SO_4 to pH < 2 immediately after collection. As they were being collected, samples were placed in plastic bags on ice in a cooler. Samples were analyzed at the UF/IFAS Environmental Water Quality Lab (EWQL) within 28 days from sampling. All water sampling procedures followed FS 2200 Groundwater Sampling. All sample handling followed Table FS 1000-4, Required Containers, Preservation Techniques, and Holding Times for Water/Wastewater Samples. Samples were delivered to EWQL with a chain of custody sheet and EWQL confirmation of requested certified analyses.

All sampling equipment and storage containers met the requirements of FS1000 General Sampling Procedures. All pumps and other equipment used in the collection of water samples were properly rinsed or purged according to FS 1004. Duplicate samples and blanks of deionized water were taken during sampling events according to FQ 1000 to ensure integrity of samples.

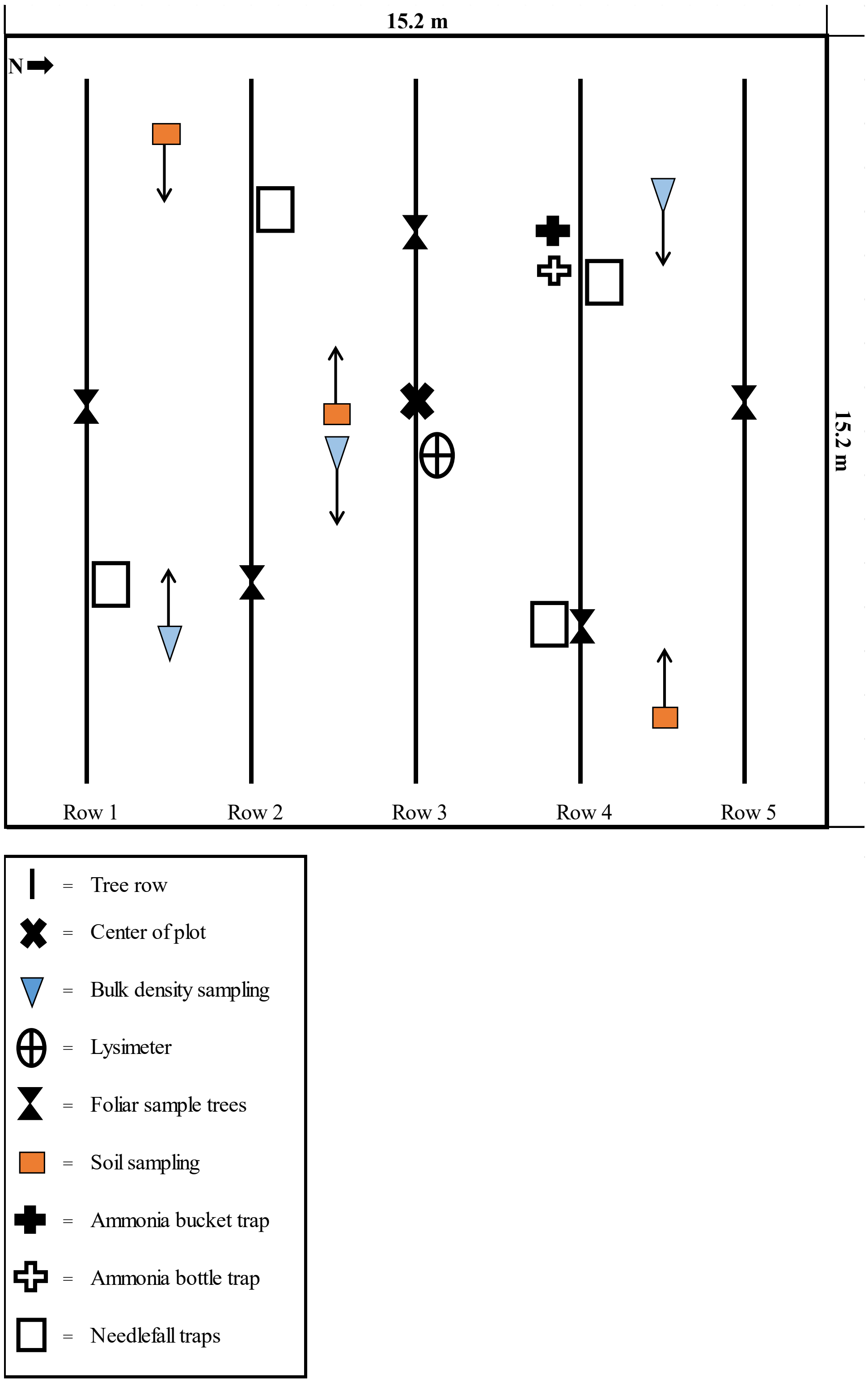

Figure M2. Layout of sampling points within measurement plots.

3.3.2 Engineering modeling: Soil and plant tissue

Soil nutrient samples were placed in labeled paper bags and kept cool in a plastic cooler during field sampling and transportation to the lab. All samples were dried in a forced air drier at less than 40º C for as long as necessary to obtain constant dry weight, then ground, and sieved to pass a 2 mm (No. 10 mesh) screen. A composite sample was formed from equal amounts of the three subsamples taken from each of the various profile depths and homogenized. Composite samples were placed in Analytical Research Laboratory (ARL) provided 473-cm^3 (1-pint) bags and delivered to ARL. Each set of samples was identified by a unique set number (assigned by ARL after receiving Sample Analysis Request Form) from the time of sample submission, through laboratory analyses, reporting of results, results QAQC, to data analyses. All processes were conducted in accordance with FS 1002 Contamination Prevention and Sampling Collection Order. All equipment used was cleaned as practical and possible according to FS1004 Container and Equipment Rinsing. Equipment used for soil sampling conformed to guidelines of equipment construction listed in DEP-SOP-001/01 Table FS 1000-1 and Table FS 1000-2.

Soil core samples were labeled, capped, placed in a shock-free container, and kept in a cool condition to maintain structural integrity. Sampling, handling, and analysis followed the standard procedures specified in the Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods (Klute, 1986).

Sampling, handling, and storage of needlefall samples followed a common sampling protocol which is described in Soil Testing and Plant Analysis (Walsh and Beaton 1973) and Plant Analysis Handbook II (Mills and Jones 1996). Each sample set was identified with a unique ARL set number from submission to data analyses.

Composite foliar tissue samples were collected in the field and transported in labeled paper bags to the laboratory. After being properly dried, tissue samples were ground to produce a homogenized composite sample, which were placed in Whirl-Pak bags and submitted to ARL. Each sample set was identified with a unique ARL set number from submission to data analyses. Sampling, handling, and storage of foliar samples followed a common sampling protocol which is described in Soil Testing and Plant Analysis (Walsh and Beaton 1973) and Plant Analysis Handbook II (Mills and Jones 1996).

3.4 Analytical Methods

3.4.1 Environmental monitoring: Groundwater and soil solution

EWQL is responsible for all sample care and testing upon submission. EWQL follows EPA methods (U.S. EPA, 1993) for their water analysis, and EWQL is NELAP certified for solution analysis (Table M2).

Table M2. Summary of analytical methods used for solution at the University of Florida EWQL Laboratory, showing the method detection limit (MDL) and the US EPA practical quantitation limit (PQL).

Nutrient analyte in solution	EPA Method # (certified)	Digestion	Accuracy (above PQL)	MDL (mg L^{-1})	PQL (mg L^{-1})
Nitrate + nitrite nitrogen (NO_x-N)	353.2	N/A	90-110%	0.1480	0.50
Ammonium nitrogen (NH_4-N)	350.1 (UF modified)	N/A	90-110%	0.0625	0.50
Total phosphorus (Pt)	365.1	Ammonium persulfate	90-110%	0.0025	0.01

3.4.2 Engineering modeling: Soil and plant tissue

The ARL laboratory follows the National Environmental Laboratory Accreditation Program (NELAP) recommendations for soil and tissue analyses, but is not NELAP certified for these analyses. For soil analyses, ARL follows SW846 according to Method of Soil Analysis in SSSA Book Series No. 5 (Sparks, 1996). For tissue analyses, ARL follows the CRC Reference Methods for Plant Analysis (Kalra, 1998). All soil and tissue analytes are tested in solution after digestion and extraction (Table M3 and Table M4).

Table M3. Summary of analytical methods used for soil at the University of Florida ARL Laboratory, showing the method detection limit (MDL) and the US EPA practical quantitation limit (PQL).

Nutrient analyte in soil	EPA Method #	Extraction/ Digestion	Accuracy (above PQL)	MDL (mg kg^{-1} DM)	PQL (mg kg^{-1} DM)
Nitrate + nitrite nitrogen (NO_x-N)	353.2	KCl	85-115%	0.74	2.5[1]
Ammonium nitrogen (NH_4-N)	350.1 (UF modified)	KCl	85-115%	0.32	2.5[1]
Total Kjeldahl nitrogen (TKN)	351.2	Kjeldahl	85-115%	12.50	50.0[2]
Total phosphorus (Pt)	365.1	HCl 6M	85-115%	1.25	5.0[3]
Phosphorus (P)	200.7	Mehlich 3	85-115%	12.50	50.0[4]
Potassium (K)	200.7	Mehlich 3	85-115%	12.50	50.0[4]
Calcium (Ca)	200.7	Mehlich 3	85-115%	50.00	200.0[4]
Magnesium (Mg)	200.7	Mehlich 3	85-115%	25.00	100.0[4]
Iron (Fe)	200.7	Mehlich 3	85-115%	5.00	20.0[4]
Aluminum (Al)	200.7	Mehlich 3	85-115%	25.00	100.0[4]

[1]reflect KCl extraction; [2]reflect Kjeldahl digestion; [3]reflect HCl digestion; [4]reflect Mehlich 3 extraction

Table M4. Summary of analytical methods used for plant tissue at the University of Florida ARL Laboratory, showing the method detection limit (MDL) and the US EPA practical quantitation limit (PQL).

Nutrient analyte in tissue	EPA Method #	Extraction/ Digestion	Accuracy (above PQL)	MDL (mg kg^{-1} DM)	PQL (mg kg^{-1} DM)
Total Kjeldahl nitrogen (TKN)	351.2	Kjeldahl	85-115%	250	1000
Total phosphorus (Pt)	200.7	HCl 6M	85-115%	125	500
Potassium (K)	200.7	HCl 6M	85-115%	500	2000
Calcium (Ca)	200.7	HCl 6M	85-115%	250	1000

3.5 Quality Control

The principal objectives of quality control measures are to ensure that the samples are representative of the source, and that the accuracy, precision, and sensitivity of the methods follow DEP SOPs, as identified below.

3.5.1 Environmental monitoring: Groundwater

During groundwater sampling, one field-cleaned equipment blank and one laboratory blank of deionized water were taken according to FQ 1000 Field Quality Control Requirements. Two replicate groundwater samples (each consisting of groundwater collected into two 20-mL sample vials to obtain the needed volume) were taken per sampling date. The two replicate groundwater samples were acidified in the field to preserve nutrient concentration and analyzed for NO_x-N, NH_4-N and Pt.

The project QA manager or the designee affixed a printed sample identification label on each sample container during field sampling. The project QA manager entered the sample ID numbers in the project data base. Accuracy ranges for each analytical method are given in Table M2. The EWQL follows NELAP quality control recommendations including running matrix spikes, method blanks, laboratory control standards, initial and continuing calibration verification, and replicates. All quality control and quality assurance requirements outlined in DEP Contract G0370 are followed by EWQL.

3.5.2 Engineering modeling: Soil and plant tissue

When dried soil or tissue samples were ground, the grinder was cleaned with compressed air to remove residual material between samples. Ground samples were placed in clean labeled plastic or paper bags and sent to ARL for analysis. Accuracy ranges for each soil and plant tissue analytical method are listed in Table M3 and Table M4. ARL follows NELAP quality control recommendations including running matrix spikes, method blanks, laboratory control standards, initial and continuing calibration verification, and replicates.

3.6 Instrument and Equipment Calibration and Maintenance

An automated weather station and soil moisture and temperature sensors were installed on-site to monitor local climatic conditions. All monitoring sensors were factory calibrated and installed per manufacture's specification. In order to minimize equipment malfunction, data was downloaded every other month, and was compared with local long-term weather station data (such as NOAA and UF/IFAS/Florida Automated Weather Network, FAWN). Equipment was examined visually during site visits to ensure that all was in good working condition. Field equipment installation, calibration, and maintenance followed procedures specified in FT 1900 Continuous Monitoring with Installed Meters.

All sampling equipment (vacuum pumps, soil corers, etc.) were cleaned after each use in accordance with FC 1000 Cleaning/Decontamination Procedures. Laboratory instruments and equipment were inspected before use and maintained in accordance with ARL/EWQL Standard Operating Procedures.

3.7 Inspection and Acceptance of Supplies and Consumables

All soil nutrient samples and groundwater samples were collected in clean new containers that meet FC 1000 Cleaning/Decontamination Procedures. Replacement parts and consumables for laboratory instrumentation were sourced from the original equipment manufacturer. Each analyte used dedicated glassware for reagent preparation. Low level analyses such as total phosphorus for groundwater used only trace metal grade acids.

3.8 Non-direct Measurements

Current and historical data from publicly available NOAA and/or FAWN weather stations has been compared with collected data and is being used in decision making.

3.9 Data Management

All paper-form field and laboratory records are stored in the Forestry Program library at the NFREC, Quincy, FL. All electronic data storage hardware and software are updated by certified IFAS Information Technology personnel only. At least two backup copies of data are updated and kept on CD or other removable storage device in addition to data kept on the University of Florida Server. All paper-form and electronic data will be retained for a minimum of five years after the end of the project. Quarterly progress reports to Michael Barr, DEP, include a copy of all current data with labeling of measured attributes, sampling dates, and units of measure. All laboratory and field records are linked by sample acquisition numbers. These numbers followed the samples from the field, to the laboratory, and back to the data base with all results. Microsoft Excel has been used for data entry and dataset management.

3.10 Statistical Analysis

Statistical analyses of the collected data were performed with SAS 9.4 software (SAS 2012). Analysis of variance, mean comparisons, and regression/trend analysis methods have been examined. Detailed description of statistical methods used for analyzing each dataset precedes discussion of the corresponding results in the 6.0 Project outcomes section.

4.0 PROJECT TASKS SUMMARIES

The environmental fate of applied N and P and pine stand responses were determined following three sequential annual applications of various rates of polymer-coated urea (ESN), a controlled-release fertilizer, plus standard P amounts using TSP, as compared to a conventional urea plus DAP treatment and a non-fertilized control, in an eight-year old slash pine stand with or without annual pine straw removal (Table M1). Specifically:

1. Groundwater NOx-N, NH_4-N, and TP concentrations were monitored weekly for four weeks prior to fertilization, then quarterly for one year following each of three sequential June fertilizations. One monitoring well was placed in the treatment area.
2. Concentrations of NO_x-N and NH_4-N were assessed in the soil solution collected by suction-cup lysimeters at 30-cm depth at 3 months, 1 month, and 2 weeks prior to the first fertilization, then at 1, 2, and 4 weeks, and at 2, 3, 6, 9, and 12 months following each fertilization.
3. Soil matrix nutrient monitoring to 180-cm depth had been done annually in May prior to each fertilization event and at 10.5 months after the third fertilization, and included a host of plant macronutrients in various forms (NO_x-N, NH_4-N, TKN, Pt, $P_{Mehlich\ 3}$, K, Ca, Mg). Soil Al and Fe concentrations were measured at these same assessment dates to facilitate

application of the Florida Phosphorus Index to evaluate leaching potential (Hurt et al. 2013). Soil pH was determined for 0 to15 and 15 to 30-cm depths at each assessment date.

4. Nutrient budgets for fertilization in pine straw production were determined by monitoring foliar nutrient status, periodic sampling of needlefall mass and nutrient content, harvested pine straw mass and nutrient content, and the measures of the soil matrix nutrients listed above.
5. Soil organic matter (OM) content within the upper 30 cm of the soil profile was analyzed at each soil matrix sampling time to evaluate the effect of straw removals and fertilization on this important index of sustainability. Soil bulk density was measured for each treatment prior to study initiation and at study completion. Soil texture will be examined prior to study completion.
6. Continuous monitoring of rainfall, tree crown rain throughfall, wind speed, air psychometric parameters, and soil moisture and temperature at various depths were recorded with solar and battery powered instrumentation on-site to help interpret the results.
7. Ammonia (NH_3) loss by volatilization were determined by using open chamber ammonia traps (bottles) (Jantalia et al. 2012) and semi-open ammonia traps (buckets) (Nômmik, 1973).

5.0 PROJECT TASKS

5.1 Impacts to Soil Nutrients

Composite soil samples were taken from each measurement plot to assess nutrient status in May 2014, prior to the first fertilization and in May of 2015 and 2016 before each annual fertilization. The last soil sampling was conducted in May 2017, 10.5 months after the third fertilization. At each assessment, a location near the center and in two quadrants of each measurement plot, representative of stand conditions, was selected for nutrient sampling and marked with a wire flag after sampling, so that these disturbed locations would be avoided in subsequent assessments. A bucket auger was used to collect loose soil samples from five depths in the upper soil profile (0 to15, 15 to 30, 30 to 60, 60 to 120, and 120 to 180 cm). Soil samples were taken from a point midway between pine rows. The same depth fractions from the three sample locations within the measurement plot were combined to form one composite sample for each depth and mixed to uniformity in the laboratory. Soil nutrient samples were analyzed for NO_{x}-N, NH_{4}- N, TKN, Pt, $P_{Mehlich\ 3}$, K, Ca, and Mg concentrations. Soil Al and Fe concentrations were also measured at these same assessment dates to facilitate application of the Florida Phosphorus Index to evaluate leaching potential (Hurt et al. 2013). Samples were analyzed by ARL.

Soil sampling frequency and number of samples:

$5_{\text{depth composites}}$ x 30_{plots} x 4_{dates} = 600 soil samples

5.2 Impacts to Soil Solution NO_x-N and NH_4-N

Ceramic cup suction-cup lysimeters were placed on the tree rows equidistant from the planted pines near the center of each measurement plot to periodically assess soil solution NO_x-N and NH_4-N concentrations. The porous cup was placed at 30 cm depth in the sandy A2 horizon (layer of maximum leaching). Soil water samples were collected at 3 months, 1 month, and 2 weeks prior to the first fertilization, then at 1, 2, and 4 weeks, and at 2, 3, 6, 9, and 12 months following each fertilization. Samples were analyzed by EWQL.

5.3 Impacts to Surficial Groundwater

To assess potential groundwater quality change, a well was installed by DEP personnel in the treatment area at the project site. Well depth was sufficient to reach surficial groundwater (estimated 6 to 9 m deep). Groundwater NO_x-N, NH_4-N, and Pt concentrations were monitored weekly for a month prior to the first fertilization, then quarterly for one year following each of three sequential June fertilizations. Samples were analyzed by EWQL.

5.4 Impacts to Soil Organic Matter

Soil organic matter (OM) content within the 0 to 15 and 15 to 30-cm depth fractions was determined concurrently with annual soil matrix nutrient sampling to evaluate the effect of pine straw removal and fertilization on this important index of sustainability.

5.5 Impacts to Soil Bulk Density

Soil bulk density was measured for each treatment plot prior to study initiation and at study completion. Soil bulk density was determined by soil core sampling at a point midway between pine rows at three locations in each measurement plot. Soil bulk density was monitored near the measurement plot center, and in two measurement plot quadrants.

5.6 Impacts to Foliar Nutrients

Foliar nutrient concentrations of the first flush of current-year growth were assessed in the dormant season prior to the first raking (December 2013 to January 2014) and after the subsequent three growing seasons. One composite foliar tissue sample from four dominant or co-dominant pines was taken within the measurement plot and placed in a paper bag. The composite samples were dried at 52 to 55 ˚C to constant weight and ground in our laboratory at the NFREC. Three aliquots of each sample were sealed in plastic Whirl-Pak bags and delivered to ARL for determination of TKN, Pt, K, Ca, and Mg concentrations.

Foliar nutrient samples from current-year pine foliage:

$$(3_{\text{aliquots}} \text{ x } 30_{\text{plots}} + 3_{\text{standards}}) \text{ x } 4_{\text{dates}} = 372 \text{ samples}$$

5.7 Impacts to Needlefall Yield and Nutrients

Litter traps were used to evaluate periodic needle cast mass and nutrient concentration responses to fertilization and raking treatments. Four litter traps (1.0 by 0.5 m) were placed in each measurement plot. Traps were placed between two trees in pine rows in areas with good crown canopy, and sampled quarterly after each of the three annual fertilization events (i.e. in September, December, March, and June ending a year after the 3rd fertilization). All non-needle material was discarded and needlefall from all four traps within a plot was combined for a composite sample and dried at 52 to 55 ˚C to determine total dry mass per plot. After grinding a composite sample, three aliquots were sent to ARL for determination of TKN, Pt, K, Ca, and Mg concentrations.

Needlefall nutrient samples from litter traps:

$$(3_{\text{aliquots}} \text{ x } 30_{\text{plots}} + 3_{\text{standards}}) \text{ x } 12_{\text{dates}} = 1{,}116 \text{ samples}$$

5.8 Impacts to Pine Straw Yield and Nutrients

The total number of bales commercially raked and removed from each plot were counted and the fresh mass of 12 bales per plot was determined in the field. A composite sample (approximately 100 g) from each of the 12 bales was placed in a sealed plastic zip lock bag and transported to our laboratory at the NFREC where percent moisture content was determined for the harvested straw, in order to estimate bale dry mass. The samples were dried at 52 to 55 ˚C. Following moisture content determination, 12 bale samples from each plot were combined for a single composite sample per plot and ground. Three aliquots of each sample were sealed in plastic Whirl-Pak bags and delivered to ARL for determination of TKN, TP, K, Ca, and Mg concentration.

Pine straw bale moisture content samples to determine bale dry weight:

$$12_{bales} \text{ x } 15_{plots} \text{ x } 4_{dates} = 720 \text{ samples}$$

Pine straw nutrient samples to determine pine straw removals:

$$(3_{aliquots} \text{ x } 15_{plots} + 3_{standards}) \text{ x } 4_{dates} = 192 \text{ samples}$$

5.9 Impacts to Ammonia Volatile Losses

In 2015, 30 semi-open ammonia chambers (buckets) were installed in 15 non-raked plots (2 per plot) to determine ammonia (NH_3) volatile losses following fertilization (2nd fertilization). Chambers were 22.7-L (6 gallons) and had the bottoms removed. Plastic blocks were installed inside the chambers to create two levels from the bottom of the chambers (10 cm and 20 cm). Foam disks (Hibco Plastics: 1370 charcoal urethane) were inserted on both levels weekly for 4 weeks and then monthly for two months. Prior to field installation, foam disks were soaked in 7.6-L (2-gallon) Ziploc bags with 150 mL of sulfuric acid solution (1M H_2SO_4 and 4%v/v Glycerol) for 24 h. Only bottom (closest to ground) disks were replaced and examined for NH_3 volatile losses. Initial field installation consisted of 60 disks (30 tops and 30 bottoms) and the bottom disks were changed out weekly for 4 weeks and then monthly for two months and examined for NH_3 volatile losses. The extraction process consisted of adding 200 mL of 2M KCl solution to each bag (with disk) and working the KCl solution into disk and then squeezing the solution out of the disk and filtering it through quantitative grade (#2) filter paper and into a 500 mL volumetric flask. Another 100 mL of KC solution was then added to the bags and the process was repeated. Analysis of the extract was conducted by the soils lab at the UF IFAS NFREC using an ammonia/nitrate analyzer (TL2X00, Timberline Instruments) (Whann 2016, see Appendix A for thesis abstract).

After the 3rd fertilization in 2016, two methods were used to measure NH_3 volatilization and were based on: (1) semi-open chamber described by Nommik (1973), Zerpa and Fox (2011), and Elliot and Fox (2014) (similar method as 2015) and (2) open chamber method described by Jantalia et al (2012). One open- and one semi-open chamber were installed near the center of each plot prior to fertilization on all raked and non-raked plots. Semi-open chambers consisted of the same chambers as the 2015 study (only non-raked plots in 2015). Open-chambers (bottle method) consisted of 2-L emptied and cleaned soda bottles with the bottoms removed. The bottom section was attached upside down to the top portion of the bottle using a pizza topper and Velcro which allowed for airflow and protection from rainfall while a suspended 89-mL cup held a 60-mL bottle which suspended landscape fabric soaked in 1M H_2SO_4 and 4%v/v Glycerol to collect NH_3 losses. Sampling was conducted weekly for 12 weeks.

Foam disc (semi-open chambers) NH_4 extraction included three sequential extractions of 100 mL of 2 M KCl and filtered into individual 500 mL volumetric flasks. Extraction of NH_4 from the 60 mL bottles and landscape fabric included three sequential extractions of 25 mL of 2 M KCl solution and filtered into 250 mL volumetric flasks. Approximately 19 mL of each extraction solution was poured into 20 mL bottles and frozen until analysis could be conducted. Analysis was conducted in the Soil and Water Science Laboratory at the University of Florida, North Florida Research and Education Center in Quincy, Florida using an ammonia/nitrate analyzer (TL2X00, Timberline Instruments) to quantify concentration of NH_4-N.

5.10 Pine Stand Response to Fertilization and Pine Straw Raking

All pines (approximately 35) within each measurement plot were identified by a unique number on a permanent metal tag placed at diameter breast height [DBH, at 4.5 ft (137 cm) from ground-line] and were measured for total live height and DBH. Additionally, an ocular estimate of disease incidence/severity and crown class was performed. Measurements were made in the dormant season prior to treatment and in the dormant season following each of the three fertilization events. Tree total live height, diameter at breast height, and crown class measurements follow standard forestry methods as described in Forest Mensuration (Avery and Burkhart, 2002).

Pine sampling intensity: $1{,}050_{trees}$ x 4_{years} = 4,200 tree samples

5.11 Weather Monitoring

Continuous monitoring of rainfall, throughfall (rain through the tree canopy), wind speed, air psychrometric parameters, and soil moisture and temperature at different soil depth fractions was recorded with solar and battery powered instrumentation to help interpret the results.

6.0 PROJECT OUTCOMES

6.1 Impacts to Soil Nutrients

6.1.1 Summary

- Analysis of variance showed a significant fertilization effect only for soil NO_x-N concentration, which was observed following the second and third annual fertilization, but measured concentrations were near the 0.74 mg kg^{-1} MDL (maximum 1.02 mg kg^{-1}) and were not dissimilar to pre-fertilization baseline values.
- Although mean comparisons among treatments or depths were not significant, ANOVA slice tests indicated significant effects of fertilization on soil NO_x-N concentrations at 30-180 cm depth fractions at 10.5 months following each fertilization (maximum 0.75 mg kg^{-1}, less than MDL).

6.1.2 Statistical analyses of soil nutrient concentration

Analysis of variance was performed for each soil variable by sample date (BF, F1, F2, F3) as a randomized complete block (RCB) split-plot design with sample depth nested within main-plots that received fertilization or raking treatments. A log transformation was required for all soil variables except pH to improve the homogeneity of variance. The covariance structure for sample depth was examined because sample depths are not randomly assigned as in a typical split-plot design. Three covariance structures were compared with respect to simplicity and Akaike's information criteria. The three structures compared were compound-symmetric (CS) with depths equicorrelated (as in the usual analysis of a split-plot design), Toeplitz with correlations identical between depths the same number of sampled depths apart, and spatial power (SP) with correlations dependent on distance between samples (Schabenberger and Pierce, 2002). The midpoint of sample depths (3, 9, 18, 36, and 60 cm) were used to determine distance between sampled depths for the spatial power model. Covariance structures were well defined in most instances, but the simplest was chosen when one structure was not decisively superior. The SP structure was appropriate for AL, Ca, Fe, K, Mg, TKN and TP where correlations were high between adjacent depths but diminished quickly toward zero with distance apart. The Toeplitz structure was appropriate for P and pH where correlation was high between adjacent depths, but zero or negative for sample depths further apart. The CS structure was best for NH_3, NO-x and percent organic matter (OM) where correlation was positive, but did not depend on distance apart. The analysis of percent OM included only the upper two sample depths.

6.1.3 Results and discussion - soil nutrient concentration

The pre-fertilization baseline sampling and each of the three sampling dates 10.5 months after sequential annual June fertilizations were analyzed separately. The full ANOVA showed significant depth effects for all measured nutrient concentrations and soil pH at all sampling dates, including the pre-fertilization baseline (Table S1). Fertilization affected soil NO_X-N concentration at 10.5 months following the second and third fertilization, but fertilization did not affect other nutrients or soil pH. A significant fertilization by depth interaction was observed for soil NO_X-N following the first and second fertilization.

Slice tests were used to examine soil NO_X-N concentration in each of the sampling depth fractions at 10.5 months after each fertilization. Following the first fertilization a significant fertilization effect was shown for NO_X-N concentration at 30-60 cm and 120-180 cm depth (Table S2). A significant fertilization effect was shown for NO_X-N concentration at 60-120 and 120-180 cm depth after the second fertilization (Table S3), and at 30-60 and, marginally (P=0.052), at 120-180 cm depth after the third fertilization (Table S4). Mean comparisons for differences among treatments or depths were not significant. The high ESN rate generally raised soil NO_X-N concentration to the greatest extent when compared to the non-treated control; however, concentrations following fertilization treatments were near 0.74 mg kg^{-1} MDL (maximum 1.02 mg kg^{-1}) and not dissimilar to baseline values for the various depths (Table S5).

Table S1. ANOVA[1] showing the significance (*P*>F)[2] of fertilization (Fert), pine straw harvest (Rake), soil depth (Depth) and the interactions of these factors for nutrient concentrations and pH in soil 1.5 months before and 10.5 months after three annual June fertilizations and 2.5 months after each of four annual February pine straw harvests.

Factor	Variable										
	NO_x-N	NH_4-N	TKN	Pt[3]	P[4]	K	Ca	Mg	Al	Fe	pH
	1.5 months before 2014 fertilization (-1.5 MAF1)[5], 2.5 months after 2014 raking										
Fert	0.141	0.923	0.804	0.173	0.906	0.644	0.541	0.823	0.492	0.202	0.866
Rake	0.222	0.662	0.259	0.936	0.597	0.409	0.607	0.724	0.340	0.719	**0.045**
Fert x Rake	0.181	0.534	0.568	0.614	0.660	0.569	0.746	0.899	0.831	0.665	0.281
Depth	**0.007**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Depth	0.687	0.256	0.892	0.614	0.675	0.582	0.723	0.961	0.796	0.191	**0.030**
Rake x Depth	0.481	0.432	0.301	**0.028**	0.942	0.887	0.716	0.834	0.763	0.415	0.086
Fert x Rake x Depth	0.987	0.455	0.921	0.463	0.658	0.868	0.971	0.957	0.553	0.439	0.485
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking										
Fert	0.062	0.924	0.904	0.412	0.953	0.977	0.906	0.840	0.151	0.544	0.998
Rake	0.919	0.360	0.138	0.944	0.545	0.520	0.811	0.874	**0.027**	0.060	0.111
Fert x Rake	0.604	0.807	0.954	0.774	0.477	0.878	0.836	0.518	0.449	0.699	0.125
Depth	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Depth	**0.005**	0.631	0.850	0.348	0.546	0.731	0.894	0.954	0.575	0.924	0.814
Rake x Depth	0.474	0.704	0.434	0.978	0.581	0.720	0.643	0.658	0.579	0.765	0.867
Fert x Rake x Depth	0.547	0.440	0.975	0.392	0.631	0.639	0.605	0.759	0.464	0.557	0.946
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking										
Fert	**0.002**	0.553	0.892	0.504	0.785	0.891	0.899	0.881	0.410	0.827	0.920
Rake	0.108	0.958	0.690	0.690	0.588	0.675	0.498	0.918	**0.043**	1.000	0.905
Fert x Rake	0.101	0.614	0.764	0.743	0.087	0.865	0.774	0.540	0.585	0.963	0.146
Depth	**0.031**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Depth	**0.003**	0.422	0.812	0.629	0.093	0.589	0.430	0.544	0.426	0.993	0.434
Rake x Depth	0.278	0.989	0.440	0.694	0.493	0.803	0.672	0.573	0.669	0.752	0.911
Fert x Rake x Depth	0.137	0.211	0.210	0.507	0.581	0.958	0.682	0.428	0.851	0.885	0.896
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking										
Fert	**0.047**	0.970	0.643	0.263	0.570	0.456	0.835	0.697	0.642	0.950	0.174
Rake	0.318	0.855	0.184	0.763	0.607	0.810	0.981	0.920	0.096	0.768	0.108
Fert x Rake	0.497	0.798	0.631	0.836	0.098	0.940	0.735	0.553	0.881	0.827	0.437
Depth	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Depth	0.686	**0.039**	0.451	0.354	0.599	0.781	0.805	0.373	0.961	0.893	0.595
Rake x Depth	0.145	**0.041**	0.240	0.319	0.438	0.971	0.800	0.636	0.763	0.543	0.411
Fert x Rake x Depth	0.109	0.435	**0.020**	0.567	0.667	0.527	0.762	0.754	0.306	0.810	0.900

[1]Separate ANOVA for each assessment date.
[2]Bold $P \leq 0.05$ denotes a significant effect.
[3]Pt = total phosphorus (6M HCl digestion).
[4]P = plant available phosphorus (Mehlich 3 extraction).
[5]MAF1 = months after the first fertilization.

Table S2. ANOVA slice tests showing the significance (*P*>F)[1] of fertilization, pine straw harvesting (raking) and interaction of these factors for nutrient concentrations and pH in soil at different depths 10.5 months after the first fertilization (2014) with urea or polymer coated urea (ESN) at different rates, which also occurred 2.5 months after the second raking (2015).

Soil depth increment (cm)	Variable										
	NO_x-N	NH_4-N	TKN	Pt[2]	P[3]	K	Ca	Mg	Al	Fe	pH
	Fertilization effect at each depth										
0-15	0.370	0.861	0.619	0.954	0.329	0.802	0.597	0.640	0.132	0.724	0.500
15-30	0.606	0.197	0.653	0.814	0.791	0.909	0.762	0.786	0.379	0.858	0.766
30-60	**0.018**	0.799	0.816	0.266	0.933	0.898	0.920	0.982	0.153	0.878	0.911
60-120	0.095	0.817	0.825	0.274	0.961	0.897	0.590	0.787	0.331	0.785	0.835
120-180	**<0.001**	0.539	0.702	0.151	0.811	0.661	0.707	0.313	0.909	0.148	0.939
	Raking effect at each depth										
0-15	0.393	0.685	0.788	0.753	0.440	0.391	0.239	0.462	0.107	0.087	0.152
15-30	0.601	0.469	0.336	0.752	0.295	0.585	0.639	0.805	0.340	0.158	0.061
30-60	0.372	0.161	0.054	0.986	0.329	0.587	0.622	0.557	0.066	0.760	0.271
60-120	0.950	0.510	0.082	0.942	0.843	0.357	0.931	0.668	0.079	0.229	0.417
120-180	0.403	0.950	0.930	0.628	0.450	0.678	0.763	0.547	0.929	0.140	0.543
	Fertilization x raking interaction at each depth										
0-15	0.349	0.512	0.969	0.998	0.219	0.976	0.439	0.804	0.080	0.719	0.368
15-30	0.858	0.291	0.929	0.976	0.701	0.967	0.939	0.973	0.646	0.400	0.369
30-60	0.059	0.869	0.598	0.188	0.938	0.861	0.997	0.996	0.099	0.981	0.267
60-120	0.263	0.890	0.714	0.331	0.994	0.942	0.930	0.933	0.128	0.858	0.771
120-180	**0.005**	0.710	0.853	0.588	0.888	0.588	0.341	0.067	0.996	0.138	0.900

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]Pt = total phosphorus (6M HCl digestion).
[3]P = plant available phosphorus (Mehlich 3 extraction).

Table S3. ANOVA slice tests showing the significance (*P*>F)[1] of fertilization, pine straw harvesting (raking) and interactions of these factors for nutrient concentrations and pH in soil at different depths 10.5 months after the second fertilization (2015) with urea or polymer coated urea (ESN) at different rates, which also occurred 2.5 months after the third raking (2016).

Soil depth increment (cm)	Variable										
	NO_x-N	NH_4-N	TKN	Pt[2]	P[3]	K	Ca	Mg	Al	Fe	pH
	Fertilization effect at each depth										
0-15	0.150	0.372	0.575	0.868	0.717	0.562	0.358	0.550	0.353	0.865	0.107
15-30	0.629	0.749	0.942	0.888	0.385	0.724	0.609	0.718	0.223	0.937	0.680
30-60	0.068	0.380	0.747	0.441	0.294	0.558	0.779	0.954	0.261	0.818	0.814
60-120	**<0.001**	0.404	0.519	0.200	0.695	0.606	0.619	0.461	0.625	0.777	0.925
120-180	**<0.001**	0.415	0.959	0.514	0.789	0.956	0.899	0.647	0.963	0.860	0.980
	Raking effect at each depth										
0-15	0.826	0.839	0.708	0.924	0.580	0.858	0.900	0.831	0.262	0.484	0.500
15-30	0.191	0.775	0.772	0.936	0.708	0.902	0.823	0.852	0.134	0.492	0.822
30-60	0.819	0.919	0.122	0.622	0.163	0.429	0.312	0.375	**0.019**	0.623	0.731
60-120	0.357	0.855	0.884	0.535	0.993	0.489	0.612	0.798	0.195	0.700	0.846
120-180	**0.015**	0.816	0.398	0.160	0.881	0.937	0.311	0.726	0.625	0.607	0.516
	Fertilization x raking interaction at each depth										
0-15	0.071	0.604	0.903	0.997	0.633	0.950	0.510	0.914	0.389	0.981	0.237
15-30	0.118	0.699	0.976	0.990	0.060	0.971	0.857	0.977	0.316	0.986	0.413
30-60	0.276	0.317	0.432	0.668	0.086	0.842	0.928	0.738	0.157	0.917	0.743
60-120	**<0.001**	0.395	0.641	0.136	0.408	0.678	0.764	0.353	0.516	0.827	0.764
120-180	**<0.001**	0.786	0.487	0.356	0.857	0.982	0.816	0.430	0.999	0.940	0.937

[1]Bold *P*≤0.05 denotes a significant effect.
[2]Pt = total phosphorus (6M HCl digestion).
[3]P = plant available phosphorus (Mehlich 3 extraction).

Table S4. ANOVA slice tests showing the significance (*P*>F)[1] of fertilization, pine straw harvesting (raking) and interactions of these factors for nutrient concentrations and pH in soil at different depths 10.5 months after the third fertilization (2016) with urea or polymer coated urea (ESN) at different rates, which also occurred 2.5 months after the fourth raking (2017).

Soil depth increment (cm)	Variable										
	NO_x-N	NH_4-N	TKN	Pt[2]	P[3]	K	Ca	Mg	Al	Fe	pH
	Fertilization effect at each depth										
0-15	0.972	0.084	0.933	0.968	0.308	0.541	0.764	0.249	0.581	0.993	**0.024**
15-30	0.995	0.985	0.908	0.989	0.463	0.361	0.854	0.369	0.842	0.978	0.129
30-60	**0.045**	0.196	**0.048**	**0.045**	0.419	0.237	0.523	0.614	0.859	0.987	0.347
60-120	0.198	0.361	0.891	0.484	0.732	0.764	0.840	0.504	0.562	0.569	0.918
120-180	**0.052**	0.501	0.632	0.108	0.993	0.692	0.833	0.929	0.655	0.847	0.850
	Raking effect at each depth										
0-15	0.609	0.051	0.432	0.632	0.609	0.910	0.720	0.264	0.196	0.439	**0.035**
15-30	0.600	0.863	0.981	0.997	0.749	0.866	0.688	0.688	0.191	0.415	0.126
30-60	0.639	0.517	**0.038**	0.431	0.386	0.900	0.886	0.858	0.056	0.748	0.332
60-120	**0.021**	0.805	0.703	0.631	0.578	0.586	0.912	0.768	0.428	0.494	0.426
120-180	0.205	0.068	0.355	0.074	0.537	0.850	0.274	0.488	0.859	0.987	0.756
	Fertilization x raking interaction at each depth										
0-15	0.985	0.166	0.977	0.998	0.697	0.876	0.857	0.502	0.510	0.989	0.052
15-30	1.000	0.768	0.921	1.000	0.131	0.847	0.874	0.720	0.869	0.983	0.121
30-60	0.074	0.413	**0.005**	0.139	0.148	0.550	0.939	0.908	0.506	0.979	0.312
60-120	**0.042**	0.470	0.720	0.443	0.397	0.824	0.923	0.455	0.472	0.778	0.936
120-180	**0.009**	0.439	0.479	0.055	0.993	0.572	0.730	0.698	0.848	0.989	0.988

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]Pt = total phosphorus (6M HCl digestion).
[3]P = plant available phosphorus (Mehlich 3 extraction).

Table S5. Soil NO_x-N concentration (mg kg^{-1}) at different depths in non-raked and raked plots 2.5 months after each of four annual February pine straw harvests (raking) and 1.5 months before or 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Soil depth increment (cm)	Non-raked					Raked				
	Fertilizer									
	ESN				Urea	ESN				Urea
	Annual nitrogen application rate (kg N ha^{-1})									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
	1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking									
0-15	0.59	0.74	0.69	0.85	0.70	0.78	0.75	0.69	1.14	0.71
15-30	0.67	0.65	0.64	0.71	0.68	0.61	0.61	0.76	0.77	0.56
30-60	0.54	0.62	0.54	0.69	0.75	0.64	0.56	0.57	0.73	0.53
60-120	0.51	0.60	0.51	0.61	0.72	0.66	0.53	0.65	0.76	0.53
120-180	0.58	0.59	0.62	0.59	0.49	0.81	0.57	0.82	0.66	0.58
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking									
0-15	0.42	1.02	0.70	0.79	0.32	0.55	0.57	0.92	0.94	0.86
15-30	0.92	0.68	0.49	0.43	0.60	0.51	0.67	0.38	0.50	0.69
30-60	-0.06	0.40	-0.13	0.59	-0.06	0.05	-0.08	-0.11	0.33	-0.01
60-120	-0.10	0.03	0.07	0.64	0.03	0.04	0.04	0.03	0.26	0.30
120-180	-0.07	-0.19	-0.33	0.68	-0.01	0.13	-0.16	-0.02	0.47	0.03
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking									
0-15	-0.51	0.03	0.18	-0.36	-0.66	-0.32	-0.68	-0.26	0.67	-0.42
15-30	-0.63	0.04	-0.51	-0.56	-0.62	-0.41	-0.68	0.00	-0.43	0.46
30-60	-0.55	0.10	-0.49	-0.06	-0.09	-0.50	-0.25	-0.60	0.46	-0.33
60-120	-0.54	-0.39	-0.43	0.75	-0.04	-0.47	-0.25	0.02	1.94	-0.50
120-180	-0.33	-0.42	-0.21	0.24	-0.47	-0.48	-0.18	0.75	2.61	-0.33
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking									
0-15	0.20	0.26	0.31	0.44	0.84	0.34	0.29	0.31	0.32	0.17
15-30	0.29	0.23	0.27	0.40	0.31	0.22	0.22	0.10	0.25	0.15
30-60	-0.57	-0.37	-0.80	-0.24	-0.86	-0.73	-0.95	-0.44	-0.12	-0.84
60-120	-0.73	-0.37	-0.59	0.29	-0.42	-0.47	-0.87	-0.68	-0.58	-0.92
120-180	-0.91	-0.62	-0.64	-0.77	-0.61	-0.71	-0.41	-0.97	0.48	-0.77

[1]MAF1 = months after the first fertilization in 2014.

Table S6. Soil NH_4-N concentration (mg kg^{-1}) at different depths in non-raked and raked plots 2.5 months after each of four annual February pine straw harvests (raking) and 1.5 months before or 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Soil depth increment (cm)	Non-raked					Raked				
	Fertilizer									
	ESN				Urea	ESN				Urea
	Annual nitrogen application rate (kg N ha^{-1})									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
	1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking									
0-15	2.87	3.20	3.14	3.70	5.50	3.19	3.32	3.27	3.76	4.66
15-30	2.29	2.95	1.98	2.08	2.15	2.82	2.53	2.34	3.31	2.03
30-60	2.13	1.28	1.64	1.70	2.37	1.45	1.33	1.58	1.95	1.12
60-120	1.64	1.46	1.93	1.53	1.95	1.86	1.69	2.06	1.66	1.35
120-180	1.94	1.44	2.98	1.63	1.46	1.43	2.02	1.61	1.43	1.86
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking									
0-15	3.48	3.26	3.18	2.02	3.51	2.93	2.55	3.38	3.97	3.29
15-30	2.72	3.59	3.68	2.16	1.83	2.23	2.33	2.83	2.65	2.30
30-60	1.41	1.39	1.28	1.58	1.77	1.26	1.38	1.06	1.26	1.24
60-120	1.61	1.27	1.34	1.75	1.18	1.11	1.42	1.22	1.42	1.36
120-180	1.11	1.38	1.19	1.93	1.12	1.16	1.36	1.32	1.32	1.52
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking									
0-15	2.76	3.46	3.96	3.04	2.83	3.04	3.30	3.19	3.98	2.82
15-30	2.19	2.88	2.42	2.37	2.23	2.36	2.24	2.69	2.12	3.07
30-60	1.70	2.08	1.71	1.77	2.38	1.78	1.75	1.73	2.71	1.83
60-120	1.75	1.91	2.12	1.73	2.63	1.85	1.63	2.26	2.33	1.86
120-180	1.79	1.95	2.14	2.18	1.85	1.71	1.66	2.40	1.93	2.05
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking									
0-15	1.67	1.41	1.39	1.50	1.34	2.11	1.63	1.53	1.57	1.54
15-30	1.20	1.18	1.36	1.31	1.15	1.39	1.31	1.09	1.17	1.33
30-60	0.86	0.90	0.95	0.93	0.90	0.70	0.84	0.87	1.05	0.92
60-120	0.82	0.77	0.82	0.89	1.01	0.78	0.89	0.94	0.72	0.91
120-180	0.85	0.82	1.03	0.91	0.89	0.71	0.83	0.82	0.75	0.88

[1]MAF1 = months after the first fertilization in 2014.

Table S7. Soil TKN concentration (mg kg^{-1}) at different depths in non-raked and raked plots 2.5 months after each of four annual February pine straw harvests (raking) and 1.5 months before or 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Soil depth increment (cm)	Non-raked Fertilizer ESN				Non-raked Fertilizer Urea	Raked Fertilizer ESN				Raked Fertilizer Urea
	Annual nitrogen application rate (kg N ha^{-1})									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking										
0-15	368	351	455	413	365	341	358	442	419	329
15-30	180	159	234	205	219	177	180	189	185	151
30-60	123	111	106	116	120	90	86	77	121	59
60-120	107	103	104	60	92	85	88	81	108	76
120-180	74	107	72	64	67	97	79	81	77	67
10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking										
0-15	422	346	448	397	362	398	354	430	386	347
15-30	267	211	263	250	214	232	211	233	217	192
30-60	176	150	141	149	159	122	138	112	151	110
60-120	176	132	156	142	137	132	128	104	128	122
120-180	120	136	105	111	106	106	119	112	96	142
10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking										
0-15	386	400	567	386	340	328	403	436	403	382
15-30	232	186	245	217	201	169	238	229	193	211
30-60	86	140	112	133	135	121	97	80	113	76
60-120	121	77	141	82	123	122	102	110	118	91
120-180	67	112	99	63	75	95	69	86	106	107
10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking										
0-15	284	285	416	313	294	282	301	274	281	257
15-30	147	124	215	184	171	163	177	147	153	193
30-60	67	69	72	83	107	83	28	63	102	39
60-120	87	66	110	58	103	81	87	72	85	65
120-180	77	83	86	65	45	78	45	59	57	67

[1]MAF1 = months after the first fertilization in 2014.

Table S8. Soil total phosphorus (Pt) concentration (mg kg^{-1}) at different depths in non-raked and raked plots 2.5 months after each of four annual February pine straw harvests (raking) and 1.5 months before or 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Soil depth increment (cm)	Non-raked					Raked				
	Fertilizer									
	ESN				Urea	ESN				Urea
	Annual nitrogen application rate (kg N ha^{-1})									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
	1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking									
0-15	104	103	121	120	82	111	97	110	107	99
15-30	76	64	86	98	88	77	68	93	83	54
30-60	99	80	63	124	109	76	54	65	115	39
60-120	171	97	154	155	167	193	170	129	252	155
120-180	171	173	213	243	153	441	299	201	286	146
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking									
0-15	100	105	113	122	84	96	97	99	102	99
15-30	109	77	77	93	82	91	72	100	81	71
30-60	81	70	50	82	88	65	131	65	88	41
60-120	194	113	160	193	165	158	201	109	263	115
120-180	231	167	198	292	217	252	170	214	378	212
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking									
0-15	101	88	122	111	96	99	90	105	109	104
15-30	86	94	93	101	80	90	75	111	90	84
30-60	100	76	59	125	97	82	92	76	88	74
60-120	257	88	169	180	173	207	212	155	216	131
120-180	267	146	260	280	161	244	306	225	316	253
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking									
0-15	87	104	109	112	86	92	86	92	95	93
15-30	69	76	83	77	84	81	70	79	77	80
30-60	66	61	79	123	101	78	58	71	127	52
60-120	180	94	208	201	203	175	198	172	225	154
120-180	265	138	316	313	130	277	274	243	364	286

[1]MAF1 = months after the first fertilization in 2014.

Table S9. Soil Mehlich 3-extractable phosphorus (P) concentration (mg kg^{-1}) at different depths in non-raked and raked plots 2.5 months after each of four annual February pine straw harvests (raking) and 1.5 months before or 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Soil depth increment (cm)	Non-raked					Raked				
	Fertilizer									
	ESN				Urea	ESN				Urea
	Annual nitrogen application rate (kg N ha-1)									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
	1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking									
0-15	33.2	55.2	52.6	53.8	31.8	46.1	33.0	31.9	43.6	36.9
15-30	19.2	25.0	34.2	24.2	18.2	22.0	18.4	20.5	22.6	29.8
30-60	2.3	10.8	5.2	7.0	4.2	6.3	5.8	3.6	7.3	4.6
60-120	-0.3	3.1	0.9	2.5	2.0	2.3	0.7	0.5	0.8	1.2
120-180	-0.2	0.2	-0.2	1.3	0.7	-0.6	0.1	0.2	-0.2	0.4
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking									
0-15	15.7	25.7	25.9	28.6	13.2	17.6	18.7	20.5	17.1	21.4
15-30	12.7	18.3	11.4	17.6	15.8	15.5	10.1	12.2	14.1	13.0
30-60	3.3	5.6	3.7	4.4	4.3	4.5	2.9	2.4	3.7	3.2
60-120	1.0	2.0	1.1	2.1	1.1	2.1	1.1	0.9	1.3	1.3
120-180	0.7	0.8	0.6	1.0	0.5	3.0	0.7	0.9	0.4	1.2
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking									
0-15	24.2	40.9	43.6	40.2	29.5	32.5	26.8	31.4	33.8	38.2
15-30	12.2	42.6	27.9	26.7	22.6	27.1	19.1	20.0	26.7	25.7
30-60	6.0	18.0	6.2	8.0	7.4	10.3	5.4	4.5	7.1	5.8
60-120	1.7	6.8	2.5	4.2	2.2	6.2	2.2	2.2	3.6	3.0
120-180	1.5	2.5	1.5	2.8	1.9	4.9	1.9	1.3	1.7	1.5
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking									
0-15	15.5	27.0	23.1	21.2	19.3	17.1	21.4	19.3	21.0	20.0
15-30	9.5	24.4	14.5	12.7	17.3	16.1	12.4	14.3	15.4	14.6
30-60	2.1	8.0	3.3	2.5	4.2	4.8	2.7	2.8	2.9	2.5
60-120	0.9	3.3	1.4	1.0	1.6	2.4	1.2	1.2	4.2	1.3
120-180	0.8	1.2	1.7	1.1	2.0	1.3	0.8	0.8	1.2	0.8

[1]MAF1 = months after the first fertilization in 2014.

6.2 Impacts to Soil Solution NO_x-N and NH_4-N

6.2.1 Summary

- All fertilization treatments increased nitrate-nitrite (NO_x-N) and ammonium (NH_4-N) concentration in soil solution collected with suction-cup lysimeters at the 30-cm depth, compared to the non-fertilized control and to pre-fertilization levels. Only the highest ESN rate (140 kg N ha^{-1} annually) was above the maximum BMP-allowable input of 280 kg ha^{-1} for any 3-year period.
- Elevated NO_x-N concentrations were observed from one to 13 or 26 weeks after each fertilization with peaks at four or eight weeks. Secondary minor spikes in NO_x-N concentration were recorded almost a year after the first and second fertilizations.
- Soil solution NO_x-N concentrations increased with increasing N application rate. The 98.4 mg L^{-1} maximum concentration, recorded four weeks after the third application of

ESN at 140 kg N ha^{-1} in non-raked plots, was more than 200-fold greater than the concentration in the non-fertilized control at that sampling date. At the same time, the lowest ESN rate (28 kg N ha^{-1}) resulted in 39.3 mg L^{-1} NO_x-N, more than 80-fold greater than the control.

- Comparison between conventional urea and polymer-coated urea (ESN) applied at the same N rate was not conclusive. We observed the advantage of ESN application only after the first fertilization, when it resulted in a smaller and later peak in NO_x-N concentration (4.6 mg L^{-1} at eight weeks) than urea (10.0 mg L^{-1} at four weeks).
- In general, NO_x-N concentration was greater in raked plots after urea application, but in non-raked plots after ESN application.
- The period of elevated NH_4-N concentration occurred between one and four weeks after the second and third fertilizations. In general, magnitude and duration of concentration increases corresponded with increasing N application rate. The peak concentrations of 16.0 and 11.56 mg L^{-1} were recorded two weeks after the second urea application in non-raked plots and one week after the third 140 kg N ha^{-1} ESN application in raked plots, respectively.
- Conventional urea resulted in greater NH_4-N increase than ESN applied at the same N rate, especially in the non-raked plots.
- Effects of pine straw harvesting (raking) were not consistent, but generally NH_4-N concentrations were greater for non-raked than raked treatments.
- Longer periods of elevated NO_x-N concentration and higher concentrations of NO_x-N and NH_4-N occurring sooner after the third fertilization, suggest a cumulative effect of the three consecutive fertilizations.

6.2.2 Statistical analyses of soil solution NO_x-N and NH_4-N concentration

Concentrations of nitrate-nitrite (NO_x-N) and ammonium (NH_4-N) nitrogen were determined for samples collected both before and after annual fertilization over a three-year period. The first three sampling dates, 14, 4 and 2 weeks before the first fertilization (-14, -4, and -2WAF1), were used to establish a baseline. Subsequently, samples were collected from 1 to 51 weeks after each fertilization (WAF) for a total of 27 sampling dates, from 14 weeks before to 155 weeks after the first fertilization (WAF1). Samples were collected more frequently around the time of each annual June fertilization.

A longitudinal analysis was performed so that post-fertilization concentrations of NO_x-N and NH_4-N could be compared to the average baseline concentration and so that treatment effects could be tested for each sampling date. The ANOVA considered blocks and treatments (fertilization x raking levels) within blocks random effects. Fertilization (Fert), raking (Rake) and sampling week (WAF1) were considered fixed effects. Sampling week was treated as a nested factor within each treatment plot and correlation of plot-level measurements over time was modeled using a spatial power structure (Littell et al. 2006) to address higher correlation for measurements made closer in time. This overall ANOVA was partitioned to provide F-tests of fertilization, raking and interaction of fertilization and raking effects for the pre-fertilization period and for each post-fertilization sampling week. The fertilization effect was also partitioned to test the effect of ESN rate and to test for differences due to the form of nitrogen applied (ESN compared to urea at 56 kg N ha^{-1}) for each sampling week. Fertilization treatment means or fertilization x raking treatment means were compared within each sampling week using the stepdown Bonferroni-Holm multiple comparison method, when appropriate. Fertilization treatment means for a given sampling week were compared to their average pre-fertilization baseline level to identify significant increases in concentration using Dunnett's adjustment for multiplicity (5 comparisons for each sampling week). All mean comparisons used a significance level of $\alpha=0.05$.

The non-Gaussian error structures in the analysis of concentrations were addressed in different ways. NO_x-N concentration values could be slightly negative due to lab procedures that avoided censoring of data and variation was observed to increase with mean concentration. The analysis of NO_x-N was performed using PROC MIXED with the natural log of (NO_x-N concentration +1) as the dependent variable. The log transformation was not effective for NH_4-N concentration because variation increased with the mean even after transformation. This was resolved by treating the non-negative right skewed NH_4-N concentration as a Gamma distributed random variable as suggested by Schabenberger and Pierce (2002) as an alternative to a log transformation. The analysis was performed using PROC GLIMMIX with a log link function (Littell et al. 2006). Standard errors for back-transformed NO_x-N and inverse-linked NH_4-N concentration LS-means were approximated using the Delta method which is based on a Taylor series approximation used by PROC GLIMMIX (Littell et al. 2006). LS-means and standard errors (SE) as described above are included in the tables, figures and text.

6.2.3 Results and discussion - soil solution NO_x-N and NH_4-N concentration

According to the overall ANOVA, NO_x-N concentration in soil solution collected by suction-cup lysimeters at the 30-cm depth was affected by the fertilization treatment (Fert), sampling week (WAF1) and Fert x WAF1 interaction, but not by raking treatment (Rake) or any interaction involving Rake (Table L1). However, partitioning the overall ANOVA to examine Fert and Rake effects for each sampling date revealed significant Rake effect or Rake x Fert interaction on a few sampling dates between two and eight weeks after the current-year fertilization (2 to 8 WAF), depending on the fertilization year (Table L2).

Table L1. Repeated measures ANOVA showing the significance (P>F)[1] of fertilization, pine straw harvest (raking), weeks after the first fertilization (WAF1) and interaction of these factors for N concentration in soil solution collected by suction-cup lysimeters at 30-cm depth at various time intervals before and after three annual June fertilizations and after four annual February pine straw harvests.

Factor	df	Nitrogen form	
		NO_x-N	NH_4-N
Fertilization (Fert)	4	**<0.001**	**<0.001**
Raking (Rake)	1	0.361	**<0.001**
Fert x Rake	4	0.242	**0.024**
WAF1	26	**<0.001**	**<0.001**
Fert x WAF1	104	**<0.001**	**<0.001**
Rake x WAF1	26	0.135	**<0.001**
Fert x Rake x WAF1	104	0.483	**<0.001**

[1]Bold $P\leq0.05$ denotes a significant effect

Fertilization treatment and ESN rate effects were significant at 2 to 13, 1 to 13, and 1 to 26 weeks after the 2014, 2015, and 2016 fertilizations, respectively. Additionally, fertilization treatment and ESN rate effects were also significant at 51WAF following the 2014 and 2015 fertilizations (Table L2). At these sampling dates we observed an increasing trend in NO_x-N concentrations with ESN application rate increase from 0 to 140 kg N ha^{-1}. Concentrations of NO_x-N were significantly greater for the highest ESN rate compared to non-fertilized control and, in most cases, compared to the ESN lowest rate (Table L2). At the peak-concentration sampling dates, 4 to 8WAF in 2014 and 2 to 4WAF in 2015 and 2016, NO_x-N concentrations following ESN application at 140 kg N ha^{-1} were greater than in any other treatment (Figure L1). In 2015 and 2016, ESN application at 28 or 56 kg N ha^{-1} resulted in greater NO_x-N concentrations than the control on these dates. The maximum NO_x-N concentration (averaged over raked and non-raked treatments) within a year following each fertilization with 140 kg N ha^{-1} ESN was detected 8WAF in 2014 (60 mg L^{-1}) and 4WAF in 2015 and 2016 (58 and 84 mg L^{-1}, respectively), while the concentration in the control was 0.72, 0.15, and 0.36 mg L^{-1} at the same dates, respectively (Table L2). We observed little difference between ESN and non-coated urea applied at the same rate (56 kg N ha^{-1}). The N form effect was significant at 4WAF in 2014 and at 4 and 8WAF in 2015, with urea resulting in greater NO_x-N concentration than ESN in 2014, but lower concentration than ESN in 2015 (Table L2).

The significance of Fert x WAF1 interactions is explained by variable durations among fertilization treatments of the period of time after application when NO_x-N concentrations were significantly greater than the pre-fertilization average. This period generally extended with increasing ESN application rate and for the highest rate lasted from 1 to 13WAF in 2014 and 2015 and from 1 to 26WAF in 2016 (Table L2). Compared to ESN, the period of elevated NO_x-N concentration after urea application at 56 kg N ha^{-1} was longer (1 to 8WAF) in 2014, shorter (1 to 4WAF) in 2015 and the same (1 to 8WAF) in 2016. We recorded a second NO_x-N concentration spike almost a year after applying ESN at the highest rate in 2014 and at any rate in 2015 (Table L2 and Figure L1). This increase did not occur in 2015 in the case of the urea treatment and was not observed for any treatment in 2016.

Raking affected NO_x-N concentrations at 4WAF in 2016 and at 8WAF in 2015 and 2016 (Table L2). Averaged across all fertilization treatments, NO_x-N concentrations at these dates were greater in non-raked (21.9, 2.1 and 2.1 mg L^{-1}, respectively) than in raked plots (11.0, 0.8, and 0.8 mg L^{-1}, respectively, results not shown). Fert x Rake interactions were significant at 4 and 8 WAF in 2014 and at 2 and 4WAF in 2016. Urea application resulted in greater NO_x-N concentrations in raked than in non-raked plots on these dates (Table L3). We observed the opposite trend for ESN fertilization, although differences were not significant in most cases.

The overall ANOVA showed significant effects of fertilization, raking and sampling date, as well as two- and three-way interactions of these factors for NH_4-N concentration in soil solution at the 30-cm depth (Table L1).

At the sampling week level, the effects of fertilization, raking and their interaction were significant from one to four weeks after the 2nd and 3rd fertilization in 2015 and 2016, respectively. None of these factors were significant during the year following the 1st fertilization in 2014 (Table L4). Additionally, Fert and Fert x Rake interactions were significant at 51WAF following the 2015 fertilization. On the dates with significant fertilization treatment effects, the NH_4-N concentrations were affected by ESN application rate and by fertilizer form (with two exceptions).

Concentrations of NH_4-N were slightly increased above the pre-fertilization level at 1 and 8WAF only for high rate of ESN in 2014 (Table L4). However, in 2015 and 2016 we observed elevated NH_4-N concentrations one and two weeks following application of any fertilizer treatment and four weeks after applying urea or the highest rate of ESN. A small increase was also recorded a year after application of ESN at the highest rate in 2015 and a year after urea application in 2016.

Significant 3-way Fert x Rake x WAF1 interaction (Table L1) resulted from fertilization treatment effects being significant only for non-raked treatment on some sampling dates, but for both raked and non-raked treatments on the other dates (Table L5). When significant, fertilization treatment effects were generally more pronounced in non-raked plots, where application of urea or ESN at 140 kg N ha^{-1} resulted in greater NH_4-N concentrations than the non-fertilized control. Lower ESN rates also increased NH_4-N concentrations over the control at 1 and 2WAF in 2015 and 2016. Urea lead to a greater NH_4-N concentration increase than the same N rate applied as ESN in non-raked plots, except for 1WAF in 2015. In the raked plots, fertilization with urea or 140 kg N ha^{-1} ESN resulted in NH_4-N concentrations greater than the control two weeks after the 2015 fertilization and one and two weeks after the 2016 fertilization. Greater NH4-N concentration in urea compared to ESN at the same N rate was only observed at 1WAF in 2016.

Table L2. NO_x-N concentration in soil solution collected by suction-cup lysimeters at 30-cm depth before (-14 to -2WAF average) and 1 to 51 weeks after (WAF) each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling Date	WAF	**Control**			**Fertilizer**												Orthogonal contrasts *P*[1] values for pre-planned comparisons				
					ESN									**Urea**							
		Annual nitrogen application rate (kg N ha^{-1})															Fert trt[2]	ESN rate[3]	N form[4]	Rake[5]	Fert x Rake[6]
		0			**28**			**56**			**140**			**56**							
		Mean[7]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE					
NO_x-N concentration (mg L^{-1}) **after 2014 fertilization**																					
3/13-6/4	-14 to -2	0.13		0.24	0.07		0.24	0.22		0.23	0.20		0.23	0.07		0.20	0.978	0.856	0.632	0.694	0.913
06/26/14	1	0.12		0.31	0.67		0.42	0.81		0.45	1.99	*	0.75	1.22	*	0.55	0.101	0.193	0.562	0.438	0.626
07/02/14	2	0.12	c	0.31	0.71	bc	0.43	1.26	bc	0.57	9.53	a*	2.63	2.54	b*	0.88	**<0.001**	**<0.001**	0.200	0.262	0.682
07/16/14	4	0.40	c	0.39	1.92	c*	0.73	0.96	c	0.53	56.65	a*	14.38	9.97	b*	2.74	**<0.001**	**<0.001**	**<0.001**	0.527	**<0.001**
08/13/14	8	0.72	c	0.48	2.75	bc*	0.94	4.76	b*	1.44	60.16	a*	15.26	4.57	b*	1.39	**<0.001**	**<0.001**	0.921	0.964	**<0.001**
09/17/14	13	0.36	b	0.38	0.64	b	0.41	1.40	ab	0.60	4.97	a*	1.49	0.61	b	0.40	**<0.001**	**0.001**	0.254	0.383	0.791
12/17/14	26	0.12		0.31	0.56		0.39	0.28		0.32	0.52		0.38	0.04		0.26	0.719	0.826	0.548	0.266	0.622
03/13/15	38	0.01		0.28	0.00		0.25	0.02		0.25	0.18		0.30	0.01		0.25	0.986	0.859	0.986	0.837	0.998
06/10/15	51	0.17	b	0.33	0.97	b	0.49	1.34	b	0.58	5.94	a*	1.73	0.62	b	0.40	**<0.001**	**0.001**	0.290	0.678	0.301
NO_x-N concentration (mg L^{-1}) **after 2015 fertilization**																					
06/24/15	1	0.25	b	0.35	1.61	ab*	0.65	1.62	ab*	0.65	5.76	a*	1.69	1.59	ab*	0.65	**<0.001**	**0.008**	0.981	0.754	0.961
07/01/15	2	0.19	c	0.33	9.25	b*	2.56	17.73	b*	4.67	54.00	a*	13.72	13.56	b*	3.63	**<0.001**	**<0.001**	0.468	0.446	0.460
07/15/15	4	0.15	d	0.32	5.06	c*	1.51	23.76	b*	6.18	57.98	a*	14.72	3.33	c*	1.08	**<0.001**	**<0.001**	**<0.001**	0.191	0.667
08/12/15	8	0.06	c	0.30	0.78	bc	0.45	2.86	ab*	0.96	5.78	a*	1.69	0.60	bc	0.40	**<0.001**	**0.001**	**0.012**	**0.022**	0.290
09/17/15	13	0.01	b	0.28	0.63	ab	0.41	0.97	ab	0.49	3.08	a*	1.02	0.17	b	0.29	**0.001**	**0.022**	0.137	0.160	0.633
12/18/15	26	0.02		0.29	0.21		0.42	0.39		0.49	1.06		0.61	0.18		0.35	0.484	0.454	0.718	0.442	0.708
03/09/16	38	0.05		0.29	0.18		0.32	0.12		0.28	0.56		0.39	0.03		0.26	0.766	0.590	0.824	0.757	0.967
06/08/16	51	0.16	c	0.32	1.35	bc*	0.59	2.60	ab*	0.90	7.88	a*	2.22	0.92	bc	0.48	**<0.001**	**0.001**	0.073	0.357	0.782
NO_x-N concentration (mg L^{-1}) **after 2016 fertilization**																					
06/22/16	1	0.07	c	0.30	2.41	b*	0.85	3.41	b*	1.10	12.89	a*	3.47	3.54	b*	1.13	**<0.001**	**0.000**	0.935	0.620	0.070
06/29/16	2	0.25	c	0.35	13.99	b*	3.74	14.55	b*	3.88	44.44	a*	11.34	14.93	b*	3.97	**<0.001**	**0.002**	0.944	0.634	**0.003**
07/13/16	4	0.36	c	0.38	13.67	b*	3.66	24.70	b*	6.41	84.47	a*	21.33	27.51	b*	7.11	**<0.001**	**<0.001**	0.765	**0.005**	**0.008**
08/10/16	8	0.12	b	0.31	0.70	b	0.42	1.71	ab*	0.68	4.27	a*	1.32	1.53	ab*	0.63	**0.001**	**0.005**	0.842	**0.012**	0.709
09/14/16	13	0.48	b	0.41	0.59	ab	0.40	0.68	ab	0.42	3.04	a*	1.01	0.49	b	0.37	**0.020**	**0.012**	0.735	0.422	0.739
12/15/16	26	0.16	b	0.35	0.77	b	0.52	1.57	ab	0.64	4.71	a*	1.42	0.68	b	0.42	**<0.001**	**0.006**	0.218	0.770	0.834
04/13/17	43	0.03		0.29	0.28		0.32	0.33		0.33	1.07		0.52	0.10		0.28	0.318	0.307	0.589	0.263	0.597
06/09/17	51	0.09		0.30	0.44		0.36	0.40		0.35	0.43		0.36	0.13		0.28	0.887	0.996	0.544	0.252	0.950

[1]Bold *P*≤0.05 denotes a significant effect.
[2]*P* values for differences among fertilization treatments (including the non-fertilized control) within a sampling date.
[3]*P* values for differences among ESN rates (28, 56, and 140 kg N ha-1) within a sampling date.
[4]*P* values for difference between ESN and urea (each @ 56 kg N ha-1) within a sampling date.
[5]*P* values for raking treatment effect within a sampling date.
[6]*P* values for significance of fertilization x raking interaction within a sampling date.
[7]LS-means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a column, LS-means signified with an asterisk are greater than a mean of three pre-fertilization sampling dates (3/13/14, 5/21/14, and 6/04/14) for that treatment using Dunnett's test at α=0.05.

Table L3. NO_x-N concentration in soil solution collected by suction-cup lysimeters at the 30-cm depth in raked and non-raked plots for sampling dates with a significant interaction of raking and fertilization treatments after the first (2014) and third (2016) annual June fertilization with urea or polymer-coated urea (ESN) at different rates.

Sampling	Weeks after fertilization		Rake	**Control**			**Fertilizer**												
Date	First (WAF1)	Current year (WAF)	treatment				**ESN**									**Urea**			
				Annual nitrogen application rate (kg N ha^{-1})															
				0			**28**			**56**			**140**			**56**			
				Mean[1]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE	
				NO_x-N concentration (mg L^{-1}) **after 2014 fertilization**															
07/16/14	4	4	Non-raked	0.8	cd	0.8	7.0	b*	2.8	0.5	d	0.6	71.8	a	25.5	3.7	bc	1.7	
07/16/14	4	4	Raked	0.1	b	0.4	0.1	b	0.4	1.6	b	0.9	44.6	a	16.0	24.5	a*	8.9	
08/13/14	8	8	Non-raked	0.8	c	0.8	6.3	b	2.6	5.6	b	2.3	61.7	a	21.9	1.4	c	0.8	
08/13/14	8	8	Raked	0.7	c	0.6	0.9	c	0.7	4.0	bc	1.8	58.7	a	20.9	12.0	ab*	4.5	
				NO_x-N concentration (mg L^{-1}) **after 2014 fertilization**															
06/29/16	106	2	Non-raked	0.2	c	0.5	24.8	ab	9.0	19.0	ab	7.0	35.2	a	12.7	6.3	b	2.6	
06/29/16	106	2	Raked	0.3	c	0.5	7.7	b	3.0	11.1	b	4.2	56.0	a	19.9	33.7	ab*	12.2	
07/13/16	108	4	Non-raked	0.5	b	0.6	39.3	a*	14.1	43.7	a	15.6	98.4	a	34.8	22.8	a	8.3	
07/13/16	108	4	Raked	0.3	d	0.4	4.3	cd	1.9	13.8	bc	5.2	72.5	a	25.7	33.2	ab	12.0	

[1]Within each sampling date, the 10 LS-means for fertilization x rake treatment interaction were compared using Bonferonni-Holm adjustment at α=0.05. LS-means within a row followed by the same letter are not significantly different. An asterisk denotes a significant difference between rake treatments for a given fertilization treatment for that sampling date.

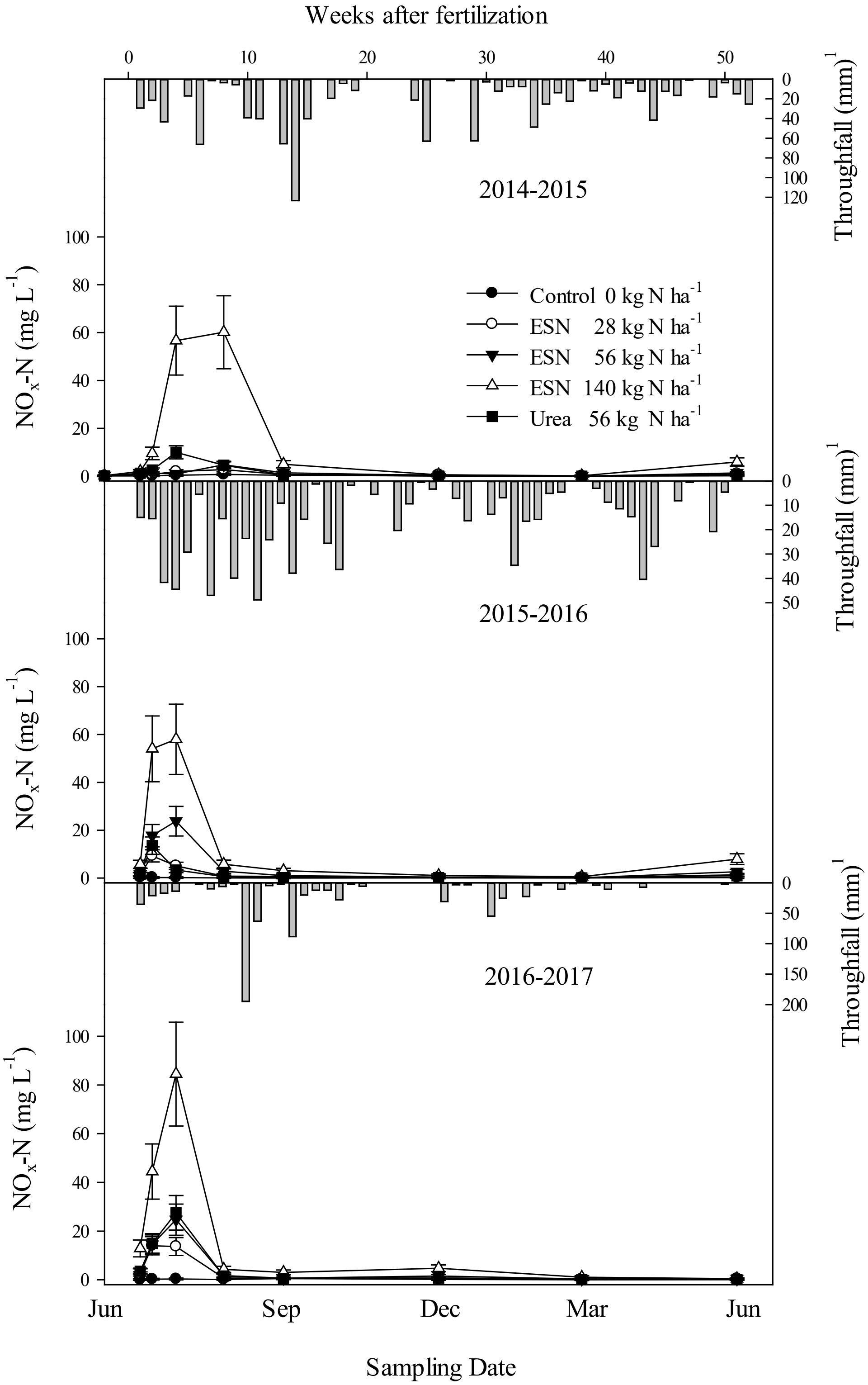

Figure L1. NO_x-N concentration in soil solution collected periodically by suction-cup lysimeters at 30-cm depth before and after three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments. Weekly total rain throughfall (through the pine canopy) is shown by bar graphs above lysimeter results. [1]Note that trough fall scales differ by year.

Table L4. NH_4-N concentration in soil solution collected by suction-cup lysimeters at 30-cm depth before (-14 to -2WAF average) and 1 to 51 weeks after (WAF) each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling Date	WAF	**Control**		**Fertilizer**								Orthogonal contrasts P^1 values for pre-planned comparisons				
				ESN						**Urea**						
				Annual nitrogen application rate (kg N ha^{-1})								Fert trt[2]	ESN rate[3]	N form[4]	Rake[5]	Fert x Rake[6]
		0		**28**		**56**		**140**		**56**						
		Mean[7]	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE					
				NH_4-N concentration (mg L^{-1}) **after 2014 fertilization**												
3/13-6/4	-14 to -2	0.12	0.01	0.12	0.01	0.11	0.01	0.12	0.01	0.12	0.01	0.994	0.972	0.877	0.811	0.997
06/26/14	1	0.13	0.02	0.15	0.03	0.17	0.03	0.24 *	0.04	0.20	0.04	0.138	0.119	0.590	0.183	0.073
07/02/14	2	0.12	0.02	0.14	0.03	0.13	0.02	0.14	0.03	0.20	0.04	0.435	0.980	0.137	0.260	0.234
07/16/14	4	0.12	0.02	0.17	0.03	0.11	0.02	0.14	0.03	0.11	0.02	0.467	0.339	0.975	0.118	0.262
08/13/14	8	0.17	0.03	0.16	0.03	0.15	0.03	0.25 *	0.04	0.16	0.03	0.276	0.102	0.899	0.425	0.700
09/17/14	13	0.19	0.03	0.19	0.03	0.20	0.04	0.20	0.04	0.20	0.04	0.999	0.972	0.974	0.998	0.999
12/17/14	26	0.10	0.02	0.10	0.02	0.09	0.02	0.11	0.02	0.12	0.02	0.922	0.840	0.394	0.522	0.850
03/13/15	38	0.16	0.03	0.20	0.04	0.16	0.03	0.18	0.03	0.20	0.04	0.852	0.747	0.427	0.737	0.954
06/10/15	51	0.07	0.01	0.08	0.02	0.09	0.02	0.10	0.02	0.09	0.02	0.891	0.883	0.902	0.093	0.944
				NH_4-N concentration (mg L^{-1}) **after 2015 fertilization**												
06/24/15	1	0.16 b	0.03	0.59 a*	0.11	0.84 a*	0.15	0.44 a*	0.08	0.78 a*	0.14	**<0.001**	**0.039**	0.775	**<0.001**	**<0.001**
07/01/15	2	0.11 e	0.02	0.52 d*	0.09	1.21 c*	0.22	4.22 a*	0.75	2.20 b*	0.39	**<0.001**	**<0.001**	**0.018**	**<0.001**	**<0.001**
07/15/15	4	0.12 c	0.02	0.12 c	0.02	0.29 b*	0.05	0.52 ab*	0.09	0.68 a*	0.12	**<0.001**	**<0.001**	**0.001**	**<0.001**	**<0.001**
08/12/15	8	0.15	0.03	0.16	0.03	0.15	0.03	0.16	0.03	0.18	0.03	0.935	0.989	0.480	0.775	0.962
09/17/15	13	0.07	0.01	0.09	0.02	0.09	0.02	0.09	0.02	0.10	0.02	0.795	0.996	0.729	0.953	0.897
12/18/15	26	0.17	0.03	0.18	0.05	0.20	0.05	0.18	0.04	0.18	0.04	0.994	0.922	0.700	0.758	0.998
03/09/16	38	0.16	0.03	0.17	0.03	0.17	0.03	0.18	0.03	0.18	0.03	0.990	0.977	0.769	0.875	0.998
06/08/16	51	0.11 b	0.02	0.13 ab	0.02	0.15 ab	0.03	0.27 a*	0.05	0.15 ab	0.03	**0.011**	**0.013**	0.972	0.057	**0.012**
				NH_4-N concentration (mg L^{-1}) **after 2016 fertilization**												
06/22/16	1	0.20 d	0.04	0.40 c*	0.07	0.22 d*	0.04	6.01 a*	1.08	1.81 b*	0.32	**<0.001**	**<0.001**	**<0.001**	**0.018**	**<0.001**
06/29/16	2	0.18 c	0.03	0.49 b*	0.09	0.34 b*	0.06	2.08 a*	0.37	1.37 a*	0.25	**<0.001**	**<0.001**	**<0.001**	**0.000**	**<0.001**
07/13/16	4	0.11 c	0.02	0.12 c	0.02	0.13 c	0.02	0.33 b*	0.06	0.82 a*	0.15	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
08/10/16	8	0.11	0.02	0.09	0.02	0.08	0.01	0.12	0.02	0.11	0.02	0.473	0.245	0.187	0.406	0.073
09/14/16	13	0.12	0.02	0.13	0.02	0.12	0.02	0.13	0.02	0.14	0.03	0.977	0.964	0.543	0.583	0.963
12/15/16	26	0.09	0.02	0.11	0.02	0.08	0.02	0.08	0.01	0.09	0.02	0.759	0.402	0.792	0.132	0.784
04/13/17	38	0.14	0.03	0.16	0.03	0.16	0.03	0.15	0.03	0.17	0.03	0.961	0.964	0.840	0.777	0.998
06/09/17	51	0.16	0.03	0.20	0.04	0.19	0.03	0.15	0.03	0.22 *	0.04	0.518	0.473	0.606	0.758	0.786

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a sampling date.
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha-1) within a sampling date.
[4]P values for difference between ESN and urea (each @ 56 kg N ha-1) within a sampling date.
[5]P values for raking treatment effect within a sampling date.
[6]P values for significance of fertilization x raking interaction within a sampling date.
[7]LS-means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a column, LS-means signified with an asterisk are greater than the mean of three pre-fertilization sampling dates (3/13/14, 5/21/14, and 6/04/14) for that treatment using Dunnett's test at α=0.05.

Table L5. NH_4-N concentration in soil solution collected by suction-cup lysimeters at the 30-cm depth in raked and non-raked plots for sampling dates with a significant interaction of raking and fertilization treatments after the second (2015) and third (2016) annual June fertilization with urea or polymer-coated urea (ESN) at different rates.

Sampling Date	Weeks after fertilization: First (WAF1)	Current year (WAF)	Rake treatment	**Control** 0 Mean[1]		SE	**Fertilizer** **ESN** 28 Mean		SE	ESN 56 Mean		SE	ESN 140 Mean		SE	**Urea** 56 Mean		SE
				NH_4-N concentration (mg L^{-1}) **after 2015 fertilization**														
06/24/15	53	1	Non-raked	0.16	b	0.04	2.17	a*	0.55	2.56	a*	0.65	0.88	a*	0.22	2.27	a*	0.57
06/24/15	53	1	Raked	0.15		0.04	0.16		0.04	0.28		0.07	0.22		0.06	0.27		0.07
07/01/15	54	2	Non-raked	0.12	c	0.03	2.58	b*	0.65	3.64	b*	0.92	10.88	a*	2.75	16.00	a*	4.05
07/01/15	54	2	Raked	0.11	c	0.03	0.10	c	0.03	0.40	b	0.10	1.64	a	0.41	0.30	b	0.08
07/15/15	56	4	Non-raked	0.12	b	0.03	0.12	b	0.03	0.32	b	0.08	1.98	a*	0.50	1.93	a*	0.49
07/15/15	56	4	Raked	0.12		0.03	0.12		0.03	0.26		0.07	0.14		0.03	0.24		0.06
				NH_4-N concentration (mg L^{-1}) **after 2016 fertilization**														
06/22/16	105	1	Non-raked	0.21	d	0.05	0.66	bc	0.17	0.23	cd	0.06	3.13	a	0.79	0.75	b	0.19
06/22/16	105	1	Raked	0.19	b	0.05	0.24	b	0.06	0.21	b	0.05	11.56	a*	2.93	4.37	a*	1.10
06/29/16	106	2	Non-raked	0.19	b	0.05	1.33	a*	0.34	0.29	b	0.07	1.92	a	0.49	2.62	a *	0.66
06/29/16	106	2	Raked	0.17	c	0.04	0.18	c	0.05	0.40	bc	0.10	2.26	a	0.57	0.72	b	0.18
07/13/16	108	4	Non-raked	0.10	c	0.03	0.11	c	0.03	0.15	c	0.04	0.46	b	0.12	4.28	a*	1.08
07/13/16	108	4	Raked	0.13		0.03	0.12		0.03	0.11		0.03	0.24		0.06	0.16		0.04

Annual nitrogen application rate (kg N ha^{-1})

[1]Within each sampling date the 10 LS-means for fertilization x rake treatment interaction were compared using Bonferonni-Holm adjustment at α=0.05. LS-means within a row followed by the same letter (or not followed by any letter) are not significantly different. An asterisk denotes a significant difference between rake treatments for a given fertilization treatment for that sampling date.

Rake effects and Fert x Rake interactions were significant for NH_4-N concentrations at 1 to 4WAF in 2015 and 2016 (Table L4). Averaged across all fertilization treatments, NH_4-N concentrations were greater in non-raked (0.3 to 2.9 mg L^{-1}) than in raked plots (0.1 to 0.8 mg L^{-1}) on these dates, with the exception of 1WAF in 2015 (results not shown). In 2015 we recorded greater NH_4-N concentrations in non-raked than in raked plots for all fertilized treatments at 1 and 2WAF and for urea and high ESN rate at 4WAF (Table L5). In 2016 the pattern was less clear with NH_4-N greater in non-raked plots for urea at 2 and 4WAF and for low ESN rate at 2 WAF, but greater in raked plots for urea and high ESN rate at 1WAF. Concentrations of NH_4-N peaked two weeks after 2015 fertilization and one week after 2016 fertilization. In 2015 the maximum NH_4-N concertation, recorded at 2WAF in non-raked plots fertilized with urea or 140 kg N ha^{-1} ESN, was 16.0 and 10.1 mg L^{-1}, respectively (137- and 93-fold greater than for the control, respectively). In 2016 the peak concentration of 11.6 mg L^{-1}, detected a week after applying the high ESN rate to raked plots, was 60-fold greater than for the control.

Our observations are consistent with expected pattern of nitrogen transformations in the soil. In the current study, the maximum soil solution concentration of NO_x-N was six-fold greater than that of NH_4-N and occurred at a later date after each fertilization. The period of elevated NO_x-N concentrations was also longer compared to NH_4-N. After application, urea is quickly hydrolyzed into ammonium (NH_4-N^+), which is less mobile than nitrate (NO_3-N^-) because of adsorption of positively charged ions by soil minerals. Small quantities of NH_4-N are directly absorbed by roots, but the majority is transformed into nitrate by nitrification, a process slower than urea hydrolysis. Therefore, NO_x-N concentration in our study continued to increase for four or eight weeks following fertilization, while NH_4-N concentration decreased past two weeks. The second substantial peak in NO_x-N concertation, 51 weeks after ESN applications 2014 and 2015, coincided with the increase of soil temperature in June. Both hydrolysis and nitrification are enhanced by adequate soil moisture and high temperature; nitrification slows down at soil temperature below 10^o C. The lack of this upsurge a year following the 2016 fertilization most likely resulted from too little precipitation, which is necessary not only for nitrification but also for NO_x-N movement through the soil profile. The total throughfall (rainfall reaching soil through pine canopy) during four weeks preceding 51WAF sampling after the 2016 fertilization was 7 mm in contrast to 74 and 61 mm after the 2014 and 2015 fertilizations, respectively and during the week immediately before 51WAF sampling date 3 mm after the 2016 fertilization compared to 31 and 35 mm following fertilizations in 2014 and 2015, respectively (Figure L1). The secondary peak at 51WAF was significant only for the high ESN rate after the 2014 fertilization but for all ESN rates after the 2015 fertilization. This suggests cumulative effect of two fertilizations. The year-after-fertilization, NO_x-N concentration increase was not significant for conventional urea applied at the same N rate as polymer-coated urea (ESN), as most of the urea had likely been converted to NO_x-N or volatilized earlier in the year. Greater NH_4-N concentrations for conventional than polymer-coated urea treatments on most dates, especially in non-raked plots, also suggests faster hydrolysis in the absence of polymer coating. When pine straw removal (raking) effect was significant, we recorded greater NH_4-N concentration in non-raked than raked plots, possibly thanks to better moisture retention and greater microbial activity enhancing urea conversions. The difference between raked and non-raked plots was less clear for NO_x-N concentration, which was greater in raked plots fertilized with conventional urea. This may reflect faster water movement through soil with reduced amount of pine litter on the forest floor.

The high ESN rate (140 kg N ha^{-1}), applied consecutively for three years, and exceeded the maximum BMP-allowable application rate of 280 kg N ha^{-1} in any three years. However, all other fertilization rates, which were below this threshold, also significantly increased NH_4-N and NO_x-N concentration in soil solution at the 30-cm depth. After the third fertilization the period of elevated NO_x-N concentration was longer, the maximum NO_x-N and NH_4-N concentrations occurred sooner and were greater for all fertilized treatments than after the first fertilization. This suggests a cumulative effect of three fertilizations with excessive amounts of nitrogen remaining in the soil. NO_x-N at great concentrations in soil solution may leach to the ground water, especially if occurring in rapid spikes preventing full uptake by trees.

6.3 Impacts to Surficial Groundwater

6.3.1 Summary

- Surficial groundwater nitrate-nitrite nitrogen (NO_x-N) and ammonium nitrogen (NH_4-N) concentrations in quarterly samples collected from well monitoring of the fertilized area did not increase through the 36-month monitoring period following the first of the three annual fertilizations, when compared to pre-fertilization baseline levels.
- Measures of groundwater NO_x-N and NH_4-N did not exceed the Practical Quantitation Limit (PQL), 0.5 mg L^{-1}, except for NH_4-N at one pre-fertilization sampling date. NO_x-N concentration was below Method Detection Limit (MDL) of 0.148 mg L^{-1}, except for two sampling dates, three weeks before the first fertilization and 6 months after the second fertilization (0.42 and 0.17 mg L^{-1}, respectively).
- NO_x-N groundwater concentrations stayed substantially below the EPA-established Maximum Contaminant Level Goal (MCLG) for nitrate or nitrite nitrogen of 10 or 1 mg L^{-1}, respectively
- Concentration of groundwater total phosphorus (Pt) fluctuated between 5.7 and 34.0 µg L^{-1}, irrespective of fertilization treatment, and a year after the second fertilization was below the pre-fertilization baseline.

6.3.3 Results and discussion – surficial groundwater

The micro-well located at the Southeast edge of the study site was used to monitor the general impact of fertilization on the surficial groundwater at the stand level, not at the treatment level. The water composition could be affected by the horizontal movement of the water in the surficial aquifer rather than directly by leaching. The sampling period was between May 23, 2014 (one month before the first fertilization; -1MAF1) and June 8, 2017 (one year after the third fertilization; 36MAF1). The water table depth in the well during this time fluctuated between 5.9 and 8.3 m.

Water parameters were recorded at each fertilization date immediately before collecting samples and following well purging (reported in Table W1). Nitrate-nitrite nitrogen (NO_x-N) concentrations remained below MDL=0.15 mg L^{-1}, except for two sampling dates (-0.75MAF1 and 18MAF1). The maximum concentration (0.42 mg L^{-1}) was recorded three weeks before the first fertilization (-0.75MAF1, results not shown). Throughout the sampling period, NOx-N groundwater concentrations stayed substantially below the EPA-established Maximum

Contaminant Level Goal (MCLG) for nitrate or nitrite nitrogen of 10 or 1 mg L^{-1}, respectively (EPA, 2017). Ammonium nitrogen (NH_4-N) concentration was also the highest (0.58 mg L^{-1}) three weeks before fertilization, and remained almost steady (0.36 to 0.49 mg L^{-1}) for the next three years.

Concentrations of total P varied from 5.74 to 9.52 µg L^{-1} before the first fertilization and fluctuated between 6.24 and 34.01 µg L^{-1} after the fertilization, falling below the pre-fertilization level a year after the second fertilization (24MAF1). We suggest that the spikes in the total P concentrations might be associated with the presence of small amounts of rusty sediment containing Fe and Al phosphates. Rusty sediment was first noticed in the purged water in December 2014 at 6MAF1. The amount of sediment visible in water varied greatly among the sampling dates and at each date dramatically decreased during purging. However, it is possible that various small amounts (visible or non-visible) of sediment remained in water which was collected for analyses. The sediment collected during purging of the well was analyzed and found to contain great concentration of P (977 mg kg^{-1}), Fe (348,495 mg kg^{-1}) and Al (16,325 mg kg^{-1}).

Table W1. Parameters of surficial groundwater sampled from a micro-well at the Southeast edge of the study area for one month before (4 weekly sampling dates) and every three months after each June fertilizations.

Sampling or fertilization date	Months after 1st fertilization (MAF1)	pH	Temperature	Conductivity	Dissolved oxygen	Turbidity
		SU	ºC	µS cm^{-1}	%	NTU
5/23/2014	-1	5.7	33.9	77	64	0.5
5/30/2014	-0.75	5.5	26.0	53	34	80.8
6/6/2014	-0.50	5.3	29.1	58	36	14.5
6/13/2014	-0.25	5.1	27.1	60	40	28.5
6/19/2017	Fertilization 1					
9/16/2014	3	5.4	24.5	54	32	8.6
12/15/2014	6	5.0	20.7	47	22	2.5
3/13/2015	9	4.9	24.9	55	20	57.0
6/10/2015	12	5.1	25.6	55	21	10.6
6/15/2017	Fertilization 2					
9/7/2015	15	5.0	25.7	50	23	5.0
12/15/2015	18	5.1	22.9	47	23	61.3
3/9/2016	21	5.0	24.4	50	18	8.5
6/8/2016	24	5.1	29.8	65	19	4.2
6/13/2016	Fertilization 3					
9/14/2016	27	5.1	24.3	47	20	21.6
12/15/2016[1]	30	.	.	.	.	1.6
3/6/2017	33	5.4	24.4	47	35	2.5
6/8/2017	36	5.5	23.5	46	20	9.8

[1]YSI meters malfunctioned

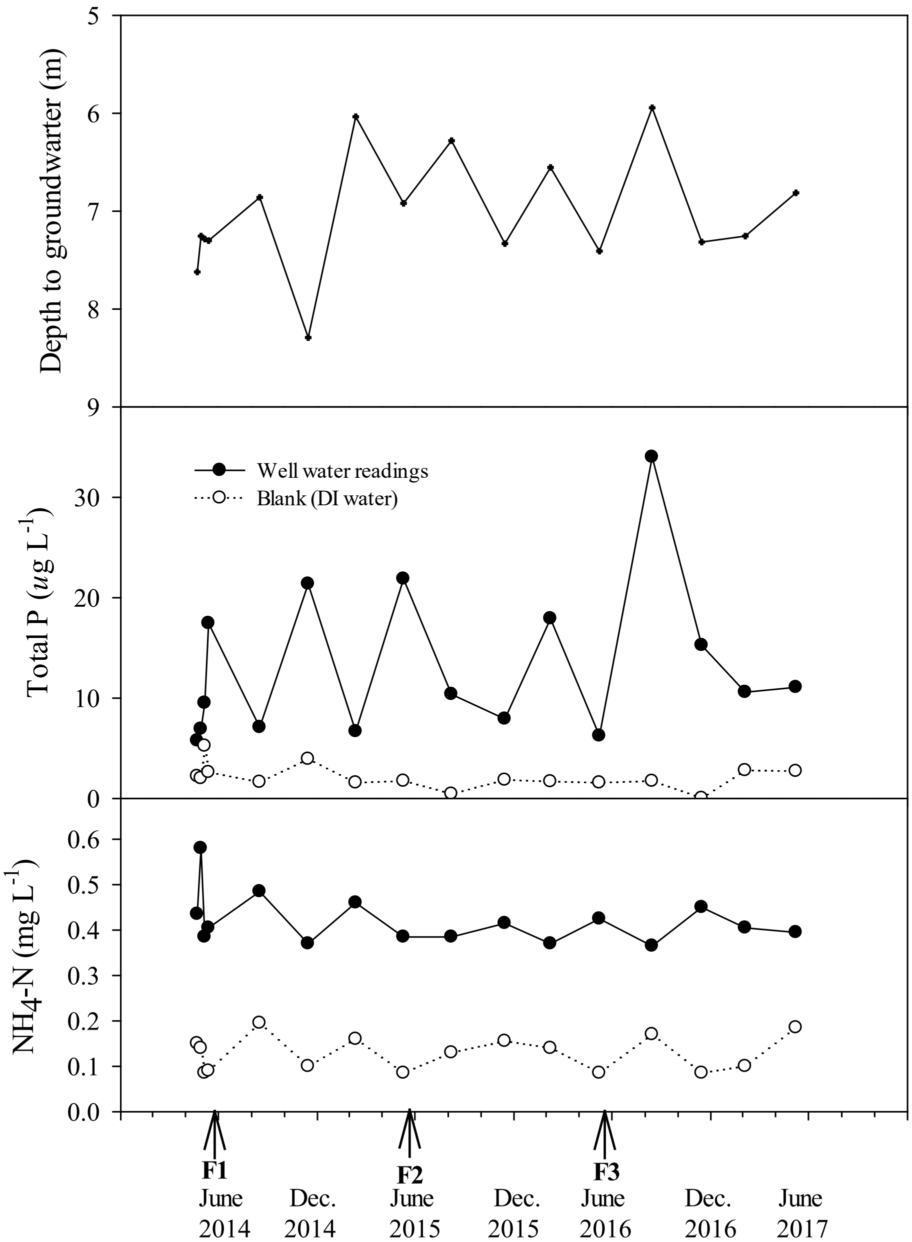

Figure W2. Depth to water table and nutrient concentrations in surficial ground water collected from a FL DEP installed micro-well at the Southeast edge of the study area four times before fertilization (-4, -3, -2 and -1 week) as a baseline, and then every three months after each of three annual June fertilizations.

6.4. Impacts to Soil Organic Matter

Pine straw raking did not affect soil organic matter content (% OM), but fertilization did have an effect following the first and second fertilization (Table O1). There was an interaction between fertilization and raking following the first fertilization (Table O2), with a decrease (*P*=0.005) in % OM for the conventional urea source in non-raked plots and a decrease (*P*=0.026) in % OM for the low ESN rate in raked plots. In contrast, following the second fertilization % OM was elevated (*P*=0.029) for the ESN treatments but not the urea treatment. Given the magnitude of fertilization rate response and the considerable variation observed, the only meaningful interpretation of these data is that raking had no meaningful effect on surface soil organic matter.

Table O1. Analysis of variance[1] showing the significance (*P*>F)[2] of fertilization (Fert), pine straw harvesting (Rake), soil depth (Depth) and the interaction of these factors for percent organic matter content in surface soil 1.5 months before the 1st fertilization and 10.5 after each of three annual June fertilizations (2.5 months after each of four annual February pine straw harvests).

Factor	Before fertilization	Fertilization year 2014	2015	2016
Fert	0.519	**0.002**	**0.046**	0.694
Rake	0.121	0.100	0.668	0.380
Fert x Rake	0.678	**0.034**	0.122	0.086
Depth	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Depth	0.963	0.141	0.953	0.917
Rake x Depth	0.401	0.785	0.200	0.738
Fert x Rake x Depth	0.968	0.232	0.480	0.897

[1]Separate ANOVA for each assessment date
[2]Bold *P*≤0.05 denotes a significant effect.

Table O2. ANOVA[1] slice tests showing the significance (*P*>F)[2] of fertilization, pine straw harvesting (raking), and the interaction of these factors for percent organic matter content in surface soil before the first fertilization and 10.5 months after each of three annual June fertilizations (2.5 months after annual February pine straw harvests).

Soil depth increment (cm)	Before fertilization	Fertilization year 2014	2015	2016
		Fertilization effect		
0-15	0.850	0.074	0.380	0.666
15-30	0.605	**0.002**	0.123	0.940
		Raking effect		
0-15	0.551	0.170	0.537	0.696
15-30	0.091	0.314	0.227	0.391
		Fertilization x raking interaction		
0-15	0.954	**0.029**	0.724	0.729
15-30	0.580	**0.009**	0.059	0.484

[1]Separate ANOVA for each assessment date.
[2]Bold *P*≤0.05 denotes a significant effect

Table O3. Organic matter content (% OM) in surface soil fractions from raked and non-raked plots 1.5 months before the first fertilization and 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates (2.5 months after each of four annual February pine straw harvests).

Soil depth increment (cm)	**Non-raked**					**Raked**				
	Fertilizer									
	ESN				**Urea**	**ESN**				**Urea**
	Annual nitrogen application rate (kg N ha-1)									
	0	**28**	**56**	**140**	**56**	**0**	**28**	**56**	**140**	**56**
	1.5 months before 2014 fertilization (-1.5 MAF1)[1], 2.5 months after 2014 raking									
0-15	1.48	1.11	1.73	1.48	1.32	1.38	1.21	1.16	1.44	1.28
15-30	0.52	0.50	0.80	0.78	0.61	0.52	0.46	0.47	0.56	0.42
	10.5 months after 2014 fertilization (10.5 MAF1), 2.5 months after 2015 raking									
0-15	0.99	1.12	1.59	1.24	0.72	1.29	0.39	0.86	1.25	0.99
15-30	0.91	0.62	0.70	0.68	0.21	0.58	0.37	0.73	0.47	0.35
	10.5 months after 2015 fertilization (22.5 MAF1), 2.5 months after 2016 raking									
0-15	1.21	1.39	2.00	1.47	1.18	1.12	1.44	1.40	1.44	1.19
15-30	0.56	0.45	0.82	0.70	0.30	0.43	0.76	0.64	0.69	0.67
	10.5 months after 2016 fertilization (34.5 MAF1), 2.5 months after 2017 raking									
0-15	0.85	1.18	1.28	1.09	0.94	1.22	1.27	0.87	0.89	0.82
15-30	0.49	0.58	0.94	0.60	0.70	0.62	0.74	0.44	0.57	0.54

[1]MAF1 = months after the first fertilization in 2014

Table O4. Organic matter content (% OM) in surface soil from raked and non-raked plots 1.5 months before the first fertilization and 10.5 months after each of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates (2.5 months after each of four annual February pine straw harvests), averaged over 0-15 and 15-30 cm soil depths.

Raking treatment	Fertilizer									
	ESN								Urea	
	Annual nitrogen application rate (kg N ha^{-1})									
	0		**28**		**56**		**140**		**56**	
	Organic matter content (%)[1]									
	1.5 months before 2014 fertilization									
Non-raked	0.88		0.75		1.18		1.08		0.89	
Raked	0.85		0.75		0.74		0.90		0.74	
Average	0.86		0.75		0.93		0.99		0.81	
	10.5 months after 2014 fertilization									
Non-raked	0.94	a	0.83	a	1.05	a	0.92	a	0.39	b
Raked	0.87	a	0.38	b*	0.79	ab	0.77	ab	0.58	ab
Average	0.91	a	0.56	ab	0.91	a	0.84	a	0.47	b
	10.5 months after 2015 fertilization									
Non-raked	0.82		0.79		1.28		1.01		0.60	
Raked	0.69		1.05		0.95		1.00		0.89	
Average	0.76	a	0.91	a	1.10	a	1.01	a	0.73	a
	10.5 months after 2016 fertilization									
Non-raked	0.65		0.82		1.09		0.81		0.81	
Raked	0.87		0.97		0.62		0.71		0.66	
Average	0.75		0.89		0.82		0.76		0.73	

[1]LS-means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. LS-mean for the raked treatment signified with an asterisk is smaller than for the non-raked within that fertilization treatment.

6.5 Impacts to Soil Bulk Density

6.5.1 Statistical analyses of soil bulk density

Soil bulk density was assessed for the upper depth fractions (0-15 and 15-30 cm), at three sampling points per plot, in the fall of 2013 before any raking or fertilization treatments, and in the fall of 2017 after four consecutive February rakings and three consecutive June fertilizations. The statistical analysis was performed using PROC GLIMMIX as a nested design with samples nested within plot and sampling year. Block, block x fertilization x raking (error term for fertilization, raking, and fertilization x raking interaction), block x fertilization x raking x sampling year (error term for sampling year effects), and block x fertilization x raking x sampling year x sample (replication of paired depth samples within plot and sampling year) were specified as random effects.

6.5.2 Results and discussion - soil bulk density

Raking, sampling year and soil depth had a significant effect on soil bulk density, and there was a significant interaction between sampling year and depth (Table B1). Comparing means for the significant main effects, non-raked plots had 2.6% greater soil bulk density than raked plots, bulk density decreased 3.8% from the 2013 pre-treatment assessment to 2017, and the 15 to 30 cm fraction had 8.8% greater bulk density than the 0 to 15 cm depth (Table B2). The significant year x depth interaction was one of scale; the reduction in bulk density from 2013 to 2017 was greater at 0 to 15 cm than 15 to 30 cm depth. Bulk density was significantly greater prior to treatment in the 15 to 30 cm fraction than at 0 to 15 cm depth, and inherent depth differences are explained in part by greater soil organic matter content in the upper fraction (improving soil porosity and structure). The important finding of these results is that raking did not adversely affect soil bulk density, which had been observed in other conditions (Haywood et al. 1998).

Table B1. ANOVA showing the significance (*P*>F)[1] of main factors and their interactions for bulk density of surface soil collected from the slash pine plantation in fall 2013 (before any treatment application) and in spring 2017 (after three consecutive June fertilizations and four consecutive February pine straw rakings).

Factor	df	*P* value
Fertilization (Fert)	4	0.876
Raking (Rake)	1	**0.023**
Fert x Rake	4	0.693
Sampling Year	1	**<0.001**
Fert x Year	4	0.750
Rake x Year	1	0.403
Fert x Rake x Year	4	0.499
Depth	1	**<0.001**
Fert x Depth	4	0.750
Rake x Depth	1	0.935
Fert x Rake x Depth	4	0.056
Year x Depth	1	**0.032**
Fert x Year x Depth	4	0.672
Rake x Year x Depth	1	0.119
Fert x Rake x Year x Depth	4	0.798

[1]Bold $P \leq 0.05$ denotes a significant effect

Table B2. Least square mean soil bulk density (g cm^{-3}) of surface soil collected from the raked and non-raked slash pine plantation in fall 2013 (before any treatment application) and in spring 2017 (after three consecutive June fertilizations and four consecutive February pine straw rakings).

Factor	Factor level	LS-mean[1]		Standard error
Rake	Non-raked	1.56	a	0.01
Rake	Raked	1.52	b	0.01
Sampling year	2013 (before any treatment)	1.57	a	0.01
Sampling year	2017 (after all treatments)	1.51	b	0.01
Soil depth	0 to 15 cm	1.47	b	0.01
Soil depth	15 to 30 cm	1.60	a	0.01
Sampling year x Depth	2013, 0 to 15 cm	1.51	c	0.01
Sampling year x Depth	2017, 0 to 15 cm	1.44	d	0.01
Sampling year x Depth	2013, 15 to 30 cm	1.62	a	0.01
Sampling year x Depth	2017, 15 to 30 cm	1.58	b	0.01

[1]LS Means for each factor followed by the same letter are not significantly different using Bonferonni-Holm adjustment at α=0.05

6.6 Impacts to Foliar Nutrients

6.6.1 Summary

- Fertilization affected pine foliar concentrations of total Kjeldahl nitrogen (TKN), K and Ca (supplied nutrients).
- Comparing treatment TKN concertation averaged across three post-fertilization years, there was a significant positive ESN rate response. All ESN treatments had greater foliar TKN than the non-treated control, and 140 kg N ha^{-1} ESN resulted in significantly greater foliar TKN than any other treatment.
- Comparing the average response for three post fertilization years, foliar TKN concentration was greater (7%) for the 56 kg N ha^{-1} ESN treatment than for the same N rate supplied as conventional urea.
- The lack of fertilization response in foliar total phosphorus (Pt) concentration may be explained by adequate inherent soil P (32-55 mg kg^{-1} at 0-15 cm depth by Mehlich 3 extraction), soil pH below 5.5 (fostering P precipitation by Al and Fe in soil), and low inherent P mobility in the soil.
- Foliar K concentration was generally higher for fertilized treatments compared to non-fertilized control and declined with increasing N fertilization rate, which may be due to corresponding mass increases.
- Foliar Ca concentration was effected only after the first fertilization, and was greater following ESN at 140 kg N ha^{-1} or conventional urea at 56 kg N ha^{-1} than observed for the non-fertilized control (Ca concentration increases of 20 or 18%, respectively).
- We did not observe a consistent effect of annual pine straw harvesting on any foliar nutrient after four years. However, after the first raking foliar Ca and Mg were approximately 8% greater in raked than non-raked plots, which may be explained by increased mineralization rates with raking disturbance and subsequent uptake by pines.

6.6.2 Statistical analyses of foliar nutrient concentration

The analysis of variance for foliar nutrients (TKN, Pt, K, Ca and Mg) was performed as a mixed-model with blocks considered random and annual foliar sampling considered a repeated longitudinal assessment of an experimental unit (plot). A preliminary analysis was performed to compare the parametric structure of the covariance matrix with respect to possible heterogeneity of variance and correlation of annual foliar samples. Compound symmetry (CS), heterogeneous compound symmetry (CSH), first-order autoregressive (AR1) and heterogeneous first-order autoregressive (ARH1) structures were compared based on AIC (Akaike 1974), AICC (Hurvich and Tsai 1989) and BIC (Schwarz 1978) information criteria using SAS PROC MIXED (Littell et al. 2006). Heterogeneous error structures were only marginally supported by AIC and AICC criteria but were the best ranked models using the BIC criteria. The heterogeneous model, where the variance can differ by sample year, was adopted based on these results: 1) the observed significant sampling year differences from the analysis of standards, and 2) the consideration that assuming variance to be constant from year to year was too restrictive when the observed sample variance was often very different for at least one year for any given foliar nutrient. The CSH error structure was selected for TKN, Pt and K, and the ARH1 error structure was selected for Ca and Mg based on AIC, AICC and BIC information criteria. Additionally, the analysis was performed on the natural log of concentration for both Ca and Mg to improve the normality of residuals.

Fertilization treatment means were compared annually and also when averaged over the three post-fertilization sampling years. An overall F-test of treatment differences was performed for both of these groupings. Individual fertilization treatment means were compared using the stepdown Bonferroni-Holm (Holm 1979) probability adjustment for multiplicity. Additional specific hypotheses tested as pre-planned comparisons were that foliar concentrations do not differ: 1) between each fertilization treatment and the non-fertilized control, 2) among the three rates of ESN (ESN rate), and 3) between conventional urea and polymer-coated urea (ESN) at the same 56 kg elemental N hectare^{-1} rate (N form).

6.6.2 Results and discussion - foliar nutrient concentration

The overall repeated measures ANOVA did not show a significant raking effect or fertilization x raking interaction on the concentration of any foliar nutrients examined (Table F1). Fertilization affected the concentration of TKN, K and Ca. Concentrations of all nutrients varied by sampling year (P<0.001), which may be explained by time from sequential annual fertilizations, changes in yearly rainfall and other temporal environmental factors. A significant fertilization by year interaction was observed for foliar TKN and K, so the response to fertilization was compared for each year.

Table F1. Repeated measures full ANOVA showing the significance (P>F)[1] of fertilization, pine straw harvesting (raking), sampling year and the interaction of these factors for nutrient concentration in slash pine foliage, collected for four years in the dormant season before and after three consecutive June fertilizations and three February pine straw harvests.

Factor	df	Foliar nutrient				
		TKN	Pt	K	Ca	Mg
Fertilization (Fert)	4	**<0.001**	0.382	**0.023**	**0.019**	0.421
Raking (Rake)	1	0.140	0.399	0.663	0.358	0.631
Fert x Rake	4	0.962	0.406	0.788	0.535	0.764
Sampling Year	3	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Year	12	**0.031**	0.170	**0.047**	0.908	0.649
Rake x Year	3	0.483	0.930	0.467	0.452	0.132
Fert x Rake x Year	12	0.276	0.640	0.119	0.687	0.283

[1]Bold P≤0.05 denotes a significant effect

Orthogonal contrasts showed that foliar TKN concertation was affected by fertilization treatment (P<0.001) every year following the first sequential annual fertilization in 2014 (Table F2). Foliar TKN concentration increased with ESN application rate each year except in 2015, explaining the significant fertilization by year interaction (P=0.031). Comparing treatment TKN concertation averaged across three post-fertilization years, there was a significant positive ESN rate response (P<0.001). All ESN treatments had greater foliar TKN than the non-treated control, and 140 kg N ha^{-1} ESN resulted in significantly greater foliar TKN than any other treatment using Bonferroni adjustment to compare multiple means. Using this mean comparison the 56 kg N ha^{-1} conventional urea treatment did not differ in TKN concentration from the control in any year, or for the three-year average. Dunnett's test was also used to compare each fertilizer treatment to the non-fertilized control (Table F2). Following the first fertilization in 2014 the medium and high ESN rates had greater foliar TKN than the control. After the second fertilization all ESN rates had greater TKN than the control, and after the third fertilization all fertilization treatments had greater TKN than the control. Using Bonferroni's adjustment to compare the average response for three post fertilization years, foliar TKN concentration was greater (7%) for the 56 kg N ha^{-1} ESN treatment than for the same N rate supplied as conventional urea.

The lack of fertilization response in foliar total phosphorus (Pt) concentration may be explained by high inherent soil P (40 mg kg^{-1} at 0-15 cm depth), soil pH below 5.5, and low inherent P mobility in the soil. At low soil pH P is precipitated by Fe and Al rendering P unavailable to plant uptake, which is particularly important in clayey soils such as these, where Fe and Al are abundant (Hurt et al. 2013).

Orthogonal contrasts showed that fertilization affected foliar K concentration in 2015, 2016 and for the average across three post-fertilization years, but not in 2014 (Table F2). This explains the significant fertilization x year interaction shown by the overall ANOVA (P=0.047). Using Bonferroni adjustment to compare multiple means, fertilized treatments did not differ in foliar K in any year or for the three-year average. These results could be expected as all fertilized treatments received the same annual amount of K, 56 kg ha^{-1}. Foliar K concentration was most responsive to the low ESN rate. Following the second fertilization in 2015, in 2016 and for the three-year average response, 28 kg N ha^{-1} ESN had greater K concentration than the non-fertilized control using Bonferroni adjustment. Using Dunnett's test all fertilized treatments differed from the control in these periods except for the medium and high ESN rate in 2015, and the high ESN rate using the three-year average. Foliar K concentration generally declined with increasing N fertilization rate, which may be due to corresponding mass increases. Orthogonal contrasts showed a significant ESN rate response only in 2015, after the second fertilization, whereby foliar K declined with increasing N rate. There were no differences in foliar K when the 56 kg N ha^{-1} rates of ESN and urea were compared.

Using orthogonal contrasts to examine the effect of fertilization on foliar Ca each year and for the three-year average (Table F3), the fertilization effect was significant only in 2014, after the first fertilization. At this assessment Ca concentration was greater following ESN at 140 kg N ha^{-1} or conventional urea at 56 kg N ha^{-1} than observed for the non-fertilized control (Ca concentration increases of 20 or 18%, respectively). All ESN treatments supplied 9.2 kg ha^{-1} Ca. There was no fertilization effect on foliar Mg concentration (Table F3), which was not supplied with any treatment.

Orthogonal contrasts showed that foliar Ca and Mg concentration was affected by the first raking in 2014 (Table F3). When averaged across all fertilization treatments (data not shown), foliar Ca and Mg concentrations were greater in raked (1.93 and 0.79 g kg^{-1}, respectively) than non-raked (1.79 and 0.73 g kg^{-1}, respectively) plots. This increase of approximately 8% for each cation may be explained by increased mineralization rates for fine forest litter, as the result of raking disturbance, and greater subsequent uptake of Ca and Mg from the soil.

Table F2. Nutrient concentration (g kg^{-1} of tissue dry mass) in slash pine foliage collected in the dormant season before fertilization (-6MAF1), and half a year after one (6MAF1), two (18MAF1) or three (30MAF1) annual June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling date	Number of fertilizations & rakings before sampling	Months after 1st fertilization (MAF1)	Fertilizer: ESN				Fertilizer: Urea		Orthogonal contrasts P[1] values for pre-planned comparisons				
			Annual nitrogen application rate (kg N ha^{-1})										
			0	**28**	**56**	**140**	**56**		Fert trt[2]	ESN rate[3]	N form[4]	Rake[5]	Fert x Rake[6]
			Nutrient concentration (g kg^{-1})[7]					SE					
							TKN						
12/17/13	0	-6	10.47	10.51	10.88	10.95	10.57	0.28	0.652	0.509	0.432	0.872	0.438
12/12/14	1	6	9.04 b	9.42 b	10.26 ab*	11.70 a*	9.55 b	0.36	**<0.001**	**<0.001**	0.181	0.142	0.956
12/08/15	2	18	11.50 b	12.84 b*	13.25 ab*	13.91 a*	12.11 b	0.31	**<0.001**	0.072	**0.017**	0.152	0.372
12/07/16	3	30	11.11 c	12.15 ab*	12.67 ab*	13.15 a*	12.10 bc*	0.26	**<0.001**	**0.044**	0.139	0.845	0.286
2014-2016 mean (post-fertilization)			10.55 d	11.47 bc*	12.06 b*	12.92 a*	11.25 cd*	0.20	**<0.001**	**<0.001**	**0.010**	0.093	0.537
							Total P (Pt)						
12/17/13	0	-6	0.98	0.97	0.95	1.04	1.02	0.05	0.693	0.433	0.299	0.563	0.356
12/12/14	1	6	1.03	0.95	0.94	0.95	0.97	0.03	0.140	0.936	0.405	0.305	0.998
12/08/15	2	18	1.19	1.16	1.07	1.06	1.14	0.04	**0.035**	0.076	0.163	0.871	0.517
12/07/16	3	30	1.05	1.10	1.05	1.01	1.06	0.04	0.519	0.220	0.860	0.529	0.360
2014-2016 mean (post-fertilization)			1.09	1.07	1.02	1.01	1.06	0.03	0.091	0.145	0.281	0.422	0.648
							K						
12/17/13	0	-6	4.11	4.24	4.21	4.26	4.17	0.20	0.979	0.976	0.883	0.740	0.606
12/12/14	1	6	4.02	4.53	4.47	4.40	4.42	0.24	0.549	0.920	0.883	0.398	0.363
12/08/15	2	18	5.42 b	7.16 a*	6.05 ab	5.78 ab	6.57 ab*	0.36	**0.017**	**0.024**	0.297	0.362	0.127
12/07/16	3	30	4.54 b	6.04 a*	5.83 ab*	5.74 ab*	5.74 ab*	0.32	**0.021**	0.776	0.827	0.642	0.677
2014-2016 mean (post-fertilization)			4.66 b	5.91 a*	5.45 ab*	5.31 ab	5.58 ab*	0.23	**0.009**	0.146	0.686	0.684	0.720

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[4]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]P values for raking treatment effect within a year or for three-year post-fertilization averages.
[6]P values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[7]Means within a row followed by the same letter, or not followed by any letter, are not significantly different using Bonferonni-Holms adjustment at α=0.05. Within a row, means signified with an asterisk are greater than the mean for the non-fertilized control using Dunnett's test at α=0.05.

Table F3. Nutrient concentration (g kg^{-1} of tissue dry mass) in slash pine foliage collected in the dormant season before fertilization (-6MAF1), and half a year after one (6MAF1), two (18MAF1) or three (30MAF1) annual June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling date	Months after 1st fertilization (MAF1)	Fertilizer: ESN, Annual nitrogen application rate (kg N hectacre^{-1}) **0** Mean[7]	SE[8]	ESN **28** Mean	SE	ESN **56** Mean	SE	ESN **140** Mean	SE	Urea **56** Mean	SE	Orthogonal contrasts P^1 values for pre-planned comparisons: Fert Trt[2]	ESN rate[3]	N Form[4]	Rake[5]	Fert x Rake[6]
		Nutrient concentration (g kg^{-1})														
Ca																
12/17/13	-6	1.67	0.10	1.57	0.09	1.60	0.09	1.80	0.10	1.70	0.10	0.340	0.124	0.395	0.666	0.160
12/12/14	6	1.68 b	0.08	1.85 ab	0.09	1.77 ab	0.09	2.02 a*	0.10	1.99 a*	0.10	**0.011**	0.061	**0.038**	**0.045**	0.424
12/08/15	18	1.88	0.18	2.01	0.20	1.94	0.19	2.22	0.22	2.24	0.22	0.581	0.580	0.296	0.653	0.888
12/07/16	30	2.15	0.15	2.14	0.15	2.11	0.15	2.38	0.17	2.11	0.15	0.645	0.366	0.992	0.850	0.797
2014-2016 mean (post-fertilization)		1.89	0.09	1.99	0.10	1.93	0.09	2.20 *	0.11	2.11	0.10	0.056	0.061	0.120	0.245	0.535
Mg																
12/17/13	-6	0.69	0.04	0.66	0.04	0.65	0.04	0.78	0.05	0.74	0.04	0.177	0.070	0.162	0.192	0.141
12/12/14	6	0.74	0.03	0.74	0.03	0.76	0.03	0.75	0.03	0.82	0.04	0.387	0.959	0.163	**0.041**	0.369
12/08/15	18	0.92	0.07	0.88	0.07	0.92	0.07	0.94	0.07	1.01	0.08	0.756	0.839	0.353	0.685	0.808
12/07/16	30	1.08	0.07	1.02	0.06	1.02	0.07	0.97	0.06	0.99	0.06	0.775	0.809	0.689	0.809	0.573
2014-2016 mean (post-fertilization)		0.91	0.04	0.87	0.04	0.89	0.04	0.88	0.04	0.94	0.04	0.669	0.919	0.343	0.226	0.308

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]*P* values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[3]*P* values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[4]*P* values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]*P* values for raking treatment effect within a year or for three-year post-fertilization averages.
[6]*P* values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[7]Means within a row followed by the same letter, or not followed by any letter, are not significantly different using Bonferonni-Holms adjustment at α=0.05. Within a row, means signified with an asterisk are greater than the mean for the non-fertilized control using Dunnett's test at α=0.05.
[8]Standard error approximated for back transformed means as exp (avg. ln (concentration)) x standard error of ln (concentration).

6.7 Impacts to Needlefall Yield and Nutrients

6.7.1 Summary

- Fertilization positively affected concentration and content of total Kjeldahl nitrogen (TKN), K and Ca (supplied nutrients) in pine needlefall and, to a lesser degree, needlefall dry mass yield (DM) and Mg content.
- Treatment effects on the nutrient contents in the needlefall were the result of combined effects on the needlefall DM and nutrient concentrations.
- DM was increased by 12% over the non-fertilized control by the second and third ESN application at 140 kg N ha^{-1}, but not by any other treatment.
- A positive needlefall TKN concentration response to ESN rate was observed after the first fertilization and increased with consecutive fertilizations, suggesting a cumulative effect.
- ESN rates of 56 or 140 kg N ha^{-1} resulted in higher TKN concentrations than non-fertilized control every year, but the greatest difference (40%) was observed after the third ESN application at 140 kg N ha^{-1}. Conventional urea application at 56 kg N ha^{-1} increased the TKN 3-year concentration average.
- Needlefall TKN content response to fertilization was similar to that of TKN concentration, except that the significant effects began after the second rather than first fertilization.
- Needlefall TKN concentration or content were not affected by fertilizer formulation (ESN versus conventional urea) when applied at the same N rate of 56 kg ha^{-1}.
- In general, needlefall total P (Pt) concentration was lower for fertilized treatments than for the non-fertilized control, but the difference was significant only after the second fertilization when highest ESN rate resulted in 20% lower Pt concentration than the control. A similar tendency was observed for needlefall Pt content, but fertilization effect was not significant in any year.
- Both needlefall K concentration and K content were higher in all fertilized treatments than in non-fertilized control. There were no differences among the fertilized treatments as they all received the same rate of K.
- Needlefall Ca concentration and content generally increased with ESN rate from 28 to 140 kg N ha^{-1}, even though Ca application rate was the same for all ESN treatments. Both concentration and content were higher for ESN applications at 140 kg N ha^{-1} than for the non-fertilized control.
- Fertilizer form significantly affected needlefall Ca concentration, and not Ca content, but both measures were generally higher following fertilization with conventional urea compared to ESN applied at the same N rate.
- Needlefall Mg concentration was not affected by fertilization, but Mg content was higher for ESN at 140 kg N ha^{-1} than for the non-fertilized control, after the second and third application.

- Out of all needlefall nutrients studied only Ca concentration was affected by pine straw harvest. It was higher in raked than in non-raked treatments by about 6% beginning with the second raking in 2015.
- Sampling timing (year, quarter and their interaction) affected all needlefall variables, which may be explained by the elapsed time from the first fertilization, changes in rainfall and other temporal environmental factors. It was included in the statistical model, but was not the subject of this study and will not be discussed.
- TKN, Pt, and K concentrations in the needlefall were generally lower than in the foliage, but the treatment effects were similar for both types of tissue.
- Mg needlefall and foliar concentrations were similar.
- Ca concentration in the needlefall was higher than in the foliage, possibly because this nutrient is least mobile in the plant and was not retrieved from foliage before senescence.

6.7.2 Statistical analyses of needlefall yield and nutrients

A repeated measures analysis was performed for needlefall dry mass, nutrient concentration and nutrient content in needlefall. The main objective of this analysis was to compare fertilization and raking treatments in terms of yearly (sampling year) needlefall dry mass (DM) and nutrient concentrations and contents after each of three annual fertilizations. The treatment plot was the repeated measures factor (subject) on which needlefall was collected every 3 months (quarter) for three years. Nutrient concentration was calculated as the average of 3 aliquots for each quarterly plot sample. There were 4 cases (out of 360) where a 2-sample average was used due to an unusually high or low reading (usually 1 order of magnitude) for an aliquot. Nutrient content was calculated for each quarter by multiplying DM by nutrient concentration.

PROC GLIMMIX was used to fit a linear model with a covariance structure (Littell et al. 2006) to account for the correlation among quarterly collections on a given plot. Covariance structures examined included unstructured (UN), compound symmetry (CS), heterogeneous compound symmetry (CSH), Toeplitz (TOEP), heterogeneous Toeplitz (TOEPH), first-order autoregressive (AR(1)), and heterogeneous first-order autoregressive (ARH(1)). Blocks were considered random and covariance structures for quarterly plot measurements were compared using AIC (Akaike 1974), AICC (Hurvich and Tsai 1989) and BIC (Schwarz 1978) information criteria. The heterogeneous structures were found to improve the model (indicative of heterogeneous variation by sampling date). The other general trend was for plot measurements made in the same quarter of different years to have higher correlations than adjacent quarterly measurements. This favored the CSH and TOEPH structures over the ARH(1) structure. The CSH structure was adopted for TKN concentration and the TOEPH structure was adopted for all the other nutrient concentrations and for needlefall DM and needlefall nutrient contents.

Fertilization and raking treatment means were compared annually and also averaged over the three post-fertilization sampling years. Overall F-tests of fertilization treatment differences, differences due to raking, or the interaction of fertilization and raking treatments were performed for the overall and annual comparisons. Individual fertilization treatment means were compared using the stepdown Bonferroni-Holm (Holm 1979) probability adjustment for multiplicity and compared to the non-fertilized controls using Dunnett's test. Additional specific hypotheses tested as pre-planned comparisons were that the means do not differ: 1) among the five fertilization treatments (Fert trt), 2) among the three rates of ESN (ESN rate), and 3) between conventional urea and polymer-coated urea (ESN) at the same 56 kg elemental N hectare^{-1} rate (N form).

6.7.3 Results and discussion - needlefall nutrient concentration

According to the overall repeated measures ANOVA, fertilization effect was highly significant (*P*<0.001) for the TKN, K and Ca concentrations in needlefall and nearly significant (*P*=0.053) for the Pt concentration (Table N1). Fertilization x sampling year interaction was highly significant (*P*<0.001) for the TKN and K and nearly significant (*P*=0.052) for the Ca concentration, indicating different fertilization effects on these nutrients in different years. Therefore, the response to fertilization was compared for each year.

Table N1. Repeated measures ANOVA showing the significance (*P*>F)[1] of fertilization, pine straw harvest (raking), sampling year and quarter, and interaction of these factors for nutrient concentration in slash pine needlefall collected quarterly for three years after each of three consecutive June fertilizations and February pine straw harvests.

Factor	df	Needlefall nutrient				
		TKN	Pt	K	Ca	Mg
Fertilization (Fert)	4	**<0.001**	0.053	**<0.001**	**<0.001**	0.369
Raking (Rake)	1	0.692	0.864	0.116	**0.010**	0.375
Fert x Rake	4	0.981	0.557	0.171	0.650	0.927
Sampling Year	2	**<0.001**	**0.046**	**<0.001**	**<0.001**	0.919
Fert x Year	8	**<0.001**	0.239	**0.001**	0.052	0.691
Rake x Year	2	0.310	0.475	0.213	0.815	0.707
Fert x Rake x Year	8	0.635	0.972	0.833	0.457	0.685
Quarter of the year (QTR)	3	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.059
Fert x QTR	12	**0.033**	**0.013**	**0.002**	0.569	0.563
Rake x QTR	3	0.079	0.367	0.115	0.708	0.304
Fert x Rake x QTR	12	0.271	0.929	0.751	0.871	0.808
Year x QTR	6	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.215
Fert x Year x QTR	24	0.188	**0.005**	**0.001**	0.245	0.714
Rake x Year x QTR	6	0.411	0.432	**0.026**	0.508	0.721
Fert x Rake x Year x QTR	24	0.333	0.864	0.226	0.998	0.784

[1]Bold *P*≤0.05 denotes a significant effect

Orthogonal contrasts showed that needlefall TKN concentration was affected by fertilization treatment (*P*≤0.001) and responded positively to the ESN rate increase every year beginning with the first fertilization in 2014 (Table N2). ESN applied at 56 or 140 kg N ha^{-1} resulted in higher TKN concentration than the non-fertilized control every year, according to the Dunnett's tests. The difference in TKN concentration between 140 and 0 kg ha^{-1} N rates increased from 16% after the first fertilization in 2014 to 40% after the third fertilization in 2016. This explains the fertilization x sampling year interaction. TKN concentration for the urea treatment at 56 kg N ha^{-1} was also higher than for the non-fertilized control, when averaged across all sampling years. No difference was observed between conventional urea and ESN applied at the same rate.

Table N2. Total Kjeldahl nitrogen (TKN), total P (Pt) and K concentration (g kg^{-1} of tissue dry mass) in slash pine needlefall collected quarterly after each of three consecutive June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over four quarters and raked and non-raked treatments.

Sampling year[1]	Number of fertilizations before sampling	Control		Fertilizer									Orthogonal contrasts P^2 values for pre-planned comparisons				
				ESN						Urea							
		Annual nitrogen application rate (kg N ha^{-1})															
		0		**28**		**56**		**140**		**56**		SE	Fert trt[3]	ESN rate[4]	N form[5]	Rake[6]	Fert x Rake[7]
		Nutrient concentration (g kg^{-1})[8]															
TKN																	
2014/15	1	3.13	b	3.27	ab	3.55	a*	3.63	a*	3.40	ab	0.10	**0.001**	**0.019**	0.267	0.651	0.698
2015/16	2	3.92	c	4.28	bc	4.55	ab*	4.97	a*	4.35	bc	0.14	**<0.001**	**0.002**	0.300	0.768	0.964
2016/17	3	3.69	c	4.16	bc	4.44	b*	5.18	a*	4.26	bc	0.17	**<0.001**	**<0.001**	0.473	0.407	0.949
2014-2017 mean		3.58	c	3.90	bc	4.18	ab*	4.59	a*	4.01	bc*	0.12	**<0.001**	**<0.001**	0.308	0.692	0.981
Pt																	
2014/15	1	0.33		0.34		0.31		0.29		0.34		0.02	0.363	0.205	0.289	0.672	0.723
2015/16	2	0.37	a	0.37	a	0.31	ab	0.29	b*	0.35	ab	0.02	**0.007**	**0.007**	0.152	0.837	0.552
2016/17	3	0.36		0.36		0.30		0.31		0.34		0.02	0.074	0.057	0.137	0.484	0.554
2014-2017 mean		0.35		0.36		0.31		0.30		0.34		0.02	0.053	**0.035**	0.144	0.864	0.475
K																	
2014/15	1	0.64		0.80		0.82	*	0.68		0.77		0.05	0.053	0.108	0.500	0.546	0.174
2015/16	2	0.81	b	1.24	a*	1.20	a*	1.11	a*	1.15	a*	0.06	**<0.001**	0.362	0.632	0.185	0.145
2016/17	3	0.86	b	1.27	a*	1.28	a*	1.33	a*	1.25	a*	0.07	**<0.001**	0.842	0.790	**0.048**	0.387
2014-2017 mean		0.77	b	1.10	a*	1.10	a*	1.04	a*	1.06	a*	0.06	**<0.001**	0.668	0.612	0.116	0.213

[1]Each sampling year starts at June fertilization and continues for four quarters.
[2]Bold P≤0.05 denotes a significant effect.
[3]P values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[4]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[6]P values for raking treatment effect within a year or for three-year post-fertilization averages.
[7]P values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[8]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a row, means signified with an asterisk are different than a mean for the non-fertilized control using Dunnett's test at α=0.05.

Table N3. Ca and Mg concentration (g kg^{-1} of tissue dry mass) in slash pine needlefall collected quarterly after each of three consecutive June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over four quarters and raked and non-raked treatments.

Sampling year[1]	Number of fertilizations before sampling	Control 0		ESN 28		ESN 56		ESN 140		Urea 56		SE	Fert trt[3]	ESN rate[4]	N form[5]	Rake[6]	Fert x Rake[7]
		Nutrient concentration (g kg^{-1})[8]											Orthogonal contrasts P^2 values for pre-planned comparisons				
		Ca															
2014/15	1	5.10	ab	5.18	ab	4.76	b	5.76	a*	5.57	a	0.21	**0.002**	**0.001**	**0.002**	0.053	0.484
2015/16	2	4.67	bc	4.63	bc	4.37	c	5.39	a*	4.96	ab	0.15	**<0.001**	**<0.001**	**0.001**	**0.017**	0.768
2016/17	3	4.53	ab	4.30	b	4.32	b	4.85	a	4.56	ab	0.16	**0.021**	**0.004**	0.199	**0.013**	0.816
2014-2017 mean		4.77	bc	4.70	bc	4.48	c	5.33	a*	5.03	ab	0.15	**<0.001**	**<0.001**	**0.002**	**0.010**	0.815
		Mg															
2014/15	1	0.71		0.76		0.78		0.80		0.77		0.03	0.485	0.683	0.810	0.606	0.876
2015/16	2	0.72		0.74		0.78		0.82		0.75		0.04	0.423	0.345	0.657	0.479	0.867
2016/17	3	0.73		0.71		0.79		0.80		0.75		0.03	0.208	0.095	0.354	0.179	0.823
2014-2017 mean		0.72		0.74		0.78		0.81		0.76		0.03	0.369	0.310	0.578	0.375	0.707

Annual nitrogen application rate (kg N ha^{-1}) for Control, Fertilizer (ESN, Urea) columns.

[1]Each sampling year starts at June fertilization and continues for four quarters.
[2]Bold P≤0.05 denotes a significant effect.
[3]P values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[4]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[6]P values for raking treatment effect within a year or for three-year post-fertilization averages.
[7]P values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[8]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a row, means signified with an asterisk are different than a mean for the non-fertilized control using Dunnett's test at α=0.05.

Nearly significant fertilization effect on needlefall Pt concentration in the overall ANOVA (Table N1) can be explained by the concentration decrease with increasing ESN rate in 2015/16 (Table N2). That year Pt concentration was lower by 20% for the ESN at 140 compared to 0 N kg ha^{-1}. This result is consistent with the lack of foliar Pt concentration positive response to fertilization and a slight foliar Pt concentration decrease with fertilization (Table F2).

Needlefall K concentration was affected by the second and third fertilization and for the 3-year average (Table N2). There were no differences among the fertilized treatments, but each resulted in K concentration higher the non-fertilized control. This could be expected because each fertilized treatment received the same rate of 56 kg ha^{-1} K with KCl annually. The K concentration increase over the control resulting from fertilization varied among the treatments form 38 to 53% in 2015/16, 48 to 55% in 2016/17 and 35 to 43% for the 3-year average.

According to the orthogonal contrasts, needlefall Ca concentration was affected every year by the fertilization treatment and ESN rate, but there was no consistent response to the ESN application rate increase (Table N3). Yearly Ca concentration was higher for ESN at 140 kg N ha^{-1} than at 56 kg N ha^{-1}, but not always significantly different from 28 or 0 kg N ha^{-1}, when compared with Bonferonni-Holm adjustment for multiple mean comparison. According to the Dunnett's test, highest ESN rate resulted in needlefall Ca concentration higher (by 12 to 16%) than non-fertilized control in 2014/15, 2015/16 and for the average of three fertilizations. At the same time, Ca concentration was affected by the fertilizer form and was higher following conventional urea compared to ESN at the same N rate.

None of the investigated factors affected Mg concentration, which as not supplied with any fertilization treatment (Table N3).

The overall ANOVA showed significant raking effect only for needlefall Ca concentration and no significant interaction between raking and fertilization or sampling year for any examined nutrient (Table N1). According to orthogonal contrasts Ca concentration was affected by raking after the second and third raking in 2015 and 2016, respectively as well as for the 3-year average (Table N3). Needlefall Ca concentration in the raked and non-raked treatments averaged across three years and all fertilization treatments and was 5.01 and 4.72 g kg^{-1}, respectively, resulting in a 6% difference.

6.7.4 Results and discussion - needlefall dry mass yield and nutrient content

According to the overall ANOVA, needlefall dry mass yield (DM) and TKN, K, Ca and Mg needlefall content were significantly affected by the fertilization treatment x sampling year interaction (Table N4), indicating different fertilization effect in different years. The main fertilization effect was significant for TKN, K and Ca content.

According to the orthogonal contrasts, needlefall DM was affected by the fertilization treatment and responded positively to the ESN rate increase only after the third fertilization in 2016 (Table N5, Figure N1). Dry mass of the needlefall collected during the year following 2016 application of ESN at 140 kg N ha^{-1} was 12% greater compared to the non-fertilized control. A significant 12% difference was also observed after the second fertilization in 2015 based on Dunnett's test (Table N5). In terms of DM, no difference between ESN and conventional urea applied at 56 kg N ha^{-1} was observed throughout the study period.

Table N4. Repeated measures ANOVA showing the significance (*P*>F)[1] of fertilization, pine straw harvest (raking), sampling year and quarter, and interaction of these factors for dry mass yield (DM) and nutrient content in slash pine needlefall collected quarterly after each of three consecutive June fertilizations and February pine straw harvests.

Factor	df	Needlefall	Needlefall nutrient				
		DM	TKN	Pt	K	Ca	Mg
Fertilization (Fert)	4	0.380	**0.001**	0.411	**0.006**	**0.007**	0.156
Raking (Rake)	1	0.396	0.637	0.670	0.199	0.331	0.707
Fert x Rake	4	0.794	0.909	0.500	0.335	0.949	0.984
Sampling Year (Year)	2	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**0.031**	**0.001**
Fert x Year	8	**0.018**	**<0.001**	0.488	**<0.001**	**0.009**	**0.038**
Rake x Year	2	0.601	0.490	**0.044**	**0.044**	0.959	0.731
Fert x Rake x Year	8	0.479	0.750	0.921	0.948	0.441	0.346
Quarter of the year (QTR)	3	<0.001	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x QTR	12	0.197	0.169	0.117	0.083	**0.014**	0.114
Rake x QTR	3	0.062	0.424	0.053	**0.016**	0.133	**0.008**
Fert x Rake x QTR	12	0.182	0.120	0.650	0.250	0.090	0.139
Year x QTR	6	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Year x QTR	24	0.071	**0.041**	0.142	**0.020**	**0.005**	0.094
Rake x Year x QTR	6	0.081	**0.017**	0.368	0.609	0.081	0.166
Fert x Rake x Year x QTR	24	0.226	**0.011**	0.387	0.105	0.467	0.584

[1]Bold $P \leq 0.05$ denotes a significant effect

Beginning after the second fertilization in 2015, needlefall TKN content was affected by the fertilization treatment, and specifically by the ESN rate, but not the fertilizer form, (Table N5). We observed a positive ESN rate response after the second and third fertilization and for the average of three fertilizations (Figure N1). At these times the highest ESN rate resulted in TKN content greater than any other treatment, although it was significantly different from the middle rate only in year 3. The 140 kg N ha^{-1} ESN rate increased TKN content over the non-fertilized control by 44% after the second fertilization, 52% after the third fertilization, and by 39% for the average of three fertilizations. According to the Dunnett's test, that increase was also significant for ESN at 56 kg N ha^{-1} (22-24%) beginning with the second fertilization and for the urea at 56 kg N ha^{-1} (16%) 3-year average (Table N5).

No significant fertilization effects were observed for needlefall Pt content. The annual 10% reduction for the highest fertilization rate compared to the non-fertilized control was not significant (Table N5).

Fertilization treatment affected needlefall K content after the second and third fertilization, as well as for the average of the three fertilizations (Table N6). However, that effect was limited to the difference between the non-fertilized control and other treatments (Figure N2), all of which received 56 kg ha^{-1} K with KCl annually. The needlefall K content increase due to fertilization was as high as 73% in case of the third ESN application at 140 kg N ha^{-1}. After the third fertilization we observed a clear trend of K content increase with increasing ESN rate, in spite of no significant differences.

Table N5. Annual needlefall dry mass yield, total Kjeldahl nitrogen (TKN) and total P (Pt) content in slash pine needlefall collected quarterly after each of the three consecutive June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling year[1]	Number of fertilizations before sampling	Control	Fertilizer: ESN			Fertilizer: Urea		Orthogonal contrasts *P*[2] values for pre-planned comparisons				
		Annual nitrogen application rate (kg N ha^{-1})										
		0	**28**	**56**	**140**	**56**	SE	Fert trt[3]	ESN rate[4]	N form[5]	Rake[6]	Fert x Rake[7]
		Dry mass (Mg ha^{-1})[8]										
2014/15	1	6.12	6.15	6.35	6.09	6.00	0.24	0.878	0.714	0.300	0.508	0.609
2015/16	2	5.84	6.25	6.22	6.57 *	6.27	0.19	0.122	0.360	0.852	0.689	0.974
2016/17	3	6.37 b	6.34 b	6.72 ab	7.15 a*	6.62 ab	0.19	**0.024**	**0.014**	0.712	0.226	0.572
2014-2017 mean		6.11	6.25	6.43	6.60	6.30	0.18	0.380	0.392	0.601	0.396	0.794
		TKN content (kg ha^{-1})[8]										
2014/15	1	18.00	18.78	21.33	21.02	19.55	1.02	0.130	0.175	0.227	0.847	0.641
2015/16	2	21.60 b	24.94 b	26.68 ab*	31.18 a*	25.70 b	1.25	**<0.001**	**0.005**	0.584	0.874	0.989
2016/17	3	22.82 c	25.36 bc	28.34 b*	34.69 a*	27.29 bc	1.26	**<0.001**	**<0.001**	0.561	0.371	0.837
2014-2017 mean		20.81 c	23.03 bc	25.45 ab*	28.96 a*	24.18 bc*	1.08	**0.001**	**0.003**	0.415	0.637	0.909
		Pt content (kg ha^{-1})[8]										
2014/15	1	1.93	2.04	1.83	1.73	1.96	0.16	0.663	0.372	0.542	0.706	0.632
2015/16	2	2.05	2.15	1.81	1.83	2.07	0.13	0.255	0.128	0.164	0.783	0.453
2016/17	3	2.28	2.18	1.90	2.05	2.17	0.14	0.326	0.344	0.153	0.170	0.528
2014-2017 mean		2.08	2.12	1.85	1.87	2.07	0.13	0.411	0.262	0.229	0.670	0.500

[1]Each sampling year starts at June fertilization and continues for four quarters.
[2]Bold P≤0.05 denotes a significant effect.
[3]P values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[4]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[6]P values for raking treatment effect within a year or for three-year post-fertilization averages.
[7]P values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[8]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a row, means signified with an asterisk are different than a mean for the non-fertilized control using Dunnett's test at α=0.05.

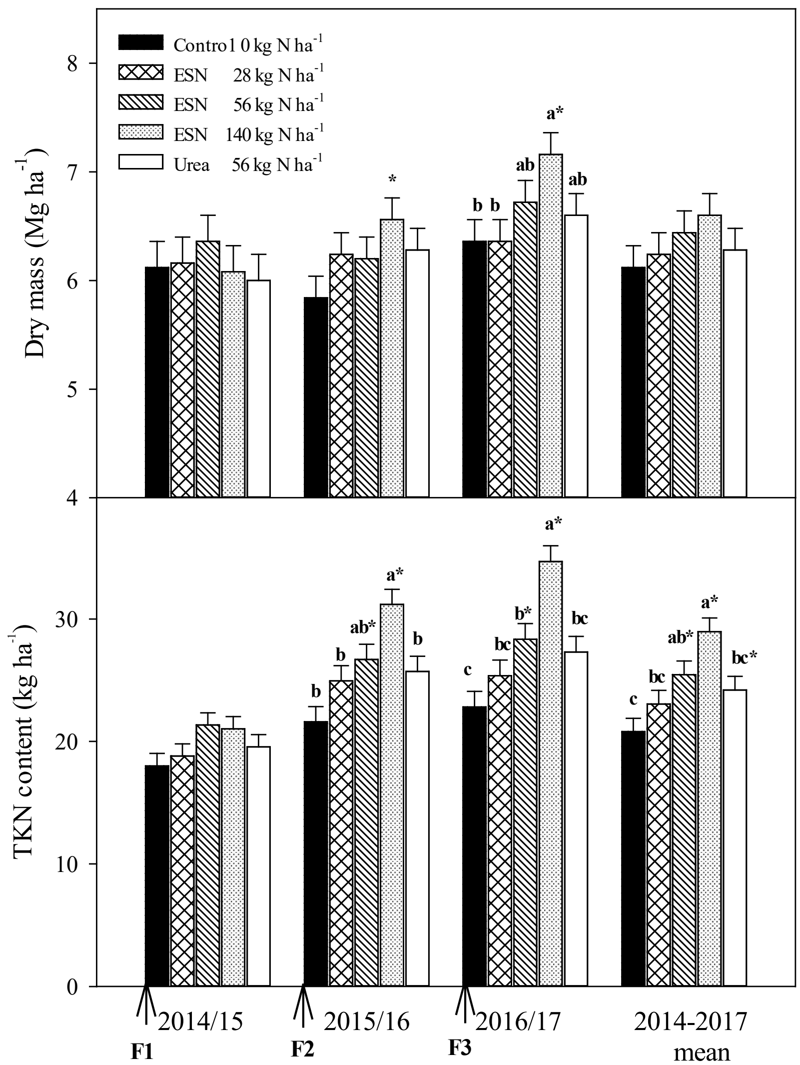

Figure N1. Annual needlefall dry mass yield and total Kjeldahl nitrogen (TKN) content in slash pine needlefall calculated from quarterly collections after each of three consecutive June fertilizations (F1-F3) averaged over raked and non-raked treatments. LS-means (+SE) within a sampling year or for an average across three years labeled with the same letter or not labeled with any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a year or for the 3-year average, fertilizer treatment means signified with an asterisk are different than the non-fertilized control using Dunnett's test at α=0.05. Each sampling year starts at June fertilization and continues for four quarters.

We observed a significant treatment and ESN rate effect on needlefall Ca content after the second, third and for the average of three fertilizations (Table N6). However, only the highest ESN rate resulted in Ca content increase over the control (by up to 31%) and there were no significant differences among other treatments (Figure N2). All ESN treatments received 9.2 kg ha^{-1} of Ca per year with triple superphosphate.

Orthogonal contrasts revealed significant fertilization treatment and ESN rate effects on needlefall Mg content only after the third fertilization in 2016 (Table N6). According to the Dunnett's test, Mg content for the ESN at 140 kg N ha^{-1} was significantly higher than for the control after the second (by 28%), the third (by 22%) fertilization.

In the overall ANOVA raking treatment or raking x fertilization interaction had no significant effect on content of any needlefall nutrient, but raking x sampling year interaction was significant for Pt and K content (Table N4). However, there were no significant differences between raked and non-raked treatments in any of the three years. The interactions were weak (P=0.044) and related to variation in the magnitude of treatment differences over sampling years in which no annual difference was large enough to be significant.

Table N6. Annual needlefall K, Ca, and Mg content in slash pine needlefall collected quarterly after each of three consecutive June fertilizations with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling year[1]	Number of fertilizations before sampling	**Control** 0		**Fertilizer – ESN** 28		**ESN** 56		**ESN** 140		**Urea** 56		SE	Fert trt[3]	ESN rate[4]	N form[5]	Rake[6]	Fert x Rake[7]
		Annual nitrogen application rate (kg N ha^{-1})											Orthogonal contrasts P[2] values for pre-planned comparisons				
		K content (kg ha^{-1})[8]															
2014/15	1	3.58		4.41		4.64		3.94		4.35		0.40	0.377	0.467	0.618	0.754	0.387
2015/16	2	4.39	b	7.03	a*	6.99	a*	6.95	a*	6.82	a*	0.48	**0.002**	0.992	0.815	0.331	0.416
2016/17	3	5.23	b	7.83	a*	8.32	a*	9.09	a*	8.21	a*	0.55	**0.001**	0.275	0.895	**0.050**	0.391
2014-2017 mean		4.40	b	6.42	a*	6.65	a*	6.66	a*	6.46	a*	0.44	**0.006**	0.911	0.768	0.199	0.335
		Ca content (kg ha^{-1})[8]															
2014/15	1	29.82		30.34		28.99		33.13		31.86		1.52	0.336	0.163	0.192	0.415	0.560
2015/16	2	26.82	b	28.40	b	26.93	b	35.26	a*	30.45	ab	1.27	**<0.001**	**<0.001**	0.062	0.319	0.997
2016/17	3	28.20	b	26.64	b	28.14	b	34.52	a*	29.78	ab	1.26	**0.002**	**<0.001**	0.365	0.413	0.972
2014-2017 mean		28.28	b	28.46	b	28.02	b	34.30	a*	30.70	ab	1.21	**0.007**	**0.002**	0.132	0.331	0.949
		Mg content (kg ha^{-1})[8]															
2014/15	1	4.24		4.57		4.81		4.70		4.51		0.28	0.668	0.832	0.470	0.962	0.894
2015/16	2	4.19		4.58		4.79		5.36	*	4.69		0.27	0.081	0.138	0.797	0.586	0.962
2016/17	3	4.58		4.47		5.24		5.58	*	4.90		0.26	**0.032**	**0.017**	0.362	0.641	0.801
2014-2017 mean		4.34		4.54		4.95		5.21		4.70		0.25	0.156	0.185	0.500	0.707	0.984

[1]Each sampling year starts at June fertilization and continues for four quarters.
[2]Bold P≤0.05 denotes a significant effect.
[3]P values for differences among fertilization treatments (including the non-fertilized control) within a year or for three-year post-fertilization averages.
[4]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[5]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or for three-year post-fertilization averages.
[6]P values for raking treatment effect within a year or for three-year post-fertilization averages.
[7]P values for significance of fertilization x raking interaction within a year or for three-year post-fertilization averages.
[8]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a row, means signified with an asterisk are different than a mean for the non-fertilized control using Dunnett's test at α=0.05.

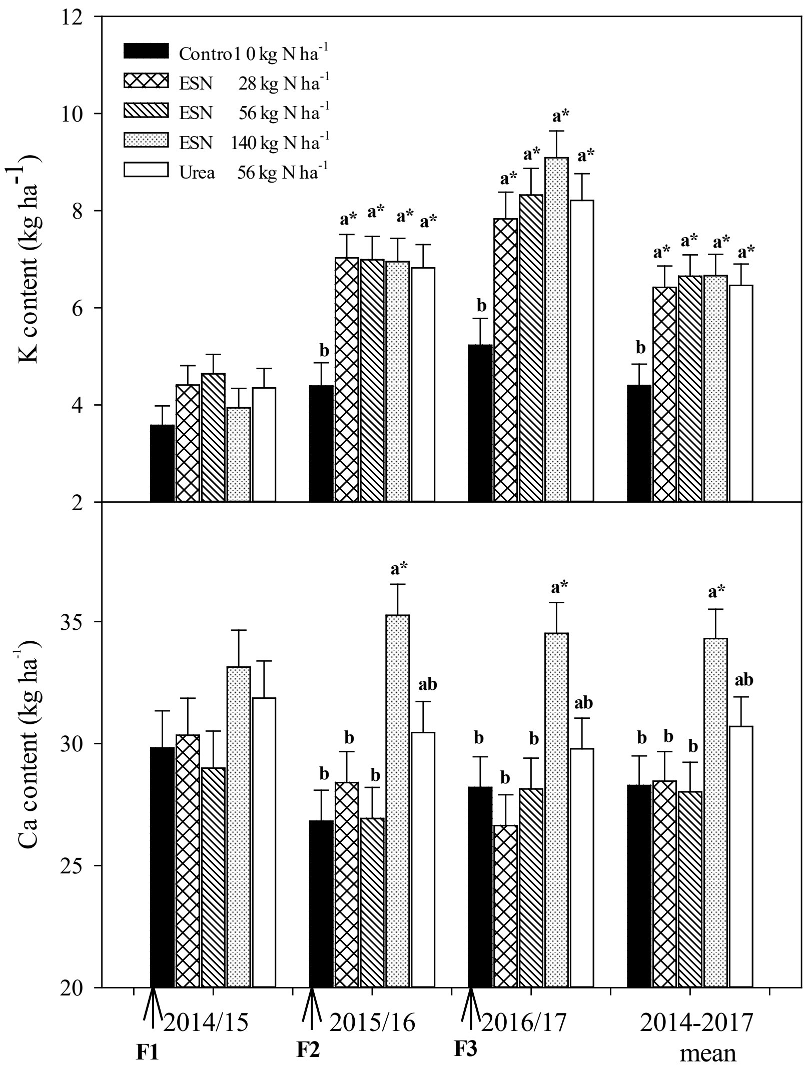

Figure N2. Annual potassium (K) and calcium (Ca) content in slash pine needlefall calculated from quarterly collections after each of three consecutive June fertilizations (F1-F3) averaged over raked and non-raked treatments. LS-means (+SE) within a sampling year or for an average across three years labeled with the same letter or not labeled with any letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a year or for the 3-year average, fertilizer treatment means signified with an asterisk are different than the non-fertilized control using Dunnett's test at α=0.05. Each sampling year starts at June fertilization and continues for four quarters.

6.8 Impacts to Pine Straw Yield and Nutrients

6.8.1 Summary

- Harvested pine straw TKN concentration was increased after two annual fertilizations with the high ESN rate, and after three fertilizations all fertilized treatments increased TKN and K concentration relative to the non-fertilized control, by as much as 29% TKN and 73% K.
- Harvested pine straw yield began to show a response following the second fertilization, at the third raking. At the forth raking bale count and dry weight was greater for the high ESN rate than all treatments, except dry weight following fertilization with conventional urea. At the fourth raking the high ESN rate increased bale count by 35% and dry mass by 30% over the non-treated control.
- Increased pine straw yields with fertilization were accompanied by greater removals of TKN, K, Ca and Mg.
- The high ESN rate resulted in the greatest cumulative nutrient removal, and increased removals relative to the control by 49% for TKN, 85% for K and 32% for Mg. The high ESN rate resulted in greater Ca removals than other fertilized treatments, but was not different from the non-treated control.
- Computing mass balance as a function of cumulative fertilization inputs and removals, the non-treated control had a deficit of -48.7 kg TKN, -4.2 kg Pt, -5.9 K, -73.9 Ca and -9.7 Mg per hectare.
- Annual applications of 28 kg N ha^{-1} as ESN compensated for removals in annual pine straw harvesting.
- Fertilized treatments had Ca deficits ranging from -33.8 to -64.6 kg ha^{-1} (27.4 kg ha^{-1} Ca was supplied in all, except for conventional urea), and Mg deficits from -9 to -12.8 kg ha^{-1}.

6.8.2 Statistical analyses of pine straw yield and nutrients

The analysis of variance for harvested pine straw nutrients [total Kjeldahl nitrogen (TKN), total phosphorus (Pt), K, Ca and Mg] was performed as a mixed-model with blocks considered random and annual straw sampling considered a repeated longitudinal assessment of an experimental unit (plot). A preliminary analysis was performed to compare the parametric structure of the covariance matrix with respect to possible heterogeneity of variance and correlation of annual pine straw samples. Compound symmetry (CS), heterogeneous compound symmetry (CSH), first-order autoregressive (AR1) and heterogeneous first-order autoregressive (ARH1) structures were compared based on AIC (Akaike 1974), AICC (Hurvich and Tsai 1989) and BIC (Schwarz 1978) information criteria using SAS PROC MIXED (Littell et al. 2006).

Fertilization treatment means were compared annually and also when averaged over the three post-fertilization sampling years. An overall F-test of treatment differences was performed for both of these groupings. Individual fertilization treatment means were compared using the stepdown Bonferroni-Holm (Holm 1979) probability adjustment for multiplicity. Additional specific hypotheses tested as pre-planned comparisons were that harvested straw nutrient concentrations do not differ: 1) between each fertilization treatment and the non-fertilized control, 2) among the three rates of ESN (ESN rate), and 3) between conventional urea and polymer-coated urea (ESN) at the same 56 kg elemental N hectare^{-1} rate (N form).

6.8.3 Results and discussion - harvested pine straw nutrient concentration

Fertilization affected the concentration of TKN and K in harvested straw. As was observed for pine foliar nutrients, concentrations of all nutrients varied by sampling year (P<0.001). This may be explained by time from sequential annual fertilizations, changes in yearly rainfall and other temporal environmental factors. A significant fertilization by year interaction was observed for foliar TKN and K concentration, which is explained by the greater effect of fertilization at the later assessments, following sequential annual fertilizations.

Table PS1. Repeated measures ANOVA showing the significance (P>F)[1] of fertilization, sampling year and interaction of these factors for nutrient concentrations in slash pine straw over four annual February harvests, beginning three months prior to the first of three annual June fertilizations.

Factor	df	Pine straw nutrient concentration				
		TKN	Pt	K	Ca	Mg
Fertilization (Fert)	4	**0.003**	0.476	**0.049**	0.080	0.083
Sampling Year	3	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Year	12	**<0.001**	0.079	**0.003**	0.302	0.736

[1]Bold $P \leq 0.05$ denotes a significant effect.

Harvested pine straw showed increased TKN concentration following the second fertilization, with the high ESN rate having greater TKN than the other treatments, 25% greater than the non-treated control (Table PS2). Following the third fertilization all fertilized treatments increased harvested straw TKN relative to the control, as shown by Dunnett's test. At this time, pine straw collected from the high ESN rate hade greater TKN than other treatments, 29% greater than the non-fertilized control. There were no differences in straw TKN concentration between ESN and conventional urea treatments.

Differences in harvested pine straw K concentration were observed only after the third fertilization, when all fertilized treatments had greater K than the non-fertilized control (50 – 73%), with no differences among them (Table PS2).

6.8.4 Results and discussion - harvested pine straw yield and nutrient removals

Fertilization affected harvested pine straw bale count and dry mass, as well as removals of TKN, K, Ca and Mg (Table PS3). As with other pine response variables, sampling year affected straw yields and all measured nutrient removals, and this temporal effect is explained by time from sequential annual fertilizations, changes in yearly rainfall and by changes in stand age. Stand age is important for straw yield in particular, since pine crowns expand through the stand ages sampled. The effects of fertilization differed by year for these variables, as indicated by the significant fertilization and year interactions described.

Annual harvested pine straw yield

Harvested pine straw yield, as measured by bale count and dry mass, began to show a response following the second fertilization, at the third raking (Figure PS1). At the third raking the high ESN rate had greater bale count and dry mass than the low ESN rate. At the forth raking bale count and dry weight was greater for the high ESN rate than all treatments, except straw dry weight following fertilization with conventional urea. At the last raking the high ESN rate increased bale count by 35% and dry mass by 30% over the non-treated control.

Cumulative pine straw yield, nutrient removals and nutrient budgets

Cumulative harvested pine straw dry mass over four annual February rakings was greater for the high ESN rate than other fertilized treatments, but did not differ from the control using Bonferroni adjustment (Table PS4). Using Dunnett's test pine straw yield with the high ESN rate was greater than the control (19%).

Cumulative nitrogen removals by raking, assessed by measures of straw TKN concentration and mass removed, were greater for the high ESN rate than other treatments, with no differences among the other treatments (Table PS4). TKN removals with the high ESN rate were 49% greater than the control. Computing mass balance as a function of cumulative fertilization inputs and removals, a deficit of -48.7 kg TKN ha^{-1} occurred in the non-fertilized control, whereas a positive balance occurred with fertilization, ranging from 36.4 (low ESN rate) to 347.9 (high ESN rate) kg TKN ha^{-1}. Annual applications of 28 kg N ha^{-1} as ESN compensated for removals in annual pine straw harvesting.

Cumulative K removals by raking were greater (85%) for the high ESN rate than the non-fertilized control, but there were no differences among the fertilized treatments using Bonferroni adjustment (Table PS4). Using Dunnett's test all fertilized treatments had greater K removal than the non-fertilized control. All fertilized treatments received 168.1 kg K ha^{-1}. Computed mass balances showed a -5.9 kg K ha^{-1} deficit for the non-fertilized control; whereas, a positive K balance was observed for fertilized treatments, with little difference among them (157.2 – 160.2 kg K ha^{-1}).

Cumulative Ca removals were greater for the high ESN rate than the other fertilized treatments, but not different from the control (Table PS4). All fertilized treatments, except urea received 27.4 kg Ca ha^{-1}. Mass balance determinations showed a Ca deficit for all treatments. The largest deficit was observed in the non-fertilized control (-73.9 kg Ca ha^{-1}), followed by the high ESN rate and urea (-64.6 and -64.5 kg Ca ha^{-1}, respectively), and a similar deficit for other fertilized treatments (-33.8 to -34.5 kg Ca ha^{-1}).

Cumulative Mg removal was greater for the high ESN rate than other treatments, with no differences among the other treatments (Table PS4). The high ESN rate had 32% greater Mg removal than the non-fertilized control. Mg was not supplied by fertilization treatments, and removals ranged from -9.0 to -12.8 kg Mg ha^{-1}).

Table PS2. Nutrient concentrations (g kg^{-1} of tissue dry mass) in slash pine straw harvested in February before (Feb-2014) and after (Feb-2015, Feb-2016 and Feb-2017) three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Fertilization date	Sampling date	Control	Fertilizer: ESN			Fertilizer: Urea		Orthogonal contrasts *P*[1] values for pre-planned comparisons		
		Annual nitrogen application rate (kg N ha^{-1})								
		0	**28**	**56**	**140**	**56**		Trt[2]	ESN rate[3]	Form[4]
		Nutrient concentration (g kg^{-1})[5]					SE			
				TKN						
	Feb-2014	2.54	2.38	2.55	2.51	2.36	0.10	0.502	0.458	0.193
Jun-2014	Feb-2015	3.28	3.26	3.78	3.67	3.32	0.17	0.165	0.126	0.087
Jun-2015	Feb-2016	2.83 b	2.86 b	3.06 b	3.54 a*	2.98 b	0.09	**0.001**	**0.001**	0.544
Jun-2016	Feb-2017	4.14 c	4.38 bc*	4.60 b*	5.34 a*	4.41 bc*	0.07	**<0.001**	**<0.001**	0.087
2014-2016 mean		3.41 b	3.50 b	3.81 ab*	4.18 a*	3.57 b	0.09	**<0.001**	**<0.001**	0.087
				Total P						
	Feb-2014	0.21	0.25	0.21	0.22	0.21	0.03	0.793	0.561	0.933
Jun-2014	Feb-2015	0.26	0.25	0.24	0.26	0.24	0.03	0.958	0.869	0.944
Jun-2015	Feb-2016	0.28	0.27	0.22	0.24	0.23	0.02	0.102	0.120	0.550
Jun-2016	Feb-2017	0.36	0.32	0.28	0.30	0.29	0.02	0.072	0.201	0.681
2014-2016 mean		0.30	0.28	0.24	0.26	0.25	0.02	0.275	0.367	0.780
				K						
	Feb-2014	0.29	0.30	0.28	0.25	0.27	0.02	0.368	0.206	0.626
Jun-2014	Feb-2015	0.30	0.36	0.34	0.34	0.37	0.03	0.479	0.869	0.492
Jun-2015	Feb-2016	0.42	0.55	0.51	0.55	0.54	0.04	0.241	0.762	0.657
Jun-2016	Feb-2017	0.52 b	0.81 a*	0.78 a*	0.90 a*	0.78 a*	0.05	**0.003**	0.228	0.939
2014-2016 mean		0.41 b	0.57 ab*	0.54 ab*	0.60 a*	0.56 ab*	0.03	**0.021**	0.529	0.722
				Ca[6]						
	Feb-2014	5.35	5.56	5.12	5.80	5.13	0.26	0.333	0.206	0.977
Jun-2014	Feb-2015	5.52	5.04	4.95	5.67	4.86	0.26	0.146	0.133	0.794
Jun-2015	Feb-2016	4.97	4.48	4.41	5.45	4.50	0.26	**0.050**	**0.018**	0.806
Jun-2016	Feb-2017	5.23	4.44	4.34	5.45	4.68	0.26	**0.026**	**0.013**	0.367
2014-2016 mean		5.24	4.65	4.57	5.52	4.68	0.22	**0.043**	**0.022**	0.732
				Mg						
	Feb-2014	0.55	0.62	0.62	0.65	0.55	0.03	0.089	0.705	0.113
Jun-2014	Feb-2015	0.68	0.69	0.72	0.77	0.69	0.03	0.219	0.176	0.449
Jun-2015	Feb-2016	0.68	0.67	0.69	0.77	0.65	0.03	0.089	0.062	0.404
Jun-2016	Feb-2017	0.71	0.68	0.73	0.78	0.71	0.03	0.246	0.089	0.599
2014-2016 mean		0.69	0.68	0.71	0.77 *	0.68	0.02	0.081	**0.045**	0.373

[1]Bold $P \leq 0.05$ denotes a significant effect.

[2]*P* values for differences among fertilization treatments (including the non-fertilized control) within a year or post-fertilization averages.

[3]*P* values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or post-fertilization averages.

[4]*P* values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or post-fertilization averages.

[5]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holm adjustment at $\alpha=0.05$. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at $\alpha=0.05$.

[6]Means for Feb-16, Feb-17 and post-fertilization averages are not different using Bonferonni-Holm adjustment or Dunnett's test.

Table PS3. Repeated measures ANOVA showing the significance (P>F)[1] of fertilization, sampling year and interaction of these factors for slash pine straw yield and nutrient removals over four annual February pine straw harvests, the first beginning four months prior to the first of three annual June fertilizations.

Factor	df	Pine straw yield		Pine straw nutrient removal				
		Bale count	Dry mass	TKN	Pt	K	Ca	Mg
Fertilization (Fert)	4	**0.041**	**0.024**	**0.015**	0.285	**0.017**	**0.018**	**0.010**
Sampling Year	3	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Year	12	**0.004**	**<0.001**	**<0.001**	**0.028**	**<0.001**	**0.001**	**0.004**

[1]Bold P≤0.05 denotes a significant effect.

Table PS4. Cumulative nutrient removals, inputs and mass balance following a regime of four annual February pine straw harvests, the first beginning four months prior to the first of three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Fertilizer treatment	Annual N application rate kg ha^{-1}	Pine straw DM Mg ha^{-1}		Nutrient (kg ha^{-1}) TKN		Pt[1]	K		Ca		Mg	
				Removals[2]								
Control	0	14.0	ab	48.7	b	4.2	5.9	b	73.9	ab	9.7	b
ESN	28	13.3	b	47.7	b	3.8	8.1	ab*	61.2	b	9.0	b
ESN	56	13.7	b	53.2	b	3.4	7.9	ab*	61.9	b	9.8	b
ESN	140	16.7	a*	72.4	a*	4.5	10.9	a*	92.0	a	12.8	a*
Urea	56	13.8	b	51.1	b	3.6	8.3	ab*	64.5	b	9.5	b
				Inputs								
Control	0			0.0		0.0	0.0		0.0		0.0	
ESN	28			84.1		37.0	168.1		27.4		0.0	
ESN	56			168.1		37.0	168.1		27.4		0.0	
ESN	140			420.3		37.0	168.1		27.4		0.0	
Urea	56			168.1		37.0	168.1		0.0		0.0	
				Balance								
Control	0			-48.7		-4.2	-5.9		-73.9		-9.7	
ESN	28			36.4		33.2	160.0		-33.8		-9.0	
ESN	56			115.0		33.6	160.2		-34.5		-9.8	
ESN	140			347.9		32.5	157.2		-64.6		-12.8	
Urea	56			117.0		33.4	159.8		-64.5		-9.5	

[1]Pt = total P.
[2]Means within a column followed by the same letter are not significantly different using stepdown Bonferroni adjustment at α=0.05. Within a column, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.

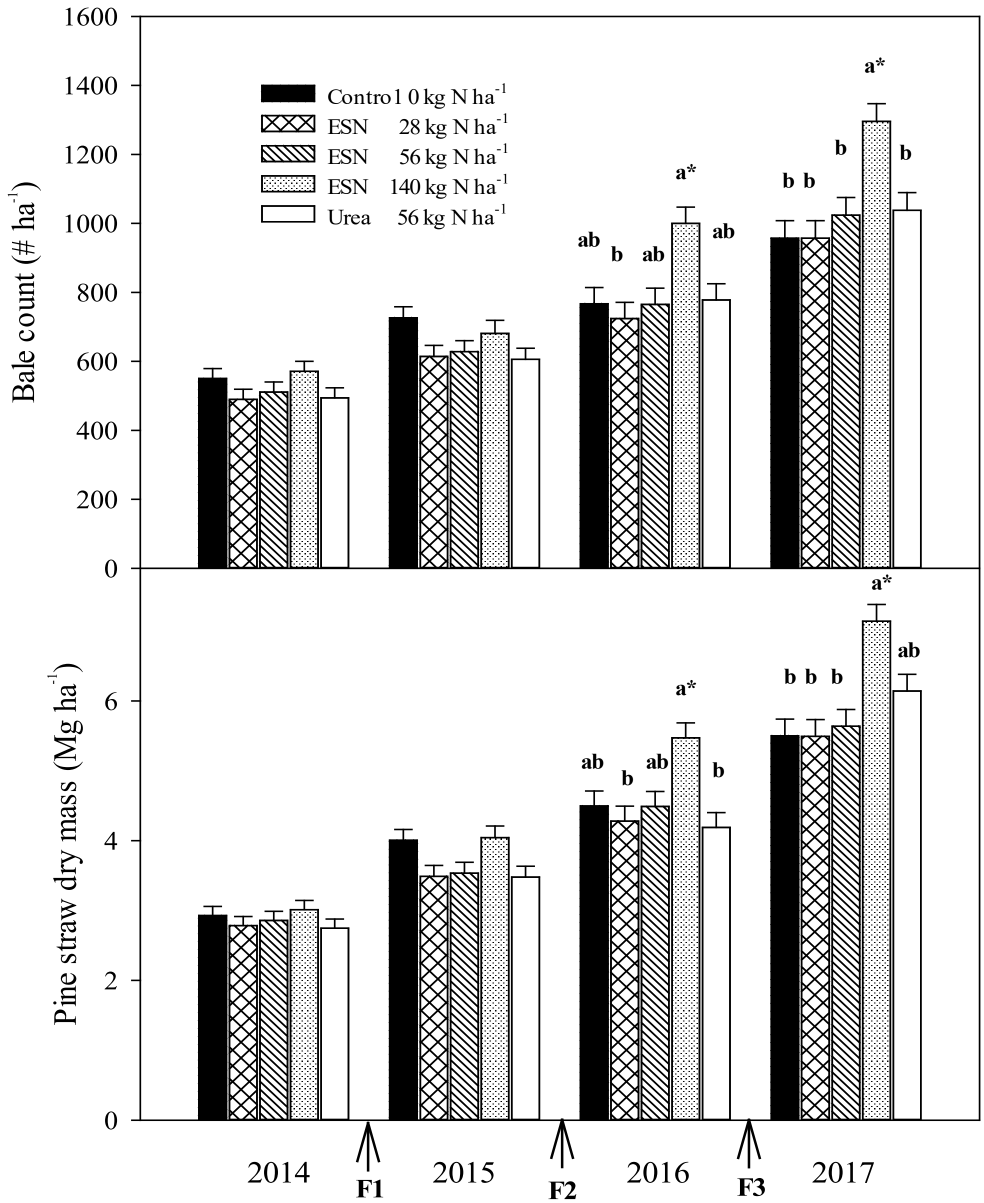

Figure PS1. Yield of slash pine straw harvested in February before (2014) and after (2015-2017) three annual June fertilizations (F1-F3) with urea or polymer-coated urea (ESN) at different rates. Means (+SE) within a sampling year labeled with the same letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a year, means signified with an asterisk are greater than the non-fertilized control using Dunnett's test at α=0.05.

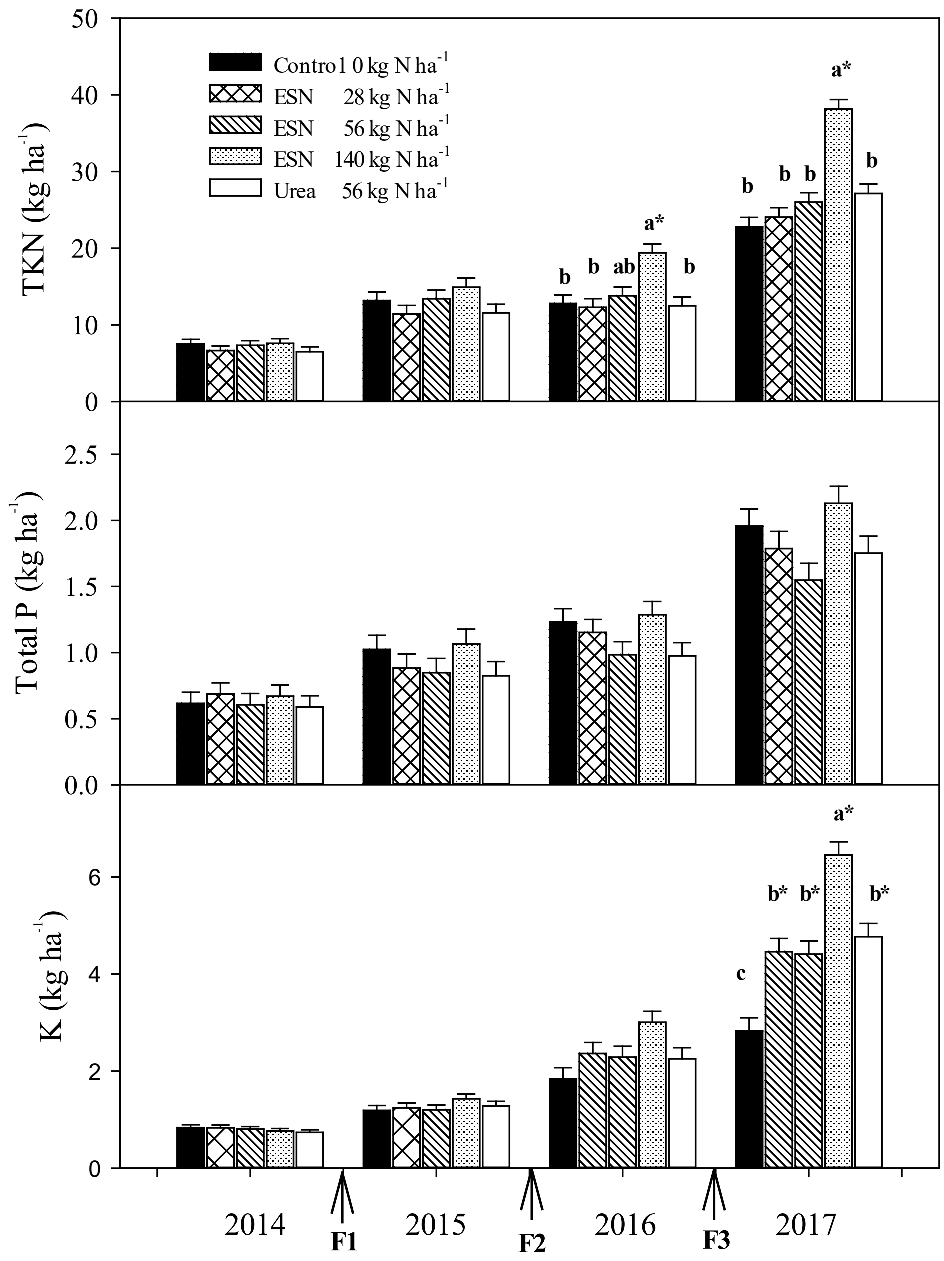

Figure PS2. Total Kjeldahl nitrogen (TKN), total phosphorous and potassium removals with pine straw harvested in February before (2014) and after (2015-2017) three annual June fertilizations (F1-F3) with urea or polymer-coated urea (ESN) at different rates. Means (+SE) within a sampling year labeled with the same letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a year, means signified with an asterisk are greater than the non-fertilized control using Dunnett's test at α=0.05.

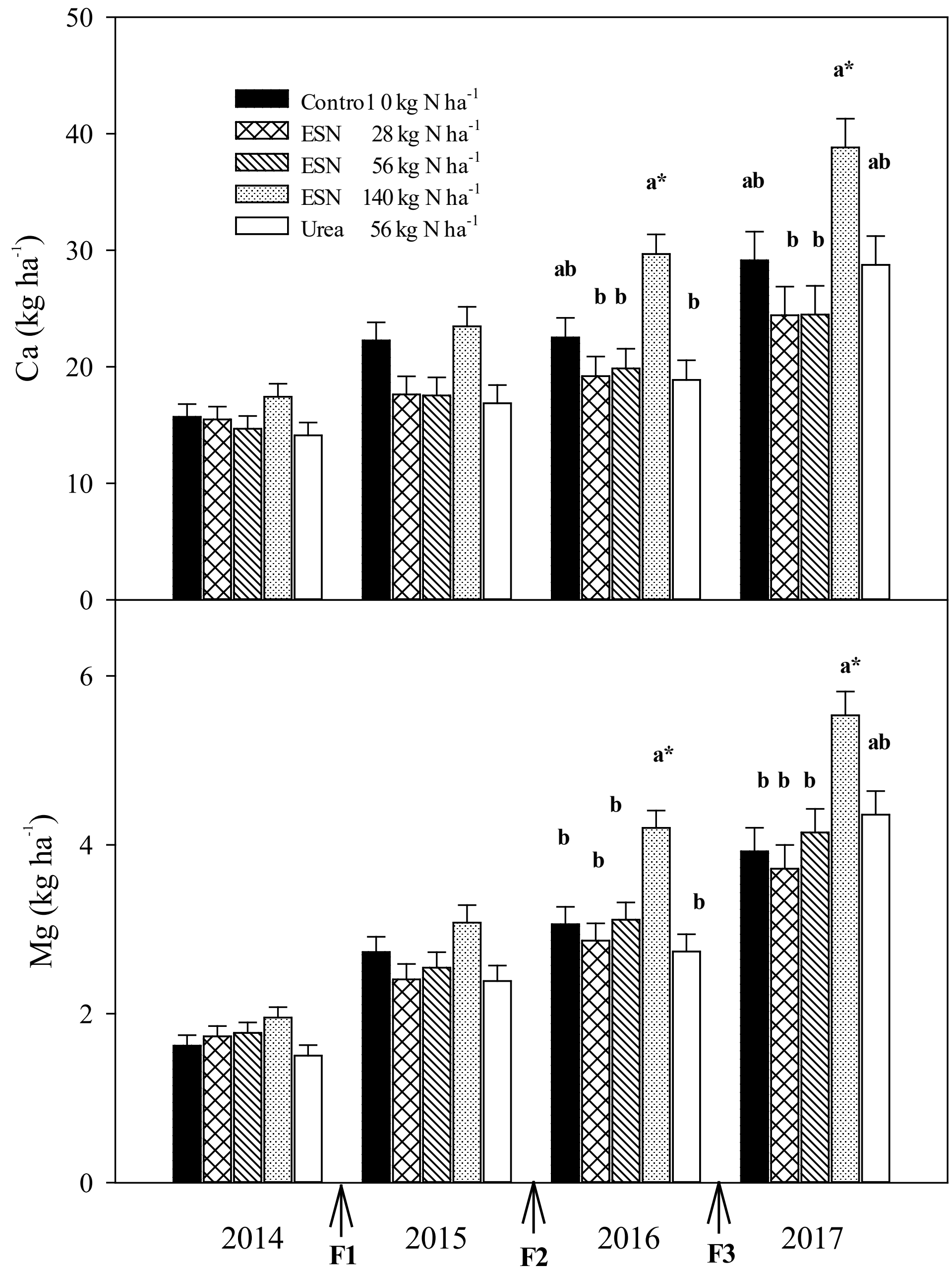

Figure PS3. Calcium and magnesium removal with pine straw harvested in February before (2014) and after (2015-2017) three annual June fertilizations (F1-F3) with urea or polymer-coated urea (ESN) at different rates. Means (+SE) within a sampling year labeled with the same letter are not significantly different using Bonferonni-Holm adjustment at α=0.05. Within a year, means signified with an asterisk are greater than the non-fertilized control using Dunnett's test at α=0.05.

6.9 Impacts to Ammonia Volatile Losses (2016)

6.9.1 Summary

- We examined the effect of pine straw raking on ammonia (NH_3) volatile losses for 12 weeks following fertilization treatments using two chamber collection methods (semi-open and open chambers).
- The 140 kg N ha^{-1} ESN and 56 kg N ha^{-1} urea treatments volatilized significantly higher amounts of NH_3 (6.71 mg L^{-1} and 6.09 mg L^{-1}, respectively) than the control (0.30 mg L^{-1}) one week after fertilization, which was 22.6 and 20.5 times greater than the control, respectively.
- The 140 kg N ha^{-1} ESN treatment yielded significantly higher amounts of volatilized NH_3 for weeks 2 thru 7 when compared to all the other treatments.
- NH_3 volatilization for the 28 kg N ha^{-1} ESN treatment was not significantly different than the control over all weeks.
- NH_3 volatile losses were significantly lower on raked plots when compared to non-raked plots over the first four weeks after fertilization.
- No significant interactions were found between fertilization rate and chamber method.

6.9.2 Statistical analysis

NH_4-N concentration was analyzed to determine if significant differences existed among fertilizer applications of: ESN (28, 56, 140 kg N ha^{-1}), urea (56 kg N ha^{-1}), and non-fertilized control on raked and non-raked plots weekly for 12 weeks directly following fertilization. Method of capturing NH_3 (30 semi-open chambers and 30 open chambers) was also examined. An analysis of variance (ANOVA) was conducted using JMP with an alpha level of 0.05 (SAS 2013). Independent variables included: fertilization treatment, raking treatment and NH_3 capture method with two-way and three-way interactions also examined. Fisher's LSD was used to compare means.

6.9.3. Results - ammonia volatilization

NH_3 volatile losses (mg/L^{-1}) were measured weekly for 12 weeks after fertilization using semi-open (bucket) and open (bottle) chambers. An Analysis of Variance (ANOVA) was conducted to evaluate chamber method and treatment effects (fertilization rate and pine straw raking) on NH_3 volatilization for each week (Table AV1). The ANOVA indicated significant differences (alpha <0.05) for weeks 1 thru 8 and week 10; however, week 10 (ANOVA=0.039) did not indicate any significant factors. Weeks 1 thru 8 indicated a significant difference in fertilization rates (Table AV2). The ESN 140 kg N ha^{-1} (6.71 mg L^{-1}) and Urea 56 kg N ha^{-1} (6.09 mg L^{-1}) treatments significantly volatilized higher amounts of NH_3 than the control (0.30 mg L^{-1}) one week after fertilization (22.6 and 20.5 times the control, respectively). Whereas, ESN 28 kg N ha^{-1} (1.50 mg L^{-1}) and ESN 56 kg N ha^{-1} (2.20 mg L^{-1}) were not significantly different than the control (4.5 and 3.1 times the control, respectively) one week after fertilization. The ESN 140 kg N ha^{-1} treatment yielded significantly higher amounts of volatilized NH_3 for weeks 2 thru 7 when compared to all the other treatments. NH_3 volatilization for the ESN 28 kg N ha^{-1} treatment was not significantly different than the control over all weeks. Over the 8 weeks that were significant, the ESN 140 kg N ha^{-1} treatment volatized an average of 26.7 times more NH_3 than the control, whereas, ESN 28 kg N ha^{-1} (3.8 times), ESN 56 kg N ha^{-1} (9.2 times), and Urea 56 kg N ha^{-1} (7.9 times) volatilized less.

NH_3 volatile losses were significantly lower on raked plots when compared to non-raked plots over the first four weeks (Figure AV1). Over the first four weeks, NH3 volatile losses were 4.1 times greater in non-raked plots with the greatest differences occurring in weeks 1 and 2 (6.7 and 5.4 times). NH_3 volatilization was significantly greater for bottle chambers at weeks 5 and 6 (2.4 and 2.2 times, respectively) (Figure AV2). Chamber method did not differ for any other week.

There was a significant interaction between fertilization rate and pine straw raking for the first four weeks after fertilization (Table AV3). NH_3 volatile losses one week after fertilization were significantly higher on non-raked plots for the ESN 140 kg N ha^{-1} and Urea 56 kg N ha^{-1} treatments. ESN 140 kg N ha^{-1} NH_3 volatile losses were significantly higher than all other treatments for weeks 2 thru 4. Over the first four weeks, non-raked plots resulted in greater NH3 losses for all treatments except the Urea 56 kg N ha^{-1} treatment at weeks 3 and 4. No significant differences were found between fertilization rate and chamber method (Figure AV3).

Table AV1. Analysis of Variance (ANOVA) for the variables examined to explain NH_3 volatile losses associated with fertilization and pine straw raking. Fertilization treatments included ESN at rates of 28, 56, 140 kg N ha^{-1}, Urea at 56 kg N ha^{-1}, and control at 0 kg N ha^{-1}. Pine straw raking treatments included plots that were raked and non-raked. Methods of trapping NH_3 volatile losses included semi-open chambers (buckets) and open chambers (bottles). Weekly sampling was conducted for 12 weeks after fertilization (WAF)

WAF[2]	1	2	3	4	5	6	7	8	9	10	11	12
	P-values[1]											
Fertilizer rate	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.895	0.068	0.235	0.059
Pine straw raking (raked/non-raked)	<0.001	<0.001	0.004	0.006	0.150	0.572	0.039	0.298	0.199	0.090	0.203	0.360
Chamber method (bottle/bucket)	0.281	0.731	0.355	0.935	0.023	0.033	0.554	0.744	0.001	0.710	0.816	0.205
Fertilizer rate x pine straw raking	<0.001	<0.001	<0.001	0.004	0.384	0.922	0.692	0.858	0.224	0.197	0.172	0.122
Fertilizer rate x chamber method	0.330	0.650	0.684	0.296	0.213	0.371	0.154	0.112	0.394	0.268	0.415	0.785
Pine straw raking x chamber method	0.372	0.858	0.213	0.008	0.902	0.011	0.001	0.087	0.538	0.055	0.238	0.042
Fertilizer rate x pine straw raking x chamber method	0.844	0.990	0.662	<0.001	0.378	0.072	0.030	0.268	0.195	0.102	0.110	0.102
ANOVA	<0.001	<0.001	<0.001	<0.001	0.002	0.001	<0.001	0.013	0.087	0.039	0.152	0.055

[1]Significance level of alpha <0.05

Table AV2. Combined chamber method (bucket and bottle) and pine straw raking (raked and non-raked) NH_3 volatile losses (mg L^{-1}) each week after fertilization (WAF) for the control (0 kg N ha^{-1}), ESN (28, 56, 140 kg N ha^{-1}), and Urea (56 kg N ha^{-1}) fertilizer treatments. Means within rows, followed by different letters are significantly different at an alpha level of <0.05.

	Control		ESN						Urea		
	Nitrogen application rate (kg N ha^{-1})										
	0		28		56		140		56		
WAF	ppm (mg L^{-1})[1]										P-value
1	0.30	b	1.50	b	2.20	b	6.71	a	6.09	a	<0.001
2	0.43	b	1.40	b	1.85	b	13.97	a	2.85	b	<0.001
3	0.27	b	1.06	b	2.11	b	11.40	a	2.38	b	<0.001
4	0.25	d	0.82	cd	1.92	b	4.21	a	1.21	bc	<0.001
5	0.08	c	0.53	bc	1.88	b	4.12	a	0.84	bc	<0.001
6	0.07	c	0.34	bc	1.15	b	2.54	a	0.55	bc	<0.001
7	0.30	b	0.60	b	0.81	b	1.64	a	0.65	b	<0.001
8	0.13	c	0.19	cd	0.46	ab	0.62	a	0.25	bc	<0.001
9	0.21		0.19		0.23		0.15		0.22		0.895
10	0.09		0.15		0.17		0.57		1.03		0.068
11	0.10		0.14		0.17		0.44		0.21		0.235
12	0.07		0.10		0.12		0.25		0.16		0.059

[1]Means within a row, followed by different letters are significantly different at an alpha level of <0.05 using Fishers LSD.

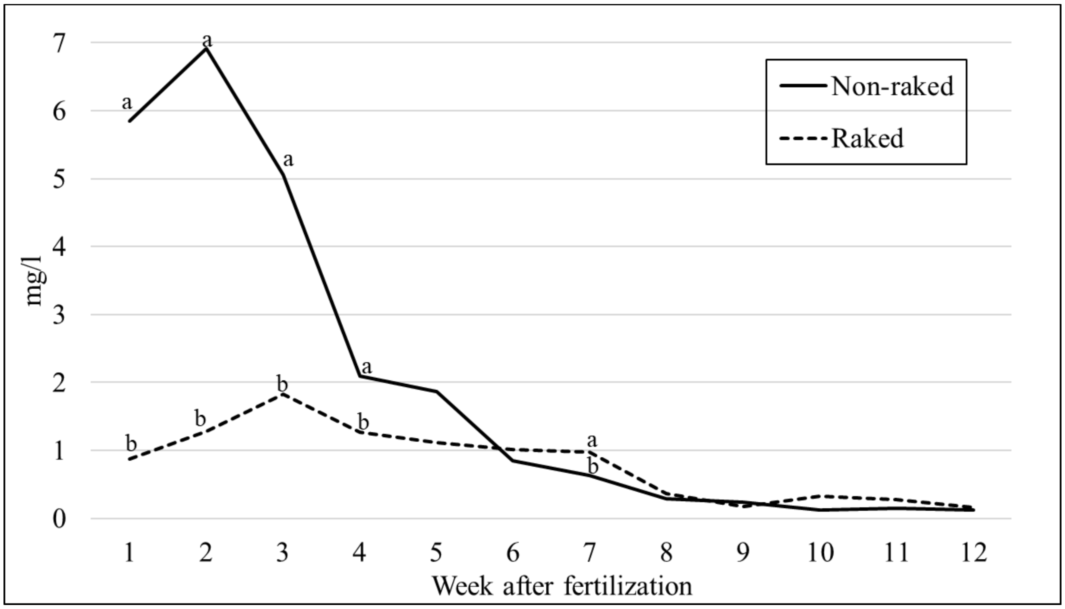

Figure AV1. Weekly mean NH_3 volatile loss (mg L^{-1}) by pine straw raking (raked and non-raked). Where present, different letters representing a significant difference between raked and non-raked plots at the significance level of <0.05.

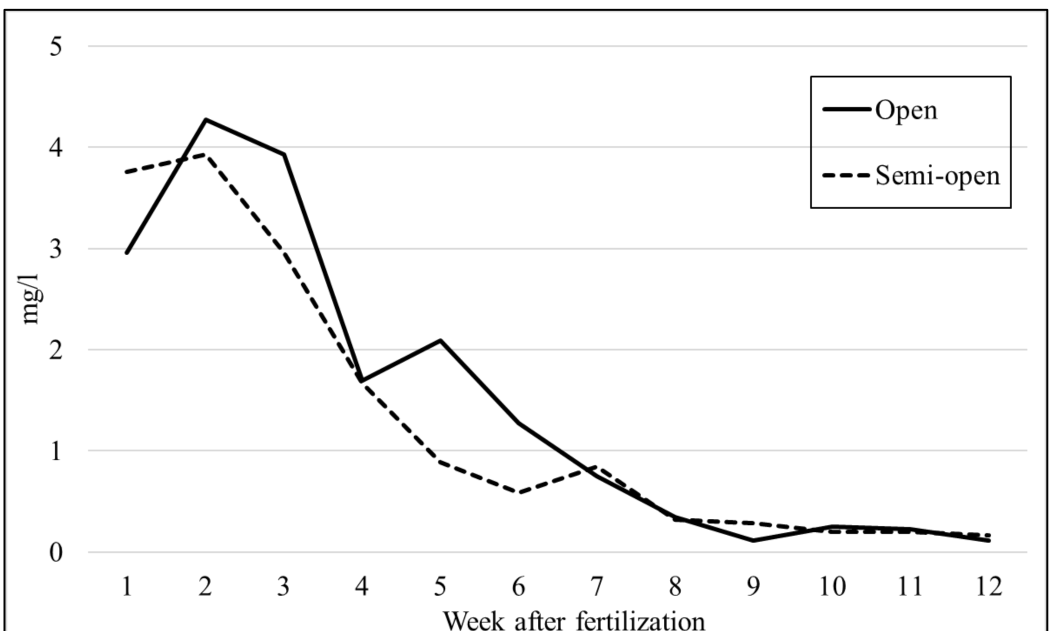

Figure AV2. Weekly mean NH_3 volatile loss (mg L^{-1}) by chamber method (open/semi-open). Where present, different letters representing a significant difference between chamber method at the significance level of <0.05.

Table AV3. NH_3 volatile losses (mg L^{-1}) associated with the interaction between fertilization rate (ESN 28, 56, 140 kg N ha^{-1}; Urea 56 kg N ha^{-1}; Control 0 kg N ha^{-1}) and pine straw raking (raked/non-raked) for each week after fertilization (WAF). Where present, different letters representing a significant difference between fertilization rate and raked and non-raked plots at the significance level of <0.05.

	Control		ESN						Urea		
	Nitrogen application rate (kg N ha^{-1})										
	0		28		56		140		56		
	Non-raked	Raked	Non-raked	Raked	Non-raked	Raked	Non-raked	Raked	Non-raked	Raked	
WAF	ppm (mg L^{-1})[1]										p-value
1	0.39 b	0.20 b	2.41 b	0.59 b	3.36 b	1.03 b	12.70 a	0.72 b	10.37 a	1.81 b	<0.001
2	0.47 b	0.38 b	2.35 b	0.46 b	2.90 b	0.79 b	25.16 a	2.78 b	3.69 b	2.00 b	<0.001
3	0.40 b	0.14 b	1.71 b	0.41 b	3.40 b	0.82 b	18.71 a	4.09 b	1.08 b	3.67 b	<0.001
4	0.27 d	0.22 d	1.19 cd	0.46 cd	2.75 b	1.10 cd	5.52 a	2.91 b	0.75 cd	1.66 bc	0.004
5	0.07	0.09	0.79	0.26	2.84	0.93	5.11	3.13	0.50	1.18	0.384
6	0.10	0.04	0.42	0.26	1.10	1.21	2.37	2.70	0.22	0.88	0.922
7	0.34	0.26	0.45	0.75	0.62	1.00	1.32	1.96	0.42	0.88	0.692
8	0.13	0.13	0.18	0.20	0.45	0.46	0.52	0.72	0.17	0.33	0.858
9	0.15	0.26	0.23	0.15	0.33	0.12	0.14	0.17	0.31	0.13	0.224
10	0.10	0.08	0.13	0.17	0.08	0.25	0.19	0.95	0.10	0.15	0.197
11	0.09	0.12	0.11	0.17	0.12	0.22	0.14	0.74	0.29	0.13	0.172
12	0.07	0.08	0.07	0.13	0.08	0.16	0.16	0.34	0.24	0.08	0.122

[1]Means within a row, followed by different letters are significantly different at an alpha level of <0.05 using Fishers LSD.

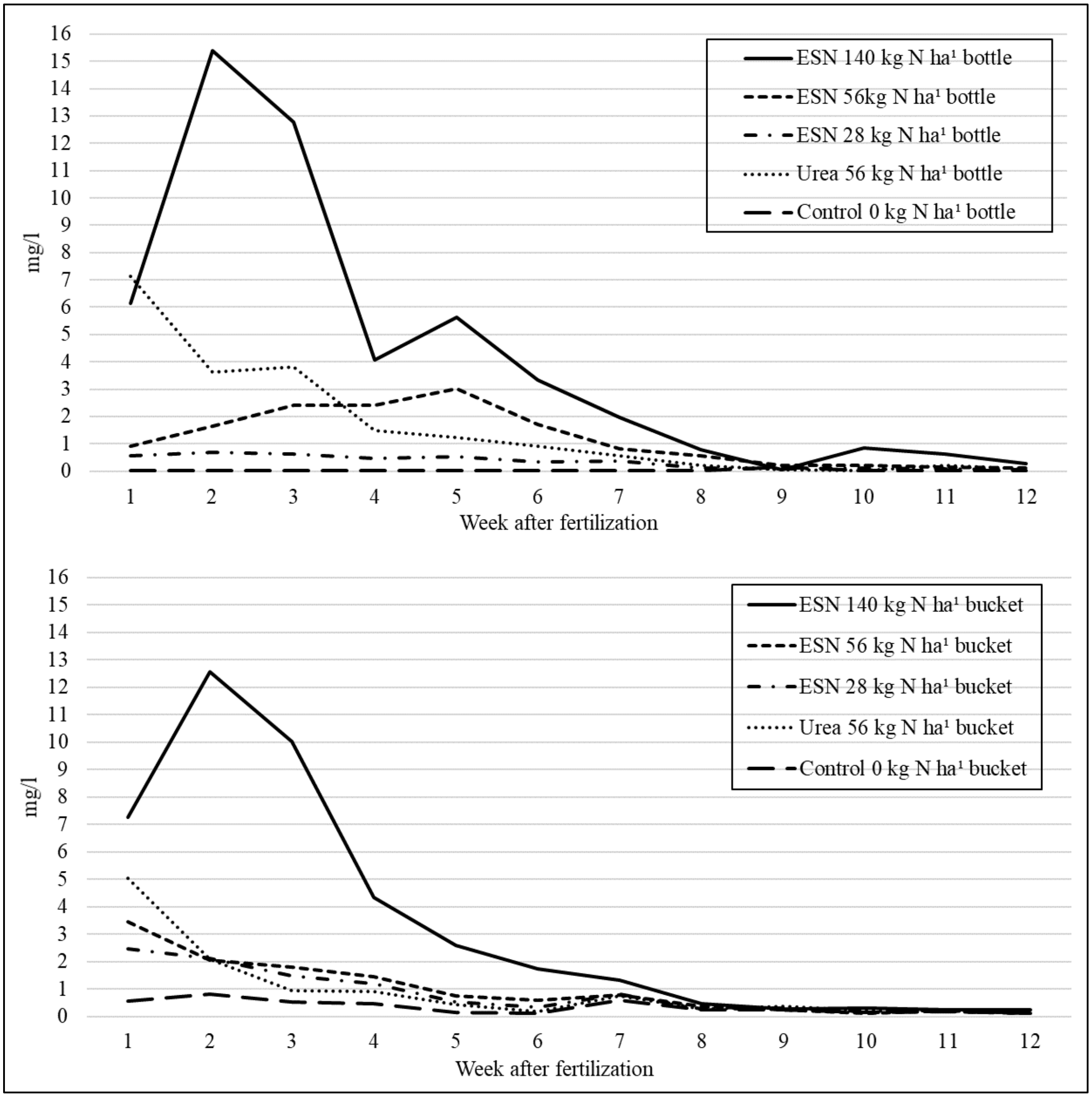

Figure AV 3. NH_3 volatile losses (mg L^{-1}) associated with the interaction between fertilization rate (ESN 28, 56, 140 kg N ha^{-1}; Urea 56 kg N ha^{-1}; Control 0 kg N ha^{-1}) and chamber method (bucket/bottle) for each week after fertilization (WAF). There was no significant difference between fertilization rate and chamber method at the significance level of <0.05.

6.9.4. Discussion - ammonia volatilization

The objectives of this research were to assess NH_3 volatile losses associated with fertilization application rates, pine straw raking, and chamber collection methods. This study found that NH_3 volatile losses were the greatest for the ESN 140 kg N ha^{-1} treatment up to eight weeks after fertilization with the highest volatilization occurring at weeks two and three after fertilization.

The Urea 56 kg N ha^{-1} treatment had volatilization similar to the ESN 140 kg N ha^{-1} one week after fertilization but then was similar to the ESN 56 kg N ha^{-1} for weeks 2 thru 8.

Pine straw raking did have an effect on NH_3 volatilization where non-raked plots volatilized more NH_3 than raked plots for the first four weeks after fertilization. Fertilizer applied to raked plots is in direct contact with the ground, whereas, fertilizer applied to non-raked plots is on top or within the pine straw which is a possibility for non-raked plots having higher volatilization. Chamber was only significantly different at weeks 5 and 6. Rainfall, wind speed, soil and outside temperatures were examined to determine impacts on NH_3 volatilization for chamber method (Figure AV4 and Figure AV5). Open chambers did have higher inside temperatures than semi-open chambers; however there was no correlation between temperatures or the other environmental factors. The open chamber method is a more refined process than the semi-open chamber method for collecting and measuring NH3; however, both methods presented similar results.

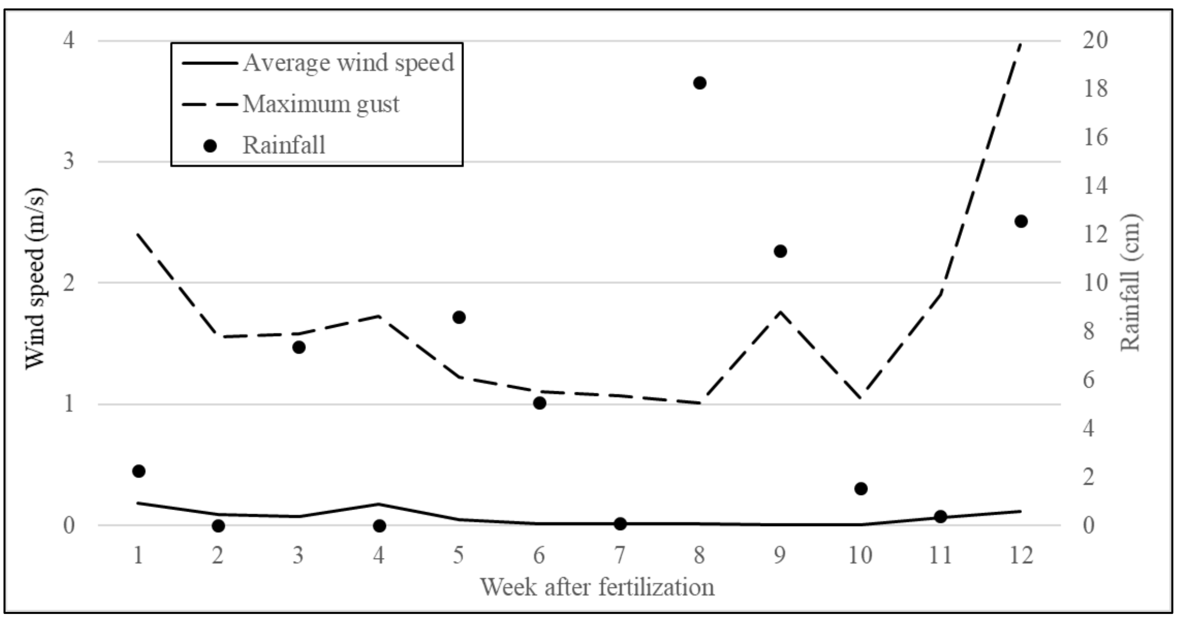

Figure AV4. Average rainfall and wind data from the onsite HOBO weather station at each week after fertilization.

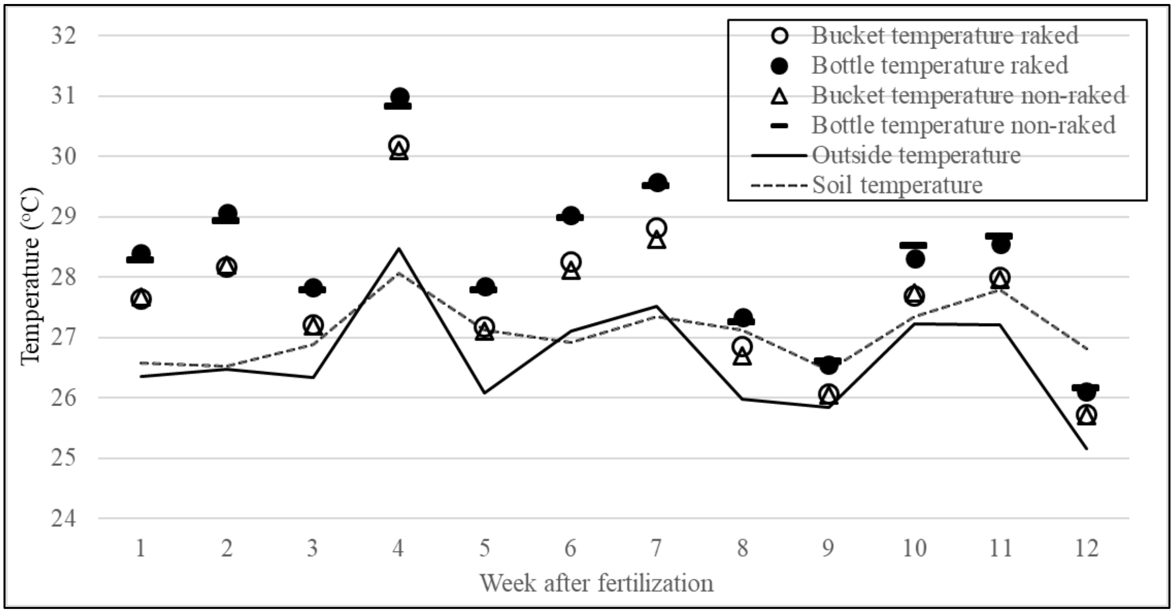

Figure AV5. Average chamber (bucket/bottle) temperature, outside temperature, and soil temperature at each week after fertilization. HOBO sensors were placed in 4 semi-open (bucket) and 4 open (bottle) chambers. Soil temperature was collected from a Campbell Station within the stand and outside temperature was collected from the onsite HOBO weather station.

6.10 Pine Stand Response to Fertilization and Pine Straw Raking

6.10.1 Summary

- The effect of annual raking was not significant on any pine response variable, nor was there any interaction between fertilization and raking treatments.
- When nitrogen was supplied as ESN pine mortality increased with increasing N rate, and at the highest rate, 125 lb N ha^{-1}, the number of pines per hectare and pine survival were significantly less than observed in the non-fertilized control.
- Conventional urea applied at the standard 50 lb N ha^{-1} rate did not differ from the non-treated control in pines per hectare or pine survival.
- Annual fertilization with the standard 50 lb N ha^{-1} rate using ESN reduced average height and height of dominant and codominant trees relative to the non-fertilized control; whereas, fertilization with conventional urea at 50 lb N ha^{-1} did not differ from the control.

6.10.2 Statistical analysis of pine response

The analysis of three-year pine survival, initial proportion of dominant and codominant trees (D&C), and initial proportion of trees with fusiform rust stem galls was performed assuming that the response variable (presence or absence, 0 or 1) is a binomial random variable. Each stem of a tree forked below diameter at breast height (4.5 feet from ground level, DBH) was considered a separate tree because each of these stems contributes to stand basal area, volume and pine straw yield. Trees were classified into two crown classes for this analysis. Trees were either classified as belonging to the combined dominant and co-dominant (D&C) crown class or combined intermediate and suppressed (I&S) crown class, based on initial tree assessments. A tree was considered to have fusiform rust at the beginning of the study if a stem gall was detected at any measurement. Fusiform rust infection occurs on young tissue but might not be detected on older stems at any given measurement. Apparent symptoms are affected by gall size, gall position and seasonal differences. Stem gall size was not considered in this analysis. Analyses were performed using SAS PROC GLIMMIX with blocks considered a random effect. The ANOVAs of initial proportion of trees in the D&C crown class and initial proportion of trees with fusiform rust stem galls consider fertilization, raking and the interaction of fertilization and raking as fixed effects. The ANOVA of survival includes the additional effects of crown class, stem rust class and the interaction of crown class and stem rust.

A repeated measures approach was used for the analysis of pine plot-level variables. Pine responses were compared for total pines per hectare (TPH), average live height of dominant and co-dominant trees (D&C HT), average live tree height (HT), quadratic mean diameter at breast height (QMD), average DBH, and stand basal area (BA). Quadratic mean diameter is the diameter of average tree basal area, commonly used in preference to mean DBH in reporting growth and yield. Total stand volume outside bark (TV ha-1) and merchantable stand volume outside bark to an 8 cm top diameter (TV8cm ha-1) were computed using a slash pine volume equation (Brister et al. 1980). The 8 cm top diameter (pulpwood) was an appropriate measure of merchantable pine volume for this point in stand development.

The analysis of plot-level pine response was also performed as a mixed-model ANOVA, with blocks considered random and annual pine measurements considered a repeated longitudinal measurement. This allows the construction of an ANOVA for 3-year pine growth response (or mortality) to test the main effects of fertilization, raking and the interaction of fertilization and raking. A preliminary analysis was performed to compare the parametric structure of the covariance matrix with respect to possible heterogeneity of variance and correlation of annual pine measurements. Compound symmetry (CS), heterogeneous compound symmetry (CSH), first-order autoregressive (AR1), and heterogeneous first-order autoregressive (ARH1) structures were compared based on AIC (Akaike 1974), AICC (Hurvich and Tsai 1989) and BIC (Schwarz 1978) information criteria using SAS PROC MIXED (Littell et al. 2006). Autoregressive error structures performed best for all pine plot-level variables. Variation increased with stand age for stand basal area, stand volumes, and stand diameters. The ARH1 error structure was selected for the analysis QMD, DBH, BA, TV ha-1and TV8cm ha-1. The AR1 error structure was selected for TPH, D&C HT, and HT.

An individual tree based analysis of covariance (ANCOVA) was also performed for D&C HT and DBH. The previous plot-level analysis used average DBH and average total live height of dominant and co-dominant trees, in which averages were based on the live tree sample for each year. The ANCOVA excludes trees that died over the study period and compares treatment averages adjusted for initial tree HT or DBH. The ANCOVA for D&C HT was performed using only dominant and co-dominant trees without broken tops. The objective of this individual tree analysis was to compare treatments in terms of average tree response. The ANCOVA was performed using a repeated measures structure for years 2014-2016 using the initial year 2013 tree measurement as the covariate (Milliken and Johnson 2002). The analysis was structured like the plot-level repeated measures analysis except that correlation of tree measurements was at the tree level. The covariance structure grouped plot-level variance by measurement year and used a first-order autoregressive error structure to describe the correlation of repeated measurements on trees.

6.10.3 Results and discussion - pine response to fertilization

As shown by repeated measures ANOVA, among pine response variables only live height (HT) and height of dominant and codominant trees (D&C HT) responded to fertilization (Table P1). The effect of annual raking was not significant on any pine response variable, nor was there any interaction between fertilization and raking treatments. Sampling year was highly significant for all pine response variables, which may be explained by pine growth with age, time from sequential annual fertilizations, and changes in yearly rainfall and other environmental factors.

A subsequent ANOVA and planned orthogonal contrasts for the 3-year change in measured pine response variables also showed a significant effect of fertilization on D&C HT (P=0.006), but not on HT (Table P2). In this analysis fertilization had a significant effect (P=0.041) on the number of trees per hectare (TPH). Again, raking did not have a significant effect on any response variable, and there was no interaction between fertilization and raking treatment.

Because raking did not affect any pine response and there was no interaction between fertilization and raking treatment, yearly means and the mean 3-year change (2013-2016) were examined to compare fertilization treatments averaged across raking regimes for each pine response variable (Table P3).

Orthogonal contrasts showed fertilization treatment and N form (ESN vs. urea) had a significant effect on live height of dominant and codominant trees in 2015 and 2016 (Table P3). In both years, fertilization with ESN generally reduced D&C HT, and the 56 kg N ha^{-1} rate of ESN significantly reduced D&C HT compared to the non-fertilized control. The 56 kg N ha^{-1} rate of urea resulted in the same D&C HT as the control, and a greater height response than the 56 kg N ha^{-1} rate of ESN. However, the response to the two N forms was pre-disposed to coincidental differences in height prior to treatment (P=0.045), whereby the initial mean D&C HT in urea plots treated with this rate was 3.5% greater than for the ESN plots. Comparing treatments for 2013-2016 D&C HT growth response, the 28 kg N ha^{-1} rate of ESN had less growth than the non-fertilized control using Dunnett's test.

Similar responses in total tree height were observed for fertilization treatment and N form in 2015 and 2016, except that 2013-2016 HT growth response did not differ among treatments (Table P3).

Over the 2013-2016 study term, pine mortality increased with increasing ESN rate, and the 140 kg N ha^{-1} rate had significantly greater mortality (-172 TPH) than the non-fertilized control (-50 TPH) using Dunnett's test (Table P3). Percent survival over the 3-year study term was effected by fertilization (P=0.008), ESN rate (P=0.043), crown class (P=0.001) and the presence of stem rust (P=0.001) (Table P4). Pine survival ranged from 91.6% in the 140 kg N ha^{-1} ESN treatment to 98.5% in the non-fertilized control, which differed using Dunnett's (Table P5). Across treatments, dominant and co-dominant pines had greater survival (99.5%) than those in the intermediate and suppressed class (82.2%). Survival was greater (98.9%) for pines without fusiform stem rust than for those with stem rust. Nitrogen fertilization accelerates the expression of tree dominance, a natural process by which stand density declines due to intra-specific competition. Trees in the dominant and co-dominant canopy class and those free of fusiform stem rust are more likely to respond to fertilization and survive.

The individual tree analysis by ANCOVA showed a highly significant effect (*P*=0.001) of initial D&C HT and DBH on the response for each of these variables, so the initial tree height or DBH was used as a covariate to better understand response to treatments (Table P6). The ANCOVA also showed a highly significant effect for treatment year, so treatments were compared for these growth response variables in each of the three years post fertilization (Table P7). Fertilization had a significant effect (*P*=0.017) on D&C HT only for the 2016 growing season, with greater height growth obtained with 56 kg N ha^{-1} urea than 28 kg N ha^{-1} ESN. The fertilization response in DBH was also only significant in 2016 (*P*=0.020), with greater DBH in the 140 kg N ha^{-1} ESN treatment than the non-treated control. The greater diameter response for the high ESN rate may be the result of "thinning", as pine density was reduced by fertilizer induced mortality.

Repeated removals of pine straw can potentially interrupt nutrient cycling, deplete site nutrients, affect stand productivity and threaten the sustainability of timber and straw production, but the response is long term. In our previous four year BMP verification study of fertilization and annual pine straw harvesting, raking had no significant effect on slash pine growth parameters except for greater D&C HT in non-raked than raked plots at a deep sandy site (Entisol) near the current study (Minogue et al., 2013).

Our previous BMP verification studies in similar aged slash pine stands also showed poor or negative pine responses to diammonium phosphate (DAP) fertilization providing 26/29, 77/87, or 129/146 kg ha^{-1} N/P (Minogue et al., 2013). At a site near Blountstown (Ultisol) having fine sandy loam or loamy sand soils the middle and high DAP rates resulted in greater four-year DBH growth than the non-fertilized control. Fertilization treatments did not differ in four-year D&C HT, but all other cumulative four-year pine responses were negative, with the middle and high DAP rates resulting in increased mortality, reduced stand basal area (a measure of stocking), and less volume growth than the low DAP rate or non-fertilized control. In contrast, at the site near Live Oak having deep fine sand (Entisol), characterized by poor nutrient holding capacity, there was an increase in four-year D&C HT growth with the high DAP rate compared to the low DAP rate or control, but the high DAP rate also resulted in greater pine mortality. At this site fertilization treatments did not differ in four-year DBH, basal area or volume growth. These BMP verification studies and the body of published literature point to the need for site-specific fertilization practices, including diagnostic assessments of nutrient needs.

Table P1. Repeated measures ANOVA showing the significance (*P*>F)[1] of fertilization, pine straw raking, sampling year and the interaction of these factors for various slash pine variables measured in the dormant season before and after each of three annual June fertilizations and three annual February pine straw harvests (raking).

Factor	df	Response variable							
		TPH	D&C HT	HT	QMD	DBH	BA	TV ha^{-1}	TV8cm ha^{-1}
Fertilization (Fert)	4	0.867	**0.026**	**0.019**	0.335	0.388	0.522	0.486	0.464
Raking (Rake)	1	0.425	0.193	0.259	0.946	0.871	0.438	0.384	0.423
Fert x Rake	4	0.331	0.308	0.244	0.403	0.382	0.596	0.570	0.626
Sampling Year	3	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**
Fert x Year	12	0.388	0.067	0.812	0.412	0.409	0.256	0.138	0.147
Rake x Year	3	0.657	0.969	0.351	0.323	0.240	0.517	0.562	0.545
Fert x Rake x Year	12	0.657	0.979	0.821	0.722	0.818	0.315	0.606	0.601

[1]Bold *P*≤0.05 denotes a significant effect.

Table P2. ANOVA and orthogonal contrasts for pre-planned comparisons showing the significance (*P*>F)1 of fertilization, pine straw raking and the interaction of these factors for the change in various slash pine variables from before (2013) to after (2016) three annual June fertilizations and three annual February pine straw harvests (raking).

Factor/comparison	df	TPH	D&C HT	HT	QMD	DBH	BA	TV ha^{-1}	TV8cm ha^{-1}
		Response variable							
Fertilization (Fert)	4	**0.041**	**0.006**	0.481	0.130	0.094	0.765	0.646	0.496
Fert vs Control[2]	(1)	0.103	**0.017**	0.944	0.066	0.068	0.855	0.761	0.919
ESN rate[3]	(2)	0.117	0.884	0.413	0.214	0.150	0.527	0.390	0.220
Urea 56 vs ESN 56[4]	(1)	0.242	**0.023**	0.148	0.621	0.652	0.297	0.245	0.256
Raking (Rake)	1	0.832	0.845	0.842	0.880	0.739	0.461	0.406	0.423
Fert x Rake	4	0.634	0.976	0.547	0.503	0.668	0.141	0.384	0.356
Fert vs Control x Rake	(1)	0.225	0.823	0.330	0.723	0.585	0.945	0.602	0.480
ESN rate x Rake	(2)	0.602	0.811	0.382	0.341	0.540	**0.037**	0.155	0.153
Urea 56 vs ESN 56 x Rake	(1)	0.867	0.721	0.677	0.930	0.862	0.846	0.786	0.799

[1]Bold *P*≤0.05 denotes a significant difference.
[2]Average of fertilized treatments vs the non-fertilized control
[3]28, 56, and 140 kg N ha^{-1}
[4]Conventional urea at 56 kg N ha^{-1} vs polymer-coated urea at 56 kg N ha^{-1}

Table P3. Slash pine response variables measured in the dormant season before fertilization (2013) and in the dormant season following annual June fertilization in 2014, 2015 and 2016 with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling year	Number of fertilizations & rakings before sample	**Control**			Fertilizer												Orthogonal contrasts P^1 values for pre-planned comparisons				
					ESN									**Urea**							
		Annual nitrogen application rate (kg N ha^{-1})															Fert trt[2]	ESN rate[3]	N form[4]	Rake[5]	Fert* Rake[6]
		0			**28**			**56**			**140**			**56**							
		Mean[7]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE					
									Trees per hectare [**TPH** (trees ha^{-1})]												
2013	0	1471		66	1442		66	1428		66	1536		66	1485		66	0.760	0.421	0.517	0.538	0.403
2014	1	1450		66	1428		66	1414		66	1485		66	1471		66	0.918	0.688	0.517	0.414	0.394
2015	2	1435		66	1392		66	1371		66	1435		66	1450		66	0.877	0.755	0.375	0.333	0.315
2016	3	1421		66	1356		66	1320		66	1363		66	1428		66	0.700	0.870	0.230	0.474	0.258
2013-2016 mortality		-50		30	-86		30	-108		30	-172	*	30	-57		30	**0.041**	0.117	0.242	0.832	0.634
									Average total height of dominant and codominant trees [**D&C HT** (m)]												
2013	0	8.42		0.20	8.49		0.20	8.17		0.20	8.45		0.20	8.46		0.20	0.164	0.056	**0.045**	0.228	0.279
2014	1	9.93		0.20	9.85		0.20	9.67		0.20	9.89		0.20	9.99		0.20	0.226	0.273	**0.028**	0.231	0.514
2015	2	11.27	a	0.20	11.01	ab	0.20	10.79	b*	0.20	11.08	ab	0.20	11.27	a	0.20	**0.009**	0.106	**0.002**	0.195	0.395
2016	3	12.41	a	0.20	12.12	ab	0.20	11.86	b*	0.20	12.12	ab	0.20	12.45	a	0.20	**0.001**	0.110	**<0.001**	0.302	0.370
2013-2016 growth		3.99		0.09	3.63	*	0.09	3.69		0.09	3.67		0.09	3.99		0.09	**0.006**	0.884	**0.023**	0.845	0.976
									Average total tree height [**HT** (m)]												
2013	0	8.10		0.21	8.03		0.21	7.79		0.21	7.91		0.21	8.06		0.21	0.102	0.173	**0.036**	0.144	0.649
2014	1	9.61		0.21	9.51		0.21	9.31		0.21	9.49		0.21	9.60		0.21	0.129	0.220	**0.025**	0.365	0.575
2015	2	10.94	a	0.21	10.70	ab	0.21	10.52	b*	0.21	10.76	ab	0.21	10.92	a	0.21	**0.011**	0.140	**0.003**	0.757	0.164
2016	3	12.03	a	0.21	11.87	ab	0.21	11.63	b*	0.21	11.90	ab	0.21	12.09	a	0.21	**0.008**	0.070	**0.001**	0.207	0.103
2013-2016 growth		3.93		0.09	3.84		0.09	3.84		0.09	3.99		0.09	4.03		0.09	0.481	0.413	0.148	0.842	0.547

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year
[4]P values for difference between ESN and Urea (each @ 56 kg N ha^{-1}) within a year
[5]P values for significance of raking treatment effect within a year
[6]P values for significance of fertilization x raking interaction within a year
[7]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holms adjustment at α=0.05. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.

Table P4. ANOVA and orthogonal contrasts showing the significance (P>F)[1] of various factors for three-year (2013-2016) tree survival after three annual February pine straw harvests (raking) and three annual June fertilizations, with urea or polymer-coated urea (ESN) at different rates.

Factor	df	Initial (2013) D&C (%)	Initial (2013) Stem rust (%)	Three-year (2013-2016) survival (%)
Fertilization (Fert)	4	0.246	0.502	**0.008**
Fert vs Control	(1)	0.080	0.314	0.100
ESN rate[2]	(2)	0.677	0.859	**0.043**
Urea 56 vs ESN 56[3]	(1)	0.645	0.182	0.137
Raking (Rake)	1	0.300	0.960	0.383
Fert x Rake	4	0.123	0.781	0.211
Fert vs Control x Rake	(1)	**0.011**	0.768	0.115
ESN rate x Rake	(2)	0.698	0.480	0.177
Urea 56 vs ESN 56 x Rake	(1)	0.647	0.853	0.729
Crown class	1			**<0.001**
Stem rust class (Rust)	1			**<0.001**
Crown class x Rust	1			0.535

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]28, 56, and 140 kg N ha^{-1}
[3]Conventional urea at 56 kg N ha^{-1} vs with polymer-coated urea at 56 kg N ha

Table P5. Initial (2013) proportion of dominant and codominant (D&C) slash pine trees, initial proportion of trees with fusiform stem rust and three-year (2013-2016) tree survival after three annual February pine straw harvests (raking) and three annual June fertilizations with urea or polymer-coated urea (ESN) at different rates.

Factor[1]	Initial (2013) D&C %		Initial (2013) Stem rust %		Three-year (2013-2016) survival[2] %		
	Mean	SE	Mean	SE	Mean		SE
Fertilization treatment (kg N ha^{-1})							
Control (0)	83.2	2.7	35.1	3.3	98.5		1.1
ESN (28)	75.6	3.0	38.8	3.4	97.1		1.5
ESN (56)	78.4	2.9	41.3	3.5	95.3		2.3
ESN (140)	74.8	3.0	41.0	3.4	91.6	*	3.6
Urea (56)	80.2	2.8	34.8	3.3	97.8		1.2
Raking treatment							
No Rake	79.9	1.8	38.2	2.1	97.2		1.3
Rake	77.2	1.9	38.1	2.2	96.2		1.7
Crown class							
Dominant and co-dominant (D&C)					99.5	a	3.4
Intermediate and suppressed (I&S)					82.2	b	5.5
Stem rust class							
Rust absent					98.9	a	0.7
Rust present					90.2	b	3.4

[1]For each factor means within a column followed by different letters are significantly different using stepdown Bonferroni adjustment at α=0.05.
[2]ANOVA showed a significant fertilization treatment effect on three-year survival (*P*=0.008), but means did not differ using Bonferonni-Holm adjustment at α=0.05.
*Survival for ESN (140) is less than for the non-fertilized control using Dunnett's test at α=0.05.

Table P6. ANCOVA showing the significance (*P*>F)1 of fertilization, pine straw raking, sampling year, interaction of these factors, and initial (2013) measurements for diameter at breast height (DBH) and height of dominant and co-dominant (D&C HT) slash pine trees measured in the dormant season after each of three annual June fertilizations and three annual February pine straw harvests (raking).

Factor	df	D&C HT	DBH
Fertilization (Fert)	4	0.140	0.149
Raking (Rake)	1	0.683	0.174
Fert x Rake	4	0.893	0.174
Sampling Year	2	**<0.001**	**<0.001**
Fert x Year	8	**0.010**	0.136
Rake x Year	2	0.885	0.268
Fert x Rake x Year	8	0.628	0.363
Initial D&C HT (2013)	1	**<0.001**	
Initial DBH (2013)	1		**<0.001**

[1]Bold *P*≤0.05 denotes a significant effect.

2013 means	n	mean	SE
D&C HT (m)	2361	8.40	0.02
DBH (cm)	2880	12.36	0.05

Table P7. Slash pine diameter at breast height (DBH) and height of dominant and codominant trees (D&C HT) measured in the dormant season following annual June fertilization in 2014, 2015 and 2016 with urea or polymer-coated urea (ESN) at different rates, adjusted by ANCOVA for pre-fertilization (2013) initial diameter or height, respectively, averaged over raked and non-raked treatments.

Sampling year	Fertilizer: ESN — Annual nitrogen application rate (kg N ha^{-1}) 0 Mean[7]	SE	28 Mean	SE	56 Mean	SE	140 Mean	SE	Urea 56 Mean	SE	Orthogonal contrasts P^1 values for pre-planned comparisons: Fert trt[2]	ESN rate[3]	N form[4]	Rake[5]	Fert x Rake[6]
Total height of dominant and codominant trees (m)															
2014	9.92	0.05	9.93	0.05	9.97	0.05	9.92	0.05	9.99	0.05	0.754	0.715	0.789	0.582	0.858
2015	11.25	0.06	11.11	0.06	11.17	0.06	11.18	0.06	11.28	0.06	0.194	0.578	0.166	0.584	0.813
2016	12.39 ab	0.07	12.17 b	0.07	12.21 ab	0.07	12.26 ab	0.07	12.45 a	0.07	**0.017**	0.636	**0.013**	0.958	0.853
Average tree DBH (cm)															
2014	13.65	0.11	13.69	0.11	13.86	0.11	13.64	0.11	13.71	0.11	0.429	0.206	0.229	0.666	0.795
2015	14.47	0.09	14.58	0.10	14.67	0.10	14.68	0.09	14.60	0.09	0.160	0.526	0.436	0.374	0.082
2016	15.19 b	0.11	15.31 ab	0.11	15.46 ab	0.11	15.54 a x	0.11	15.46 ab	0.11	**0.020**	0.123	0.965	0.189	0.067

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year
[4]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year
[5]P values for raking treatment effect within a year
[6]P values for significance of fertilization x raking interaction within a year
[7]Means within a row followed by the same letter or not followed by any letter are not significantly different using Bonferonni-Holms adjustment at α=0.05. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.

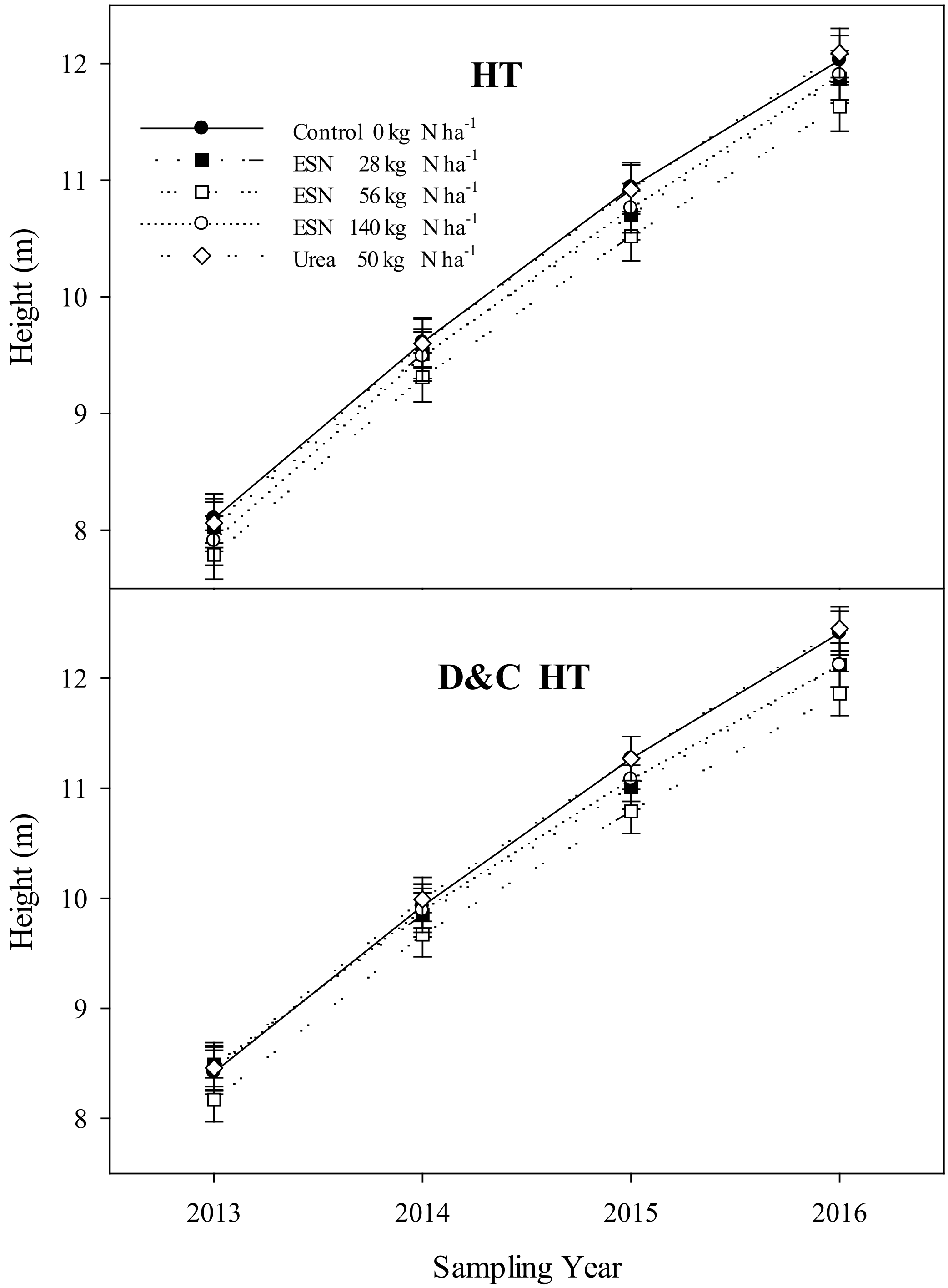

Figure P1. Average total height (HT) and average total height of dominant and codominant (D&C HT) slash pine trees measured in the dormant season before fertilization (2013) and in the dormant season following annual June fertilization in 2014, 2015, and 2016 with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

6.11 Improvements, additions, and changes

- Sampling of volatile ammonia loss was added to the proposed work to compare fertilization treatments and qualitatively quantify N fate.
- A distant reference well was installed approximately 1 km from the monitoring well in the fertilized area. However, three weeks before the first fertilization, Pt concentration in the distant well was 252.9 µg L^{-1} compared to 8.4 µg L^{-1} in the treatment well. Therefore, it was not suitable as a reference well.
- We improved the accuracy of the fertilizer application rate within a 1 m^2 area around each lysimeter by protecting this area during fertilization of the measurement plots and subsequently applying precisely weighted amounts of fertilizer.
- Since 2013 we experienced a few failures of the HOBO weather station data logger and sensors resulting in short periods of some missing weather data.

7.0 EDUCATIONAL GOAL

This environmental monitoring project includes applied and basic research questions regarding the fate of applied nitrogen and phosphorus in pine forests. Three Agrium ESN polymer-coated urea rates: 28, 56, 140 kg N ha^{-1} (25, 50, 125 lb N $acre^{-1}$) plus a common triple super phosphate (TSP) rate, 28 kg P_2O_5 ha^{-1} (25 lb $acre^{-1}$) were compared to typical urea plus diammonium phosphate (DAP) treatment, 56 kg N and 28 kg P_2O_5 ha^{-1} (50 lb N, 25 lb P_2O_5 $acre^{-1}$) and a non-fertilized control. We are examining forest stand level nutrient budgets and effects of pine straw removal on nutrient cycling, tree growth, straw harvest yields, and soil chemical and physical properties. The goal is to determine biological and economic thresholds for fertilization in pine straw production, as well as to ensure soil resource sustainability and protection of water quality through refinement of Florida Silviculture BMPs.

8.0 EDUCATIONAL TASKS

This research is supporting our University Extension program outreach to pine straw producers in Florida and the region to provide improved guidelines for efficient use of fertilizer materials. Few published studies or on-going research address the use of controlled release nitrogen fertilizers in forestry, largely because of their higher cost. However, these costs may be justified by greater nutrient use efficiency and the high product value ($100 to $200 $acre^{-1}$) that annual pine straw harvesting affords, which is in addition to timber revenue. Another important educational message is the higher cost is also justified by mitigation of the significant potential adverse social and environmental effects of excessive fertilization. In 2015 we published a peer-reviewed Extension publication "*Guide to Fertilization for Pine Straw Production on Coastal Plain Sites*" (Osiecka et al. 2015), which is available on-line to growers throughout the region. This provides a review of important diagnostic tools to refine fertilization practices and improve efficiencies. A planned follow up to this is a similar peer reviewed Extension publication aimed at addressing cost-effectiveness for forest fertilization in pine straw specifically.

We will also continue our educational outreach to growers though Extension Workshops (see Executive Summary, Education) which have been supported by this and two previous DEP 319 grants to refine silviculture fertilization BMPs. Specific objectives of our Extension program include:

1. Educate pine straw producers concerning appropriate fertilization practices for various soils and stand conditions to optimize profits while avoiding over-fertilization, with the Florida Sand Ridge and areas with unconfined aquifers being the highest priority.
2. Provide pine straw producers research-based silvicultural guidelines for appropriate pine species, optimum tree spacing, vegetation management practices, nutrient management, sustainable harvesting frequency, and the integration of pine straw production with production of conventional wood products.

Planned Publications:

Osiecka, A. and P.J. Minogue. (2018 submission). Overview of pine straw production in the Coastal Plain. University of Florida, EDIS (Peer-reviewed Extension publication available on-line).

Minogue P.J. and A. Osiecka. (2018 submission). Nutrient removals and fertilization recommendations for annual pine straw raking in slash pine stands. For submission to Forest Ecology and Management. (In Preparation)

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Appendix A. Graduate Thesis Abstract

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

FATE OF APPLIED NITROGEN FROM UREA AND POLYMER COATED UREA IN SILVICULTURAL FERTILIZATION

By

Alexandria Whann

August 2016

Chair: Patrick Minogue

Major: Forest Resources and Conservation

Polymer coated urea fertilizers provide a controlled release of nitrogen (N) in forest fertilization, and may have better nutrient use efficiency than standard N fertilizers. Leaching of applied N is of particular concern in the Lower Suwannee Valley where surficial groundwater is close to the surface and soils are prone to nutrient leaching. Three rates of polymer coated urea (PCU) plus triple super phosphate fertilizer (28, 56, 140 kg N ha^{-1} and 28 kg P ha^{-1}), a urea plus diammonium phosphate (DAP) standard treatment (56 kg N ha^{-1} and 28 kg P ha^{-1}) and a non-fertilized control were compared in a nine-year-old slash pine plantation near Live Oak, Florida. Changes in soil solution N concentration at 30 cm depth and changes in soil N at various depths to 183 cm were monitored over time. Volatile losses of ammonia were measured using two trap methods. From 2 through 4 weeks after fertilization, nitrate/nitrite N (NO_x-N) concentrations in soil solution were significantly greater for the urea plus DAP standard treatment than for the same rate of N from PCU (56 kg N ha^{-1}). In this same period, the high PCU rate (140 kg N ha^{-1}) had significantly greater NO_x-N concentration in soil solution than all other treatments through week 13. Though soil NO_x-N concentration did not differ between mid-rate PCU and urea plus DAP, high rate PCU resulted in significantly higher concentration11 months after fertilization. Ammonium and total Kjeldahl N concentrations measured in soil did not differ among fertilization or raking treatments. Ammonia volatilization at one month after fertilization, as measured by acid-trapped ammonium, was greater from PCU than from urea plus DAP at equal elemental nitrogen rates. Significantly higher volatile losses were measured one week following fertilization from the standard urea plus DAP treatment than from the mid-rate PCU, and high rate PCU had significantly higher losses at several sampling dates after fertilization. This study suggests that for similar sites PCU has less potential to be lost to leaching and volatilization than a standard urea fertilizer, as long as a practical rate of 56 kg N ha^{-1} is applied.

Appendix B. Additional tables

Table ApPS1 (Results for figure PS1). Yield of slash pine straw harvested in February before fertilization (Feb-14) and in 2015, 2016 and 2017 following previous year June fertilization with urea or polymer-coated urea (ESN) at different rates.

Fertilization	Sampling	Number of fertilizations before harvest	Control			Fertilizer												Orthogonal contrasts P[1] values for pre-planned comparisons		
						ESN									Urea					
			Annual nitrogen application rate (kg N acre^{-1})																	
			0			**28**			**56**			**140**			**56**			Trt[2]	ESN rate[3]	Form[4]
			Mean[5]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE			
			Bale count (# ha^{-1})																	
	Feb-14	0	550		29	490		29	511		29	571		29	494		29	0.255	0.163	0.691
Jun-14	Feb-15	1	726		32	614		32	628		32	681		38	606		32	0.271	0.484	0.659
Jun-15	Feb-16	2	767	ab	47	724	b	47	765	ab	47	1,000	a*	47	778	ab	47	**0.015**	**0.005**	0.852
Jun-16	Feb-17	3	957	b	51	957	b	51	1,024	b	51	1,296	a*	51	1,038	b	51	**0.007**	**0.003**	0.846
2014-2016 total (post-fertilization)			2,449		109	2,295		109	2,417		109	2,977	*	110	2,422		109	**0.035**	**0.013**	0.976
			Pine straw dry mass (Mg ha^{-1})																	
	Feb-14	0	2.93		0.13	2.78		0.13	2.86		0.13	3.01		0.13	2.75		0.13	0.629	0.481	0.564
Jun-14	Feb-15	1	4.01		0.16	3.49		0.16	3.54		0.16	4.04		0.17	3.48		0.16	0.060	0.070	0.801
Jun-15	Feb-16	2	4.50	ab	0.21	4.28	b	0.21	4.49	ab	0.21	5.47	a*	0.21	4.19	b	0.21	**0.011**	**0.006**	0.343
Jun-16	Feb-17	3	5.50	b	0.24	5.50	b	0.24	5.64	b	0.24	7.14	a*	0.24	6.14	ab	0.24	**0.003**	**0.001**	0.167
2014-2016 total (post-fertilization)			14.01	ab	0.56	13.27	b	0.56	13.67	b	0.56	16.66	a*	0.56	13.81	b	0.56	**0.011**	**0.003**	0.859

[1]Bold $P \leq 0.05$ denotes a significant effect.

[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year or post-fertilization averages.

[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or post-fertilization totals.

[4]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or post-fertilization totals.

[5]Means within a row followed by the same letter or not followed by any letter are not significantly different using stepdown Bonferroni adjustment at α=0.05. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.

Table ApPS2 (Results for figure PS2). Nutrient removals with slash pine straw harvested in February before fertilization (Feb-14) and in 2015, 2016 and 2017 following previous year June fertilization with urea or polymer-coated urea (ESN) at different rates.

Fertilization	Sampling	Number of fertilizations before harvest	Control			Fertilizer												Orthogonal contrasts *P*[1] values for pre-planned comparisons		
						ESN									Urea					
			Annual nitrogen application rate (lb N acre^{-1})																	
			0			28			56			140			56			Trt[2]	ESN rate[3]	Form[4]
			Mean[5]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE			
												TKN (kg ha^{-1})								
	Feb-14	0	7.49		0.61	6.63		0.61	7.31		0.61	7.56		0.61	6.49		0.61	0.580	0.523	0.344
Jun-14	Feb-15	1	13.17		1.12	11.40		1.12	13.41		1.12	14.89		1.19	11.55		1.12	0.269	0.159	0.271
Jun-15	Feb-16	2	12.77	b	1.13	12.26	b	1.13	13.78	ab	1.13	19.40	a*	1.13	12.48	b	1.13	**0.015**	**0.008**	0.435
Jun-16	Feb-17	3	22.76	b	1.25	24.02	b	1.25	25.98	b	1.25	38.13	a*	1.25	27.10	b	1.25	**<0.001**	**<0.001**	0.538
2014-2016 total (post-fertilization)			48.70	b	3.27	47.68	b	3.27	53.17	b	3.27	72.41	a*	3.30	51.14	b	3.27	**0.008**	**0.004**	0.669
2014-2016 average from SAS output			16.23		1.09	15.89		1.09	17.72		1.09	24.14		1.10	17.05		1.09			
												Total P (kg ha^{-1})[6]								
	Feb-14	0	0.62		0.08	0.69		0.08	0.61		0.08	0.67		0.08	0.59		0.08	0.876	0.767	0.886
Jun-14	Feb-15	1	1.02		0.11	0.88		0.11	0.85		0.11	1.06		0.11	0.82		0.11	0.442	0.362	0.878
Jun-15	Feb-16	2	1.23		0.10	1.15		0.10	0.98		0.10	1.29		0.10	0.97		0.10	0.176	0.155	0.952
Jun-16	Feb-17	3	1.96		0.13	1.79		0.13	1.55		0.13	2.13		0.13	1.75		0.13	0.112	**0.048**	0.296
2014-2016 total (post-fertilization)			4.21		0.31	3.82		0.31	3.38		0.31	4.48		0.32	3.55		0.31	0.172	0.103	0.700
												K (kg ha^{-1})								
	Feb-14	0	0.84		0.06	0.83		0.06	0.80		0.06	0.76		0.06	0.73		0.06	0.641	0.685	0.431
Jun-14	Feb-15	1	1.19		0.10	1.24		0.10	1.20		0.10	1.43		0.12	1.28		0.10	0.610	0.376	0.621
Jun-15	Feb-16	2	1.84		0.23	2.36		0.23	2.29		0.23	3.00	*	0.23	2.25		0.23	0.069	0.107	0.923
Jun-16	Feb-17	3	2.83	c	0.27	4.46	b*	0.27	4.41	b*	0.27	6.45	a*	0.27	4.77	b*	0.27	**<0.001**	**0.001**	0.369
2014-2016 total (post-fertilization)			5.86	b	0.47	8.06	ab*	0.47	7.89	ab*	0.47	10.88	a*	0.47	8.30	ab*	0.47	**0.009**	**0.014**	0.570

[1]Bold $P \le 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year or post-fertilization averages.
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or post-fertilization totals.
[4]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or post-fertilization totals.
[5]Means within a row followed by the same letter or not followed by any letter are not significantly different using stepdown Bonferroni adjustment at α=0.05. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.
[6]Means for Feb-17 are not different using Bonferroni adjustment or Dunnett's test.

Table ApPS3 (Results for figure PS3). Nutrient removals with slash pine straw harvested in February before fertilization (Feb-14) and in 2015, 2016 and 2017 following previous year June fertilization with urea or polymer-coated urea (ESN) at different rates.

Fertilization	Sampling	Number of fertilizations before harvest	Control			Fertilizer: ESN									Fertilizer: Urea			Orthogonal contrasts *P*[1] values for pre-planned comparisons		
			Annual nitrogen application rate (lb N acre^{-1}): 0			28			56			140			56			Trt[2]	ESN rate[3]	Form[4]
			Mean[5]		SE	Mean		SE	Mean		SE	Mean		SE	Mean		SE			
			Ca (kg ha^{-1})																	
	Feb-14	0	15.69		1.10	15.48		1.10	14.68		1.10	17.44		1.10	14.12		1.10	0.334	0.241	0.730
Jun-14	Feb-15	1	22.25		1.56	17.63		1.56	17.53		1.56	23.48		1.67	16.88		1.56	**0.043**	**0.042**	0.773
Jun-15	Feb-16	2	22.51	ab	1.68	19.19	b	1.68	19.86	b	1.68	29.67	a*	1.68	18.88	b	1.68	**0.005**	**0.002**	0.689
Jun-16	Feb-17	3	29.13	ab	2.46	24.42	b	2.46	24.48	b	2.46	38.82	a*	2.46	28.76	ab	2.46	**0.012**	**0.003**	0.248
2014-2016 total (post-fertilization)			73.89	ab	5.32	61.24	b	5.32	61.88	b	5.32	91.98	a	5.35	64.52	b	5.32	**0.011**	**0.003**	0.733
			Mg (kg ha^{-1})																	
	Feb-14	0	1.62		0.12	1.73		0.12	1.77		0.12	1.95		0.12	1.51		0.12	0.199	0.432	0.158
Jun-14	Feb-15	1	2.73		0.18	2.41		0.18	2.55		0.18	3.08		0.21	2.39		0.18	0.151	0.080	0.553
Jun-15	Feb-16	2	3.06	b	0.21	2.87	b	0.21	3.11	b	0.21	4.20	a*	0.21	2.74	b	0.21	**0.003**	**0.002**	0.224
Jun-16	Feb-17	3	3.92	b	0.28	3.72	b	0.28	4.15	b	0.28	5.53	a*	0.28	4.36	ab	0.28	**0.008**	**0.003**	0.607
2014-2016 total (post-fertilization)			9.71	b	0.58	8.99	b	0.58	9.81	b	0.58	12.82	a*	0.59	9.48	b	0.58	**0.006**	**0.002**	0.700

[1]Bold $P \leq 0.05$ denotes a significant effect.
[2]P values for differences among fertilization treatments (including the non-fertilized control) within a year or post-fertilization averages.
[3]P values for differences among ESN rates (28, 56, and 140 kg N ha^{-1}) within a year or post-fertilization totals.
[4]P values for difference between ESN and urea (each @ 56 kg N ha^{-1}) within a year or post-fertilization totals.
[5]Means within a row followed by the same letter or not followed by any letter are not significantly different using stepdown Bonferroni adjustment at α=0.05. Within a row, means signified with an asterisk are greater than a mean for the non-fertilized control using Dunnett's test at α=0.05.

Table ApP1. Slash pine response variables measured in the dormant season before fertilization (2013) and in the dormant season following annual June fertilization in 2014, 2015 and 2016 with urea or polymer-coated urea (ESN) at different rates, averaged over raked and non-raked treatments.

Sampling year	Number of fertilizations & rakings before measurement	Fertilizer									
		ESN								Urea	
		Nitrogen application rate (kg N ha^{-1})									
		0		28		56		140		56	
		Mean[7]	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
		Quadratic mean DBH [**QMD** (cm)]									
2013	0	12.56	0.20	12.56	0.20	12.35	0.20	12.44	0.20	12.03	0.20
2014	1	13.95	0.23	13.93	0.23	13.85	0.23	13.90	0.23	13.35	0.23
2015	2	14.84	0.23	14.93	0.23	14.76	0.23	15.10	0.23	14.35	0.23
2016	3	15.60	0.28	15.83	0.28	15.74	0.28	16.13	0.28	15.30	0.28
2013-2016 growth		3.04	0.18	3.27	0.18	3.40	0.18	3.70	0.18	3.27	0.18
		Average tree DBH (cm)									
2013	0	12.29	0.21	12.25	0.21	12.10	0.21	12.06	0.21	11.77	0.21
2014	1	13.68	0.23	13.60	0.23	13.58	0.23	13.57	0.23	13.07	0.23
2015	2	14.57	0.22	14.59	0.22	14.47	0.22	14.77	0.22	14.07	0.22
2016	3	15.29	0.27	15.51	0.27	15.46	0.27	15.83	0.27	15.01	0.27
2013-2016 growth		3.01	0.19	3.26	0.19	3.37	0.19	3.77	0.19	3.25	0.19
		Stand basal area [**BA** (m^2 ha^{-1})]									
2013	0	18.2	0.7	17.7	0.7	17.1	0.7	18.7	0.7	16.9	0.7
2014	1	22.1	1.0	21.7	1.0	21.3	1.0	22.6	1.0	20.6	1.0
2015	2	24.8	1.0	24.2	1.0	23.3	1.0	25.8	1.0	23.4	1.0
2016	3	27.0	1.1	26.5	1.1	25.5	1.1	28.0	1.1	26.2	1.1
2013-2016 growth		8.8	0.5	8.7	0.5	8.5	0.5	9.3	0.5	9.3	0.5
		Total stand volume o.b. [**TV ha^{-1}** (m^3 ha^{-1})]									
2013	0	82	4	80	4	75	4	84	4	76	4
2014	1	114	6	111	6	107	6	116	6	106	6
2015	2	140	6	135	6	129	6	145	6	132	6
2016	3	165	8	160	8	151	8	169	8	160	8
2013-2016 growth		83	4	80	4	77	4	85	4	84	4
		Merchantable stand volume o.b. to 8 cm top [**TV8cm ha^{-1}** (m^3 ha^{-1})]									
2013	0	68	4	65	4	61	4	68	4	61	4
2014	1	100	6	97	6	93	6	102	6	91	6
2015	2	127	6	122	6	116	6	132	6	118	6
2016	3	152	7	147	7	139	7	157	7	146	7
2013-2016 growth		84	4	82	4	78	4	89	4	85	4

Table ApP2. Slash pine response variables measured in the dormant season before (2013), and after one (2014), two (2015), or three (2016) annual February pine straw harvests (rakings), averaged over all fertilization treatments.

Sampling year	Number of rakings and fertilizations before measurement	Raking treatment			
		No Rake		**Rake**	
		Mean	SE	Mean	SE
Trees per hectare [**TPH** (trees ha^{-1})]					
2013	0	1490	46	1455	46
2014	1	1472	46	1427	46
2015	2	1444	46	1389	46
2016	3	1398	46	1358	46
2013-2016 mortality		-92	19	-98	19
Average total height of dominant and co-dominant trees [**D&C HT** (m)]					
2013	0	8.45	0.18	8.34	0.18
2014	1	9.92	0.18	9.81	0.18
2015	2	11.14	0.18	11.02	0.18
2016	3	12.24	0.18	12.14	0.18
2013-2016 growth		3.79	0.06	3.80	0.06
Average total tree height [**HT** (m)]					
2013	0	8.04	0.19	7.92	0.19
2014	1	9.54	0.19	9.47	0.19
2015	2	10.78	0.19	10.76	0.19
2016	3	11.95	0.19	11.85	0.19
2013-2016 growth		3.92	0.06	3.93	0.06
Quadratic mean DBH [**QMD** (cm)]					
2013	0	12.40	0.13	12.37	0.13
2014	1	13.81	0.15	13.78	0.15
2015	2	14.74	0.15	14.85	0.15
2016	3	15.72	0.18	15.72	0.18
2013-2016 growth		3.32	0.11	3.35	0.11
Average tree DBH (cm)					
2013	0	12.11	0.13	12.07	0.13
2014	1	13.50	0.15	13.49	0.15
2015	2	14.42	0.14	14.57	0.14
2016	3	15.41	0.17	15.43	0.17
2013-2016 growth		3.30	0.12	3.36	0.12

Table ApP3. Slash pine stand volume measured in the dormant season before (2013), and after one (2014), two (2015), or three (2016) annual February pine straw harvests (rakings), averaged over all fertilization treatments.

Sampling year	Number of rakings and fertilizations before measurement	Raking treatment			
		No Rake		**Rake**	
		Total stand volume o.b. [**TV ha^{-1}** (m^3 ha^{-1})]			
2013	0	81	3	78	3
2014	1	113	4	108	4
2015	2	138	4	134	4
2016	3	164	5	158	5
2013-2016 growth		83	3	80	3
		Merchantable stand volume o.b. to 8 cm top [**TV8cm ha^{-1}** (m^3 ha^{-1})]			
2013	0	66	3	63	3
2014	1	99	4	95	4
2015	2	125	4	121	4
2016	3	151	5	145	5
2013-2016 growth		85	3	82	3

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