

THE EFFECT OF SOIL MOISTURE AND
FERTILIZATION ON NITROGEN AVAILABILITY IN
A LOBLOLLY PINE (*PINUS TAEDA*) PLANTATION

By

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Abstract: The Southeast is considered to be one of the more vulnerable regions in the United States to climate change. This will have an impact on future southern pine productivity, specifically loblolly pine (*Pinus taeda* L.), one of the most intensively managed forest ecosystems in the region. Because of this, it is important to understand how shifts in the soil nitrogen (N) supply under varying degrees of soil moisture and fertilization will impact loblolly pine productivity. Doing so would allow forest landowners to adapt their management practices in order to more efficiently utilize fertilizer inputs while maintaining productivity. The primary objective of this study was to examine the influences of soil moisture and fertilization on the belowground processes affecting loblolly pine productivity by assessing how fertilization with projected changes to the precipitation regimes in the southeastern United States will influence soil N availability. This study was located on a seven-year-old loblolly pine plantation in McCurtain County near Broken Bow, OK. A randomized complete block 2x2 factorial design was utilized, incorporating two levels of fertilization (none or fertilized) and rainfall manipulation (none or 30% throughfall reduction). Ion exchange resin bags and intact soil cores were used to index N availability and determine N mineralization rates over the course of 486 days. Previous literature estimates net mineralization rates in loblolly pine plantations around 22.4 to 96.4 kg N ha⁻¹ soil yr⁻¹. The mineralization rates in this study ranged from 37.84 (wet), 51.71 (dry), 25.59 (wet+fert), and 30.22 (dry+fert) kg N ha⁻¹ soil yr⁻¹. The major finding in this study was that fertilization increased N mineralization rates as hypothesized, particularly for nitrate. While not significant, there were also indications supporting this for NO₃ accumulation on the core resins as well. The second major finding of this study was the fluctuations in N mineralization rates did not follow the patterns observed in previous studies, which is attributed to unexplored fluctuations in the microbial community.

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CHAPTER I

INTRODUCTION

Background and Rationale

The timberlands of the southeastern United States are among the most intensively managed forest ecosystems in the world (Allen and Campbell, 1988; Kelting et al., 1999; Conner and Hartsell, 2002). Dominating approximately 30 million acres (Sheffield and Knight, 1982; Allen et al., 1990; Dickens et al., 2003), loblolly pine (*Pinus taeda*) is a leading supplier of wood and fiber products. It also contributes other goods and services, such as providing clean air and water, sequestering carbon to mitigate climate change (Lal, 2005; Sundquist et al., 2008; Lorenz and Lal, 2010), providing wildlife habitat, facilitating recreational activities, and esthetics making it one of the most important commercial species in the region (World Resources Institute, 1996; Prestemon and Abt, 2002; Phelan and Allen, 2008; Huang et al., 2011).

The Southeast is considered one of the more vulnerable regions in the United States to climate change (Karl et al., 2009; Bastola, 2013). These changes are predicted to bring intense hurricanes, flooding, and more extensive and frequent droughts than currently being experienced (Karl et al., 2009; Ingram, 2013). This will have a significant impact on loblolly pine productivity because of the influence precipitation has on soil processes such as net mineralization and soil respiration (e.g., Cassman and Munns, 1980; Addiscott, 1983; Orchard and Cook, 1983; Pastor and Post, 1988; Ellert and Bettany, 1992; Luxmoore et al., 1993; Renault and Sierra, 1994;

Sierra, J., 1997; Fernandez et al., 2000; Zaman and Chang, 2004; Warren et al., 2009; MacKay et al., 2012). Soil moisture influences microbial activity which drives nitrogen mineralization rates, supplying the largest source of bioavailable nitrogen to plants (Henderson and Harris, 1975; Wollum and Davey, 1975; Binkley and Hart, 1989). Too high soil water content from flooding and intense precipitation or an insufficient one from drought can be detrimental to soil microbial communities, resulting in lower mineralization rates and subsequently nutrient availability. If conditions are prolonged this will lead to a loss of productivity and will be detrimental to the region's economy.

There has been a shift in focus to forest soil - site productivity relationships in order to understand the interactions between forest productivity and soil nutrient availability (Pastor et al., 1984; Nadelhoffer et al., 1985; Zak et al., 1989; Allen et al., 1990; Cole et al., 1990; Gower and Son, 1992; Jokela and Martin, 2000; Wilson and Maguire, 2009). Nutrient deficiencies within forests can lead to suboptimal wood and leaf area production (Vose and Allen, 1988; Colbert et al., 1990; Albaugh et al., 1998, 2004). This has resulted in the fertilization of over 6.5 million ha of forested land in the Southeastern United States in order to enhance nutrient availability and improve productivity (Albaugh et al., 2007). This will impact water availability because an increase in leaf area production from fertilization leads to higher and faster water depletion (Linder et al., 1987). This could in turn decrease leaf stomatal conductance, limiting water loss from the canopy (Ewers et al., 1999) and decrease photosynthesis limiting stemwood production (Munger et al., 2003).

The majority of past research on southern pine productivity has been focused upon the impacts of increasing water availability (Jokela et al., 2004; Samuelson et al., 2008). Given the prospect of escalating droughts in the southeastern United States, investigating the interaction between fertilization combined with diminishing precipitation on nutrient availability becomes imperative in order to determine its significance for southern pine productivity. One group

working to increase this knowledge is the PINEMAP (Pine Integrated Network: Education, Mitigation, and Adaptation) project. One of three coordinated agricultural projects funded in 2011 by the USDA, their primary goal is to adapt forest management practices to improve productivity in order to counter climate change and to harness that productivity to increase carbon sequestration. Focused on the 20 million acres of managed pine forests in the Southeastern United States, it endeavors to integrate research, education and extension in order to improve forest resiliency and support the economic reliance on the forest industry. This research took place on one of their Tier III sites, designed to examine the influences of fertilization and reduced soil moisture on soil nitrogen (N) availability by manipulating soil moisture and fertilization levels on a loblolly pine plantation.

Objectives

The overall objective of this study was to characterize the influences of soil moisture and fertilization on loblolly pine productivity by assessing how fertilization and projected changes to the precipitation regimes in the southeastern United States will influence soil nitrogen (N) availability. This was done by examining shifts in the soil N supply under varying degrees of soil moisture and fertilization in a loblolly pine plantation. To accomplish this, measurements were performed on soil chemistry and correlated to environmental conditions occurring over the course of the study.

Hypothesis

H1: Highest N mineralization rates will occur with fertilization and no throughfall reduction.

H2: As soil moisture decreases net nitrogen mineralization rates will decline, leading to lower nitrogen availability, however the addition of fertilizer in combination with decreased soil moisture will result in higher N mineralization rates compared to treatments without fertilization.

CHAPTER II

REVIEW OF LITERATURE

General Characteristics of Loblolly Pine (*Pinus taeda*)

Loblolly pine (*Pinus taeda* L.) is a fast growing conifer native to North America. It is also recognized by the names North Carolina pine, Arkansas pine, bull pine, and oldfield pine.

Loblolly pine's natural range covers the southeastern United States from southern New Jersey to Florida and extends westward into eastern Oklahoma and Texas (Figure 1), and is generally managed as either even- or uneven-aged natural stands. The timber is an ideal economic resource for the region due to fast growth in plantations for fiber, coupled with high strength saw timber.

Within its native range, the climate for loblolly pine is primarily subtropical consisting of hot summers and mild winters with adequate to excessive precipitation. When compared to other southern pine species, loblolly pine is considered to be fastest growing when cultivated on well-drained sites (Shiver et al., 2000). The least productive sites are either highly waterlogged with shallow or deep sandy soils without a high water table or clay lens to hold moisture near the roots (Fowells, 1965). The majority of soils existing within the native range of loblolly pine are Ultisols, however there are also some Alfisols and few pockets of Entisols and scattered Spodosols present (Allen et al., 1990; Baker and Langdon, 1990).

The progression of loblolly pine into territories further north is hampered by the colder

temperatures and subsequent ice damage during the winter months, and western expansion beyond Oklahoma and Texas is restricted by inadequate precipitation during the growing season (Fowells, 1965). However, loblolly pine also has the potential of becoming acclimatized to areas along the outer perimeter of its natural range and in addition has been shown to be successfully established in other countries.

Soil Quality and Productivity

Soil quality has been defined as “the capacity of a living soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and animal health” (Doran et al., 1998). Forest site quality is understood to be contingent upon readily accessible resources, such as soil nutrients and water availability (e.g., Allen et al., 1990; Albaugh et al., 1998; Kelting et al., 1999; Piatek and Allen, 1999, 2001; Jokela and Martin, 2000; Gough et al., 2004; Jokela et al., 2004; Fox et al., 2007; Samuelson et al., 2008). Long term studies support that the gap between the productivity and biological potential of loblolly pine can be diminished by improving soil quality and nutrient availability (Adegbedi et al., 2002). Silviculturists need to be aware, however, of their primary responsibility to prevent the mismanagement of existing resources that could lead to site degradation (Ford, 1983). As Gessel (1981) states, “It is less costly to maintain and/or enhance productivity than it is to restore it”.

Previous research has attempted to identify indicators of forest soil quality in order to predict future productivity (Polglase et al., 1992; Burger and Kelting, 1998; Kelting et al., 1999; Heumann et al., 2012), which is summarized as the ability of soils to adequately supply nutrient demands for biomass production. Nitrogen (N) is the most limiting nutrient in forest soils, with current silvicultural practices promoting the use of N fertilizers to make up for any deficits in the

soil N pool and improve soil fertility (Reich and Schoettle, 1988; Tang et al., 1999; Allen et al., 2001). Mineralizable N has the greatest potential to become an indicator for soil quality and productivity, as it is the N that is actively cycling within the soil pool (Keeney, 1980; Powers et al., 1998; Knoepp et al., 2000). Soil quality has been shown to improve as mineralization rates increase and more N becomes available. Because of this, soil N mineralization rates should be considered a significant factor in predicting future productivity (Gregorich and Carter, 1997).

Southern Pine Nutrition

When any tree species has such an extensive range, differences in productivity will likely occur due to the considerable variability in environmental conditions (Sampson and Allen, 1999).

Previously it had been believed that water availability was the most limiting resource in enhancing southern pine productivity. However, it is now understood that soil nutrients are the primary drivers to improve their growth rates (Albaugh et al., 1998, 2004; Sampson and Allen, 1999; Jokela and Martin, 2000; Jokela et al., 2004).

Loblolly pine is highly adaptable to the infertile soils of the southeastern United States. However, the need for soil nutrient amendment is still needed as a stand ages due to the soil no longer being able to supply sufficient levels of N for maximum growth (Miller, 1981; Piatek and Allen, 1999, 2001). Because of this, fertilization is utilized on the majority of southern pine stands in order to promote optimal productivity (e.g., Gough et al., 2004; Will et al., 2005; Fox et al., 2007; Samuelson et al., 2008) and research shows that with additional N inputs, average growth increases lasting from 8 - 10 years can occur (Fox et al., 2007). For example, field trials in the Southeast for loblolly pine have shown that with a single fertilizer application of approximately 150 to 225 lb N ac⁻¹, a growth response of 50 ft³ ac⁻¹ yr⁻¹ (1.5

ton $\text{ac}^{-1} \text{yr}^{-1}$) can last for more than 6 years (Hynynen et al., 1998; Amateis et al., 2000; Fox et al., 2007).

Recent experiments and empirical models support claims that current productivity levels for southern pine in the southeastern United States remain far lower than what is achievable (Allen and Lein, 1998; Martin et al., 1999; Sampson and Allen, 1999; Jokela et al., 2000; Landsberg et al., 2001; Yin and Sedjo, 2001). Studies indicate that with sufficient inputs growth rates exceeding $360 \text{ ft}^3 \text{ ac}^{-1} \text{ yr}^{-1}$ ($10.8 \text{ ton ac}^{-1} \text{ yr}^{-1}$) are entirely feasible (Yin et al., 1998, Fox, 2000). So while initial costs per acre including fertilization may be higher, the financial gains in costs per ton of wood due to higher productivity can be considerable (Allen et al., 2005).

Soil Moisture and Nitrogen Availability in Forest Soils

The mineral soil serves as a repository for the nutrient reserves in an ecosystem. In forests, a rate of approximately 1 to 3 % of total soil N is available yearly for trees (Binkley and Hart, 1989). The largest source of biologically available N in forest soils is from the production of ammonium (NH_4) and nitrate (NO_3) due to mineralization from the decomposition of soil organic matter (SOM) and root turnover (Figure 2) (Henderson and Harris, 1975; Wollum and Davey, 1975; Binkley and Hart, 1989).

Nitrogen mineralization is governed by microbial activity, which is influenced by environmental conditions such as soil water content, temperature, aeration, and pH (Addiscott, 1983; Orchard and Cook, 1983; Ellert and Bettany, 1992; Renault and Sierra, 1994; Sierra, J., 1997). Soil water content can both stimulate N cycling by increasing mineralization rates and increase N losses through the leaching of excess from the forest ecosystem (Jager and Bruins, 1975; Orchard and Cook, 1983; Pastor and Post, 1988; Cabrera, 1993). This is due in part to the influence soil water content has on soil microbial communities (Cassman and Munns, 1980;

Orchard and Cook, 1983). Nitrogen mineralization is also influenced by soil moisture through its regulation of oxygen distribution within the soil volume, which also impacts microbial activity by decreasing 'habitable space' (West et al., 1988a; West et al., 1988b; Renault and Sierra, 1994). Microbial communities shift as moisture content changes allow more desiccation-tolerant and anaerobic species to thrive (Sommers et al., 1981). This would decrease overall microbial growth rates as anaerobic activity is considered less efficient than aerobic. It is also noted that within multiple drying and rewetting cycles, SOM will show an increase in N mineralization after a subsequent wetting (Jager and Bruins, 1975; Orchard and Cook, 1983; Cabrera, 1993). However, even at permanent wilting point (1500 kPa), some N mineralization will still occur (Macduff and White, 1985; Howard and Howard, 1993; Grundmann et al., 1995).

In recent years research has examined the effects of water availability in loblolly pine plantations (Jokela et al., 2004; Samuelson et al., 2004, 2008; Tang et al., 2004; Albaugh et al., 2006; Fox et al., 2007; Karl et al., 2009; Campoe et al., 2013). A number of studies have found that fertilization in combination with irrigation increases biomass productivity in mid-rotation loblolly pine (Albaugh et al., 2006; Campoe et al., 2013). A fertilization-throughfall reduction study conducted by Tang et al. (2004) on an 18-yr old plantation, found that leaf net photosynthetic rate decreased with throughfall exclusion and biomass increased with fertilization in non-excluded treatments. However a similar study by Coyle et al. (2008) looking at irrigation alone or in combination with fertilization found no growth response within a 4-yr old stand. Considering the future likelihood of increased droughts in the southeastern United States (Karl et al., 2009; Seager et al., 2009), it becomes even more relevant to understand the interactions between reduced water availability and fertilization on the productivity of southern pines.

Use of Ion Exchange Resins in Soil Nutrient Analysis

Ion exchange resins (IER) are becoming a popular alternative to estimating soil nutrient availability (Binkley, 1984; Hart and Binkley, 1985; Binkley et al., 1986; DiStefano and Gholz, 1986; Lundell, 1989; Hubner et al., 1991). Ion exchange resin materials consist of labile ions that can be exchanged with other ions in the soil through the processes of anion and cation exchange. Ion diffusion regulates nutrient concentrations at the root surface. The adsorption rate of soil nutrients to IERs is determined by the mineralization rate of the soil nutrient, their competition with other soluble ions, and the mobility of the given ion. When IERs are buried they become exposed to the same conditions as the plant roots, therefore the nutrients recovered from them serve as a representation of nutrient availability to the plant. IERs are incapable of offering direct competition with soil microbes for bioavailable N, preventing the skewing of any estimates for inorganic N.

Concerns over N loss on the resins themselves during incubation can be disregarded, as fluxes between ionic N species do not occur on them (Schnabel, 1983). In addition, IERs are responsive to soil water content due to their influence on nutrient mobility. Because nitrate is a highly mobile nutrient in soil, IERs will generally take it up in greater quantity when compared to a less mobile nutrient, like NH_4 . With respect to that, NH_4 recovery using IERs is more dependent upon the volume of water percolating through soil than NO_3 (Fisher and Binkley, 2000). The two methods most commonly used with IERs are single- or mixed-ion resin bags and resin bags used in combination with intact soil cores (Eno, 1960; DiStefano and Gholz, 1986; Johnson et al., 2005).

The main benefit to using IER bags to assess soil nutrient availability is their nondestructive physical and biological disturbance of soil and relative ease in use. They allow measurements at the same location over time with no loss of the substrate when compared to

standard soil sampling methods. However, unlike soil sampling where the values can be correlated back to a specific volume of soil, IER measurements are expressed as a function of weight or moles of nutrient per unit weight of resin (Hart and Binkley, 1985; Binkley et al., 1986; Kjønaas, 1999; Johnson et al., 2005). Because of this, IER bags serve better as an index of nutrient availability rather than as an exact value at a given point of time under field conditions (Binkley et al., 1986; Fisher and Binkley, 2000; Schimel and Bennett, 2004).

A study by Binkley and Matson (1983) comparing IER bags to other methods for nutrient assessment determined that IERs provide more utility than laboratory incubations due to their responsiveness to field conditions. Positive correlations with IERs exist when evaluating N transformations with soil and plant nutrient uptake (e.g., Lajtha, 1988; Huang and Schoenau, 1997; Kjønaas, 1999). The use of ion exchange resins *in situ* have been very effective differentiating between fertilized and unfertilized stands (Binkley and Matson, 1983; Hart and Binkley, 1985), illustrating their suitability in this study.

Use of Intact Soil Cores in Soil Nutrient Analysis

Forest productivity is well correlated to the rates of *in situ* mineralization and N availability (e.g. Adams and Attwill, 1986; Adams et al., 1989; Hart and Firestone, 1989). Intact soil cores consisting of a PVC tube used in combination with one or two IER bags are inserted into the soil profile to remain *in situ* for a predetermined time. Mineralization can subsequently be calculated by taking the difference between the soil N prior to incubation and what is extracted from the core after. Incubation intervals generally range between 1-2 weeks and up to 8 weeks (e.g., Adams et al., 1989; Hart and Firestone, 1989).

Field incubations using intact soil cores have benefits over the use of IER bags alone or laboratory incubations for a number of reasons. Because fewer disruptions of abiotic and biotic

factors occur within a core under field conditions, a more accurate representation of the microenvironmental processes that regulate N fluxes is produced (Nadelhoffer et al., 1985; DiStefano and Gholz, 1986; Raison et al., 1987; Sierra, J., 1997). While more labor intensive, the use of intact soil cores allows monitoring of these N fluxes by estimating mineralization and immobilization rates over time in a way that IER bags alone cannot, and laboratory methods are incapable of taking into consideration the influence of field conditions on these processes (DiStefano and Gholz, 1986). This study uses IER bags in combination with a modified intact soil cores technique, whereby a single mixed-ion exchange resin bag was placed at the bottom of the soil core to catch throughfall and the percolating soil solution.

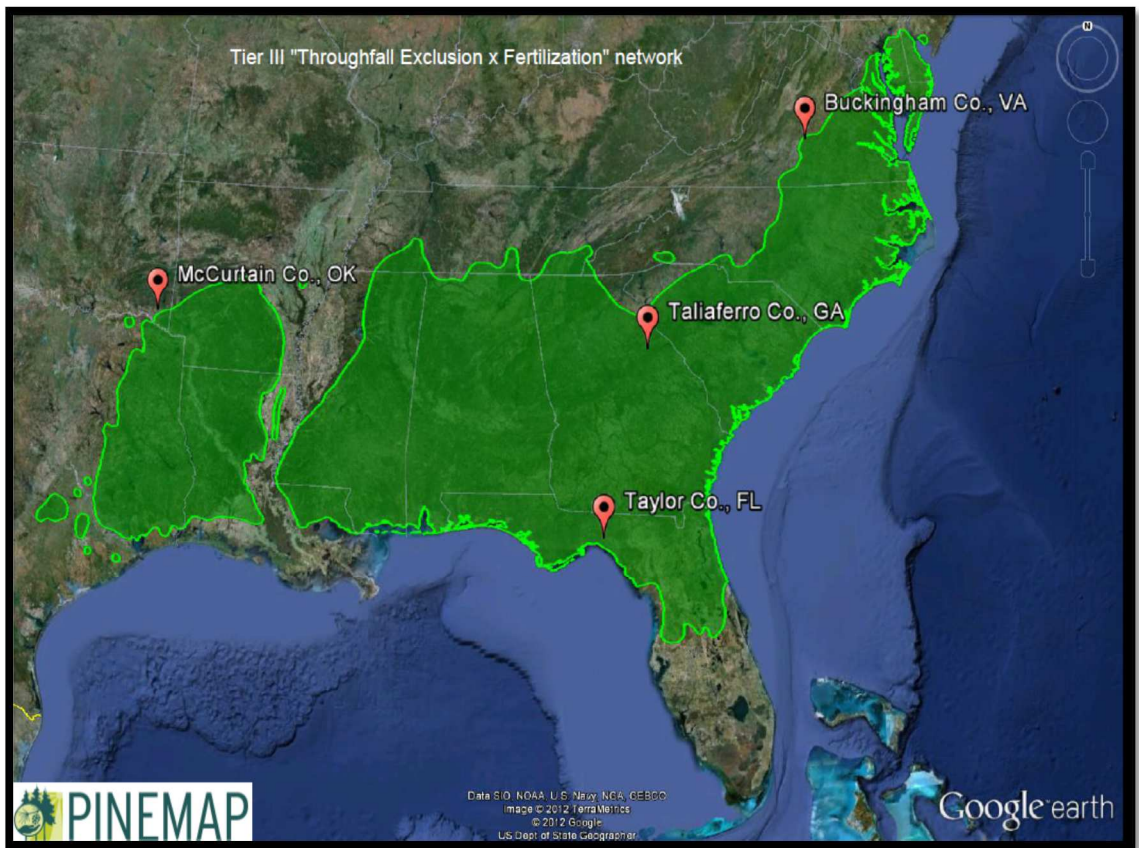


FIGURE 1. Natural range of loblolly pine (green area). The red flags show the locations of the Tier III fertilization x throughfall exclusion field experiments. This study took place on the McCurtain Co, OK site. [Remote sensing image: Google Earth; Range map: USDA Forest Service].

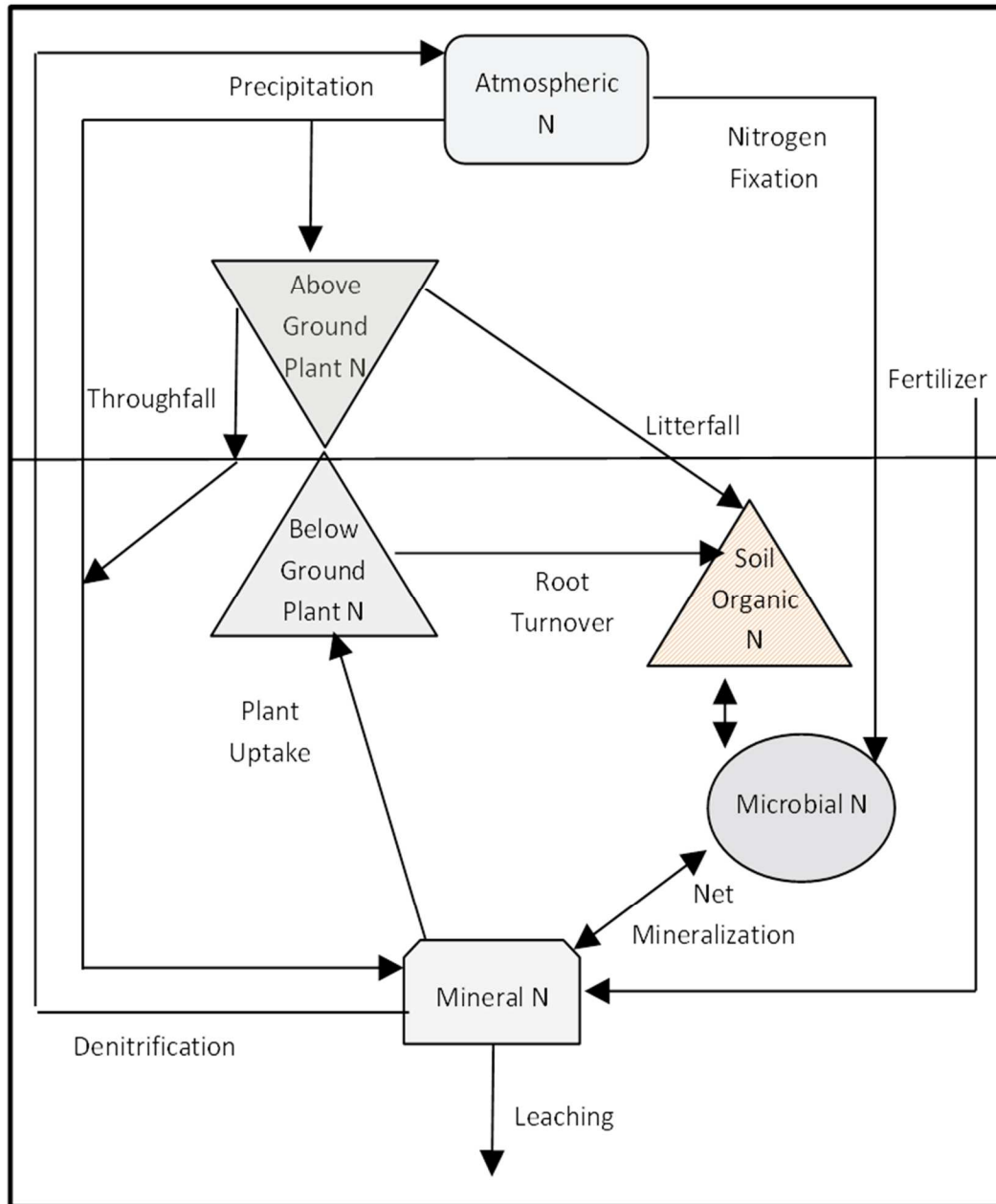


FIGURE 2. Diagram of nitrogen cycling. The largest source of biologically available N present in soils is due to mineralization and root turnover (Henderson and Harris, 1975; Wollum and Davey, 1975; Binkley and Hart, 1989). [Modified from: Brierley et al., 2001]

CHAPTER III

METHODOLOGY

Study Location and Soil Characteristics

This study was conducted on a 7 year old loblolly pine (*P. taeda* L.) plantation located in McCurtain County near Broken Bow, Oklahoma, USA (34°01' N , 94°49' W) at an elevation of 153 m. The mean annual temperature in McCurtain County is 17°C; with a 30 year average annual precipitation around 1371 mm (Oklahoma Climatological Survey, 2000). The annual snowfall rate is approximately 9 cm with the first freeze occurring around November 3 and the last freeze approximately March 30 (Oklahoma Climatological Survey, 2000).

The soils are characterized as a Ruston series (a fine-loamy, siliceous, semiactive, thermic Typic Paleudults), which is a well-drained, very deep fine sandy loam soil formed from marine or stream deposition on the Upper Coastal Plains (Soil Survey Staff, 2013). Soil pH was measured for each plot and averaged by treatment type with a glass electrode using a 1:1 (w:v) ratio of soil and deionized water (Kalra, 1995). From the center of each control (wet) plot, soil bulk density was measured using 5 cm by 5cm cores (Blake, 1965) and volumetric water content using tempe cells (Klute and Dirksen, 1986).

Treatments and Experimental Design

The trees at this site originated from an orchard mix of improved Western Gulf 1-0 bare-root seedlings that were planted in spring 2008. The gross treatment plot size is approximately 0.4 ha, containing measurement plots of approximately 0.1 ha. These plots had approximately 620 trees per ha at spacing of 2.1 m by 3.0 m. A randomized complete block 2x2 factorial design was utilized in this study incorporating two levels of fertilization (none or fertilized) and rainfall manipulation (none or 30% throughfall reduction), (Figure 3).

The operational standard fertilization rate for loblolly pine plantations was broadcast applied by hand April 2012. The fertilized plots received 224 kg·ha⁻¹ N, 27 kg·ha⁻¹ phosphorus and 56 kg·ha⁻¹ K applied as 432 kg·ha⁻¹ urea, 140 kg·ha⁻¹ diammonium phosphate, and 112 kg·ha⁻¹ potash, respectively. Additionally, granular oxysulfate micronutrient mix (Southeast Mix, Cameron Chemicals, Inc., Virginia Beach, VA, USA) consisting of 6% sulfur, 5% boron, 2% copper, 6% manganese, and 5% zinc was applied at a rate of 22.4 kg·ha⁻¹ to eliminate micronutrient deficiencies. Nitrogen volatilization was minimized through the application of Agrotain® Ultra (Koch Agronomic Services, LLC, Wichita, KS, USA) at a rate of 0.43 mL·kg⁻¹ of urea.

The following treatments were replicated in four blocks:

1. Control plot with no fertilization and no exclusion (wet)
2. No fertilization with exclusion (dry)
3. Fertilization with no exclusion (wet + fert)
4. Fertilization with exclusion (dry + fert)

The precipitation reduction was achieved using throughfall excluders over the entire gross plot which was calculated to cover 30% of the measurement plot. Raised covered troughs measuring 50 cm wide were constructed using 2x4 wood panels and opaque UV protected polyethylene plastic to run between the entire rows of the treated plots (Figure 4). To eliminate water entering the measurement plot from excluder overflow, drainage pipes were added to both ends of each excluder to direct water outside the plot (Figure 5). In addition, excess surface water flowing into the plots from outside of the measurement zone was avoided by incorporating a surrounding buffer zone around each plot consisting of an extra row of excluders and trees. Complete weed control was initiated on all plots using glyphosate (2% a.i., Roundup[®], Monsanto Co., St. Louis, MO, USA) at a rate of approximately 28 liters per hectare in early 2012 and maintained throughout the duration of the study.

Field Study and Laboratory Analysis

Field Study

Three methods were used to determine the plant available nitrogen in the soil near eight randomly selected trees per plot from May 2013 to September 2014. The same trees were used for the duration of the study. There were eight collection intervals, over the course of 486 days. During the growing season (spring through fall), they were spaced at approximately 4 to 6 week intervals, and 6 to 8 weeks during the winter months. For each collection (incubation) interval an attempt was made to keep each of the three methods within 20 cm of each other.

Method one (Bulk Soil Sample): At the beginning of each collection period, near the selected trees a bulk soil sample was taken from the upper 15 cm of the mineral soil. The samples were kept separate and transported on ice to the laboratory and stored at 2°C until extracted. These bulk samples were used to assess the soil gravimetric water content and initial ammonium

and nitrate (NH_4 and NO_3) pools available for plant uptake prior to each incubation interval. It is also used to calculate mineralization rates using the difference between starting N and *Method three* for each incubation interval.

Method two (Bulk Resin Bag): Mixed ion exchange resin (IER) bags were used to provide an index of bioavailable N within each plot for each collection interval over the duration of the study, and to serve as a comparison to the resins used in *Method three*. They quantified the amount of soil N not taken up by microbial communities or plants or lost through volatilization, denitrification or leaching (Sibbesen, 1977; Binkley and Matson, 1983). At the beginning of each collection interval, an IER bag containing 10 g (wet weight) mixed-ion exchange resin beads was inserted to 5 cm depth in the mineral soil at each of the selected trees. The IER bags were created from a nylon-polyester blend material using Ionac® ASB-1P OH^- and Ionac® C-267 H^+ IERs (Lanxess Corp., Pittsburgh, PA, USA) which were hand-mixed at a 1:1 ratio. The functional groups for the resins are quaternary amine and sulfonic acid, respectively. The bags were formed by weighing 10 g of the mixed IER within 15 cm by 15 cm squares of material and secured with zipties (Figure 6). Prior to placement, the bags were rinsed with deionized (DI) water, drained, and then refrigerated in sealed plastic bags until deployed. At the next collection interval the previous bags were removed from the field and placed within plastic bags and stored on ice for transport to the laboratory and kept cold at 2°C until extracted.

Method three (Intact Soil Core): Field net N mineralization (N_{min}) using an intact soil core in combination with a single resin bag, a technique modified from DiStefano and Gholz (1986) measured in-field N availability. It was calculated for each collection interval from the differences in N between the bulk soil and the intact soil core. The intact soil cores were made from polyvinyl chloride (PVC) tubes 18 cm long and 4.5 cm (internal diameter) wide. At the beginning of each collection interval, a PVC tube was inserted to 18 cm of the mineral soil and then removed. Approximately 3 cm of soil was removed from the bottom of the PVC tube and a

20 g (wet weight) mixed-resin bag inserted in place of the removed soil, ensuring no gaps remained between the resin bag and the wall of the tube (Figure 7). This results in 239 cm³ mineral soil plus 20 g IER bag per intact soil core. The PVC tube was then returned to the original hole for incubation (Figure 8). At the beginning of the next collection interval, the core was removed and transported on ice to the laboratory for analysis.

The 20 g mixed-resin bags were made by doubling the IER amount used in *Method two* and contained within 18 cm by 18 cm square material. Within each of the plots, two additional intact soil cores were placed besides two of the locations to serve as a comparison to the first cores. This second group of tubes were capped to prevent precipitation from entering the tube to use as a comparison to the open cores, resulting in ten intact soil cores total per plot (8 open / 2 capped). All of these samples were transported back to the laboratory following the same procedures in *Method one* and *Method two*. The IER bags used in *Method two* and *Method three* were formed using fresh mixed-ion exchange resin beads for each incubation interval. The ion exchange capacities for the two IERs used in this study are shown in Table 1. The following equation was used to determine the exchange capacity per kg (mol_c · kg⁻¹) of resin for each IER

$$R = C_{\text{resin}} \times \frac{1}{D_{\text{resin}}} \quad (1)$$

where R is the resin exchange capacity per kg (mol_c · kg⁻¹), C_{resin} is the total capacity of the IER (mol_c · L⁻¹), and D_{resin} is the bulk density of the resin (kg · L⁻¹). The exchange capacity per bag (mmol_c · bag⁻¹) was calculated as

$$B = R \times b \times k_l \quad (2)$$

where B is the exchange capacity per resin bag (mmol_c · bag⁻¹), R is the resin exchange capacity (mol_c · kg⁻¹), b is the resin bag weight (kg), and k_l is a unit conversion factor (mmol_c per mol_c).

From the above we can estimate the ion or nutrient (NH₄ or NO₃) adsorption capacity per IER bag, as shown below

$$A = R \times \frac{1}{m} \times M_w \times k_2 \times b \times S \quad (3)$$

where A is the nutrient adsorption capacity per bag (mg · bag⁻¹), R is the resin exchange capacity (mol_c · kg⁻¹), m is the molar charge per ion (mol_c), M_w is the molecular weight of the nutrient (g · mol⁻¹), k₂ is a unit conversion factor (mg per g), b is the resin bag weight (kg), and S is the percent of solid resin per gram of total resin (g).

Laboratory Analysis

All of the soil and resin samples were analyzed in triplicate for ammonium and nitrate by colorimetric techniques using a BioTek® Instruments Synergy H1 Hybrid (BioTek Instruments, Winooski, VT, USA) microplate reader and reported on a dry weight basis. Nitrate (NO₃) analysis was conducted using a modified vanadium III chloride method from Doane and Horwath (2003). Ammonium (NH₄) analysis was based on a sodium salicylate/sodium hydroxide method (Weatherburn, 1967). For samples that exceeded the level of the calibration standards which ranged from 0 to 10 ppm, the elutriant was analyzed a second time using a 1:10 dilution and the results multiplied by 10.

Soil Extraction (Methods one and three): Each of the soil samples were air dried and homogeneously mixed in preparation for extraction. Soil ammonium and nitrate were extracted using 5 g of soil in a 2 M potassium chloride (KCl) solution at a ratio of 1:5 (w:v). The resulting elutriant was stored cold at approximately 2°C until analysis. For each sample the soil moisture content was determined gravimetrically by drying a subsample at 105°C for 24 hours. The results

for each of the extracted soil samples were expressed as milligrams of NH₄ or NO₃ per kilogram of dry weight soil using the following equation:

$$F = N_{ppm} \times \left[\frac{Y}{\phi_d} \right] \quad (4)$$

where F represents the final level of NH₄ or NO₃ (mg · kg⁻¹) present, N_{ppm} is the concentration of NH₄ or NO₃ (ppm) from the colorimetric analysis, Y is the total volume of KCl (ml) used for the extraction, and ϕ_d is the dry weight of the extracted soil sample (g).

IER Extraction (Methods two and three): After removal from the field, the IER bags from *Method two* were extracted by adding 20 ml of a 2 M KCl solution to 5 g of resin from an opened 10 g IER bag and shaken for 1 hour. The elutriant was then poured from the resin mixture, and the process repeated using the same 5 g resin. This produces a total solution of 5 g resin and 40 ml KCl, which was combined and refrigerated for 24 hours. The following day, the combined KCl-resin mixture was shaken for 1 hour and filtered. The 20 g IER bags (*Method three*) were extracted by doubling the amount of KCl and resin used in *Method two* resulting in a 10 g resin and 80 ml KCl combined solution. The filtered elutriant from each method was stored cold at 2°C until analysis.

The moisture content for each resin sample was determined gravimetrically by drying a subsample from each IER bag at 60°C for 24 hours. As with the results of the soil analysis, all of the IER bags were expressed in milligrams of NH₄ or NO₃ per kilogram of dry weight resin by correcting for the total volume of KCl used in the resin extraction and substituting the dry weight of the extracted resin for that of the soil in equation 4.

Fresh mixed-ion exchange resin beads were used for each deployment in *Method two* and *Method three*. Any IER bag that became damaged or lost resin during the incubation period was

discarded and not analyzed. If the damaged bag was inside a soil core, the soil inside that core was discarded as well.

Additional Calculations and Rationale

Total inorganic N (N_i) was calculated as the sum of NH_4 and NO_3 .

$$N_i = NH_4 + NO_3 \quad (5)$$

Net ammonification (ΔNH_4): The changes in the ammonium concentration after the incubation period ($NH_{4(\text{final})}$) and the initial bulk soil ammonium concentration prior to incubation ($NH_{4(\text{initial})}$). This was computed for soil within the root exclusion tubes, and the sum of soil changes and IER NH_4 accumulation.

$$\Delta NH_4 = NH_{4(\text{final})} - NH_{4(\text{initial})} \quad (6)$$

Net nitrification (ΔNO_3): The changes between the nitrate concentration after the incubation period ($NO_{3(\text{final})}$) and the initial bulk soil nitrate concentration prior to incubation ($NO_{3(\text{initial})}$). Again, this analysis was for soil differences alone, or soil plus IER nitrate.

$$\Delta NO_3 = NO_{3(\text{final})} - NO_{3(\text{initial})} \quad (7)$$

Net mineralization (N_{min}): The net mineralization rate was estimated using the sum of net ammonification (ΔNH_4) and net nitrification (ΔNO_3). Immobilization occurs if N_{min} is a negative value.

$$N_{min} = \Delta NH_4 + \Delta NO_3 \quad (8)$$

Net Nitrogen uptake (N_{up}): The plant uptake during an incubation period was calculated by the net mineralization of the soil only (not including IER associated nitrogen) (N_{min}), minus

any changes (losses) in the soil inorganic N pool from the bulk soil (Δ bulk soil N) at the beginning of the next incubation interval and leaching.

$$N_{up} = N_{min} - [\Delta\text{bulk soil N}] - \text{leaching} \quad (9)$$

Denitrification will be assumed to be negligible (Wollum and Davey, 1975; Keeney, 1980). Leaching potential will be estimated by comparing the difference in concentration between the uncapped (leaching) and capped soil cores (*Method three*).

Water-filled Pore Space (WFPS): The water-filled pore space was calculated from the total porosity (*TP*) of the soil and the gravimetric (%) water content using the following equation

$$WFPS = [(BD \times G) \times TP] \times 100 \quad (10)$$

where BD is the soil bulk density, G is the gravimetric water content (%), and *TP* is the total porosity of the soil using $TP = [(1 - (BD/\text{mineral soil particle density})) \times 100]$, where the mineral soil particle density is 2.65 g cm^{-3} .

Gravimetric soil moisture (θ) was calculated as $\theta =$

$$\frac{(\text{soil wet wt} - \text{soil dry wt})}{\text{soil wet wt}} \times 100 \quad (11)$$

Statistical Analysis

All statistical analysis was performed using PROC MIXED in SAS for Windows, version 9.4 (SAS Institute Inc., Cary, NC, USA). A randomized complete block 2-way factorial analysis of variance (ANOVA) at eight subsamples per plot was used to test the effect of the treatments on N mineralization rates. Random effects were plots nested within treatment, and location nested within plot. Significance using the Kenward-Roger test was determined when $p < 0.1$ between

the levels of fertilization in combination with each level of rainfall manipulation. LSMEANS was used to compute means. We used the following model

$$Y = \mu + F + E + (F * E) + D + (D * F) + (D * E) + (D * F * E) + U_i + V_{ij} + \epsilon \quad (12)$$

where F is fertilized, E is throughfall excluded, D is deployment, U_i is the random effect for plot, V_{ij} is the random effect for sample point, and ϵ is the residual error.

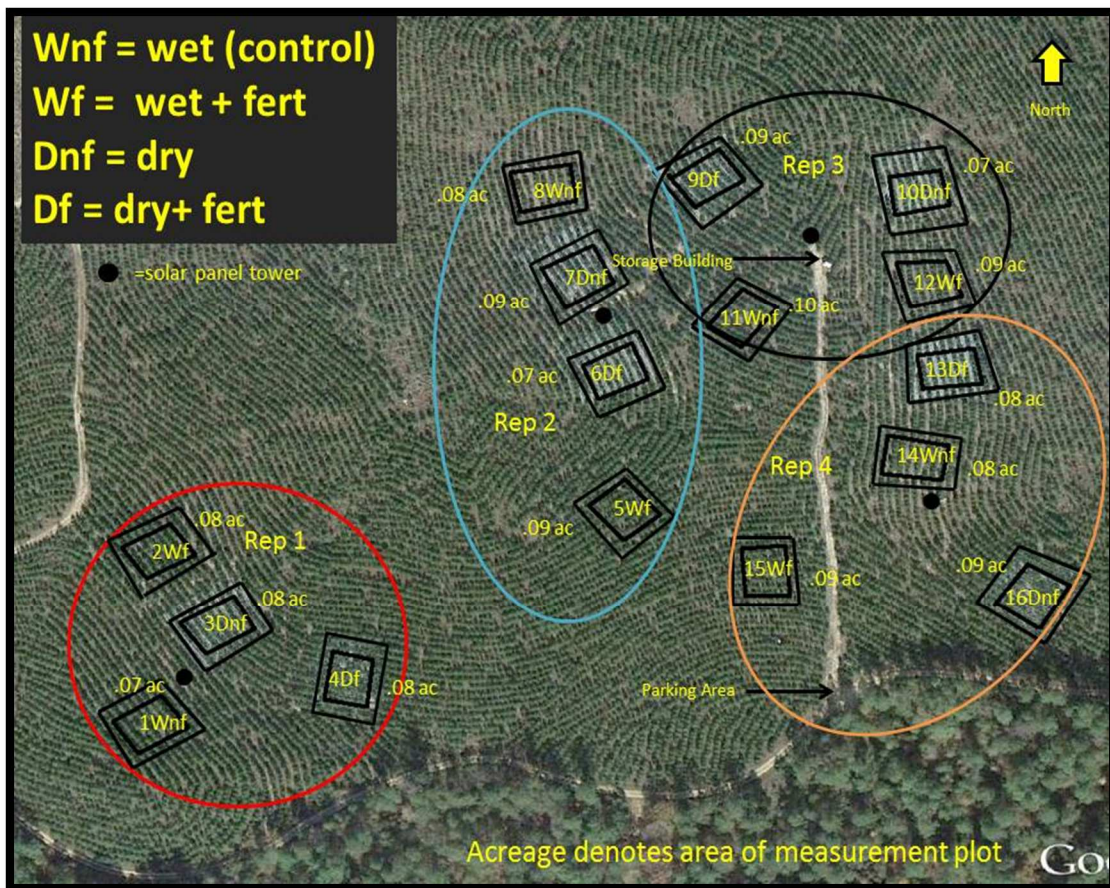


FIGURE 3. Site map showing layout of plots and treatments: wet (control), wet+fert, dry, and dry+fert. The white areas on the map are the plots receiving the throughfall exclusion. Source: “OK Tier III”. 34°01’ N and 94°49’ W. May 22, 2013. [Remote sensing image: Google Earth]



FIGURE 4. Images of the $\frac{1}{3}$ throughfall excluder placement through the understory of a measurement plot of a loblolly pine (*P. taeda* L.) plantation in McCurtain County, Oklahoma. The excluders were constructed as two 50 cm troughs containing a 50 cm gap between. [Source: Middle and bottom photos courtesy of Duncan Wilson, 2012]



FIGURE 5. Images of the $\frac{1}{3}$ throughfall excluders showing drainage design which directs precipitation away from the measurement plots in McCurtain County, Oklahoma. [Source: Photos courtesy of Duncan Wilson, 2012]

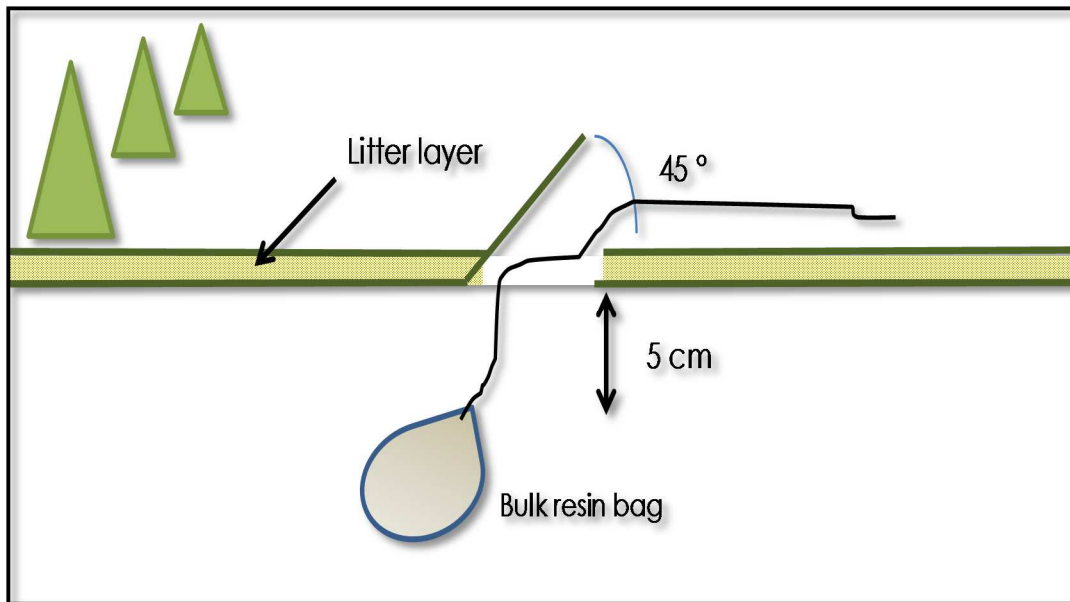
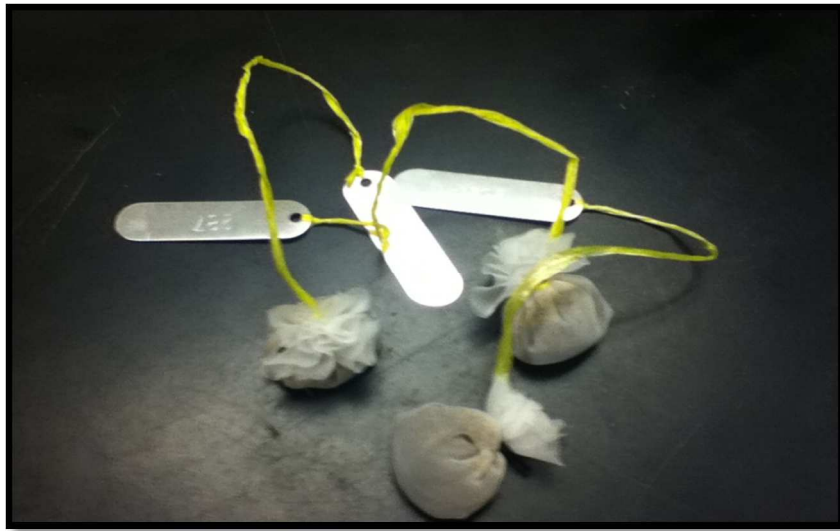


FIGURE 6. (*Method 2*) Photo of 10 g mixed-ion exchange resin (IER) bags prior to deployment and a diagram of placement. The bags contain 5 g each of Ionac® ASB-1P OH⁻ and Ionac® C-267 H⁺ IERs (Lanxess Corp., Pittsburgh, PA).

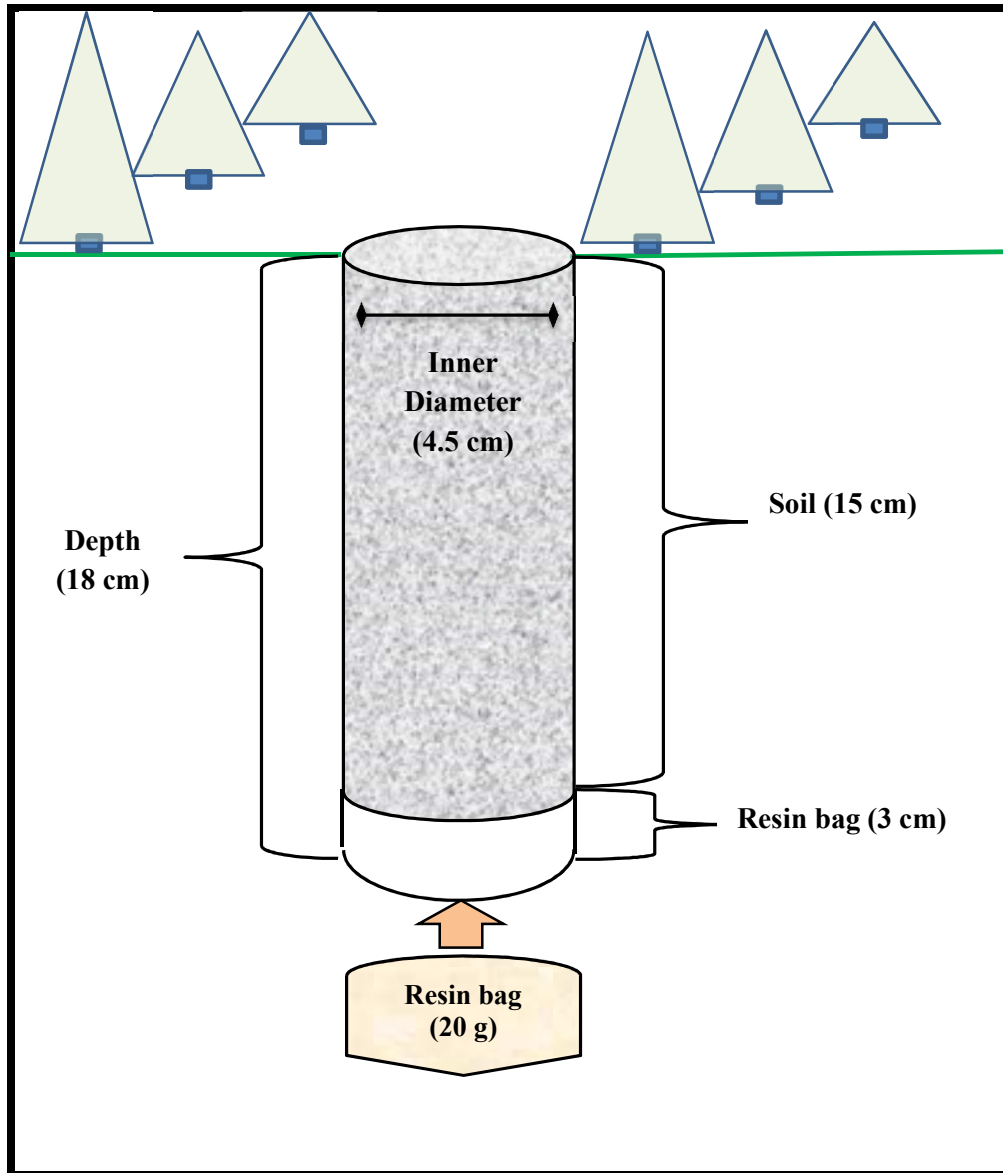


FIGURE 7. Diagram of an intact soil core. A 20 g mixed-ion exchange resin bag (approximately 3 cm in height) is placed in the bottom of a 4.5 cm diameter wide by 18 cm long PVC tube and buried beneath the mineral soil surface.



FIGURE 8. Photo showing placement of *Method two* and *Method three* within a measurement plot of a loblolly pine plantation, McCurtain County, Oklahoma.

TABLE 1. Ion exchange resin beads used in this study with their exchange capacity. Commercially purchased single bed resins were homogeneously hand-mixed at a 1:1 ratio prior to bag formation.

Label	Resin Type	Ionic Form	Mesh Size (mm)	Resin Weight per Bag (wet resin)	Exchange Capacity ²		mg Ion per bag (wet resin) ^{1,2}
					mol _e kg ⁻¹ (dry resin)	mmol _e bag (wet resin)	
Ionac - ASB-1P	Strong base anion	OH ⁻	16-50	5 g	1.76	8.79	436.55
				10 g	1.76	17.58	873.10
Ionac - C-267	Strong acid cation	H ⁺	16-50	5 g	2.38	11.90	173.89
				10 g	2.38	23.80	347.78

¹ Wet weight based on resin solid content of 80% for anion (NO₃) and 81% for cation (NH₄).

² The values shown represent a conservative estimate of the maximum capacity for the given amount of resin.

CHAPTER IV

RESULTS

Soil Environment and Initial Soil N Pools

Soil Environment

Mineral soil properties were measured for the upper 0 to 15 cm of the soil profile. The bulk density was taken from the center of the control plots at 5 cm increments and had a mean value of 1.45 g cm⁻³, with an average clay content of 8.4% (Table 2). The mean volumetric water content at -33kPa and -1500 kPa was 0.13 and 0.04 cm³ cm⁻³, respectively (Table 2). There was no significant difference between treatments in the mean soil pH, which was measured at a depth of 0 to 15 cm and ranged from 4.48 to 4.91 (Table 3).

It should be noted that all of the seasonal effect was significant for percent soil moisture, bulk N pools, N adsorption to the bulk resin bags, and net mineralization due to results being significantly higher or lower depending on the given season.

Percent soil moisture, based off the soil dry weight, was measured to compare the bulk (initial) percent soil moisture against the percent soil moisture within the intact soil cores (tubes) after incubation. The mean percent bulk soil moisture ranged from 2.7% to 24.9%, which corresponds to a water filled pore space (WFPS) of 8.62% (wet) to 79.73% (wet+fert) (Figure 9). The intact soil core percent soil moisture varied between 4.7% [WFPS 15.05%] (dry+fert) and

24.3% [WFPS 77.84%] (wet) (Figure 9). My results showed an overall seasonal effect and a seasonal*fertilizer*excluder interaction in the bulk soil and within the intact soil cores (Table 4). This is because the trend for percent soil moisture was higher in the wet+fert treatment for all of the incubations except fall for the bulk soil. In the intact soil cores the percent soil moisture was significantly higher at $p=0.1$ in the wet+fert treatment for all of the incubations except late summer 2013 and late spring 2014. Comparing the mean values for the excluded and unexcluded treatments between the percent soil moisture for the bulk soil and the intact cores, the intact cores had higher moisture levels late spring and fall of 2013, and spring of 2014.

Bulk Soil N Pools

There were significant seasonal*fertilizer and seasonal*excluder interactions on the starting ammonium pool (Table 5). Because of fluctuations in the ranking of the mean values among treatments, the F x S interaction was significant. The E x S interaction was significant because NH_4 was significantly greater in the excluded treatments from late spring 2013 to fall and again in summer 2014 (Table 6). The bulk soil NH_4 concentration of each incubation interval comprised the largest component of the KCl extractable mineral N pool, and was approximately 4 times higher than the concentrations for initial soil NO_3 from winter to spring of 2014 (Table 6). The ammonium pools measured from 1.91 mg N kg^{-1} soil (wet+fert) in late summer 2013 to 12.80 mg N kg^{-1} soil (dry) the summer 2014.

There was a significant seasonal*fertilizer interaction on the initial NO_3 pools (Table 5), because while fertilization increased NO_3 on all sample dates, the magnitude of the increase varied. When testing individual dates, the effects of fertilization were only significant spring 2013. Initial soil NO_3 pools varied from 0.30 mg N kg^{-1} soil (dry) in spring 2014 to 12.41 mg N kg^{-1} soil (dry+fert) spring 2013. The highest NO_3 concentrations were noted for spring 2013

within the wet+fert and dry+fert treatments, measuring 8.04 and 12.41 mg N kg⁻¹ soil, respectively (Table 6), and were significant spring 2013.

Between the fertilized and unfertilized treatments in the bulk soil total inorganic N pools, a significant fertilizer*seasonal interaction existed, which is attributed to the increases in NO₃ with fertilization that varied in magnitude among dates (Table 5). Total inorganic N pools ranged from 3.36 mg N kg⁻¹ soil in the control plot during fall (2013) to 19.80 mg N kg⁻¹ soil (dry+fert) in spring 2013 (Table 6).

N Sorption to Bulk Resin Bags

The bulk resin bags (*Method Two*) were used to help quantify N transformations and potential plant availability at the soil surface prior to incubation. Except for the seasonal effect, no factors in the model were statistically significant on NH₄ concentrations in either the fertilizer or excluder treatments (Table 7). Net ammonium concentrations on the bulk resins ranged from 0.09 (dry+fert) to 1.09 (dry+fert) mg N kg⁻¹ resin day⁻¹ (Figure 10A). The highest NH₄ concentrations were measured in spring and late summer 2013, ranging from 0.81 to 1.09 mg N kg⁻¹ resin day⁻¹. Seasonal fluctuations in NH₄ concentrations on the bulk resins were fairly uniform and did not appear to be correlated to initial % soil moisture (Figure 10A).

There was a significant fertilizer effect on NO₃ adsorption on the bulk resins indicating that fertilization increased nitrate adsorption (Table 7). This was likely due to the mobility of nitrate in the soil at that time compared to ammonium. However, no relationship appeared to exist between the initial % soil moisture and final NO₃ concentrations on the resins. Nitrate bulk resin concentrations varied between 0.14 (dry) and 0.80 (wet+fert) mg N kg⁻¹ resin day⁻¹ (Figure 10B).

There was no significant treatment effect or interaction for either fertilization or throughfall exclusion with total inorganic N adsorption on the bulk resins (Table 7). The bulk resin concentration for total inorganic N fluctuated between 0.26 (dry+fert) and 1.57 (dry+fert) mg N kg⁻¹ resin day⁻¹, and did not appear to fluctuate in relation to the initial soil moisture (Figure 10C).

Net Mineralization Using Intact Soil Cores

There were no significant treatment effects of interactions related to ammonification using intact soil cores, except at a seasonal level as mentioned previously (Table 8). With the exception of fall and spring 2014, total net ammonification levels were predominantly negative, fluctuating between -0.11 (dry) to 0.09 (dry) mg N kg⁻¹ day⁻¹ (Figure 11C). Ammonium adsorption on the core resins showed a significant F x E x S treatment interaction and was significantly higher for both fertilization and throughfall exclusion for spring, early summer, and fall 2013, indicating more ammonium was captured by the resins instead of remaining in the bulk soil during these incubations (Table 9). Ammonium concentrations on the core resins varied between 0.008 (dry+fert) to 0.005 (dry+fert) mg N kg⁻¹ day⁻¹ (Figure 11B).

There was a significant fertilization interaction showing fertilization increased nitrate 37% (Table 8). Total nitrate N_{min} rates were overall net positive and fluctuated between -0.001 (wet+fert) and 0.19 (dry) mg N kg⁻¹ soil day⁻¹ (Figure 12C). Nitrification rates were the greatest in spring 2013 at the start of the growing season and then gradually declined until winter (Figure 12A, C). In 2014, nitrification rates were approximately half that of the previous year. Nitrate concentrations on the core resins measured between 0.003 (dry) and 0.02 (wet+fert) mg N kg⁻¹ soil day⁻¹ (Figure 12B), and there was a significant seasonal*fertilization treatment interaction on the core resins from spring to late summer 2013 (Table 9). Overall, there was twice as much

nitrate adsorbed to the resins compared to ammonium, regardless of the core soil moisture level (Figure 12B).

There was a significant fertilization effect on total inorganic N_{min} (Table 8), which is attributed to the fertilization effect for nitrification. With the exception of winter and summer 2014, total N_{min} were primarily net positive, and total N mineralization rates varied between -0.08 (dry) and 0.16 (dry) $\text{mg N kg}^{-1} \text{ soil day}^{-1}$ (Figure 13C). The incubation periods with the greatest increases in initial soil moisture, fall (144.0%) and spring 2014 (48.5%) resulted in the highest mineralization rates (Figure 13A, C). Total inorganic N accumulation on the core resins ranged from 0.45 (dry) to 2.21 (wet+fert) $\text{mg N kg}^{-1} \text{ soil day}^{-1}$ (Figure 13B). Like nitrate adsorption to the core resins, a significant seasonal*fertilization interaction was found for total inorganic N on the core resins (Table 9). The reason for this interaction is that both nitrate and ammonium showed a significant F x S interaction for N resin accumulation, and total inorganic N adsorption was higher in the fertilized treatments from late spring to fall 2013(Figure 13B).

Comparing the % soil moisture between the capped and uncapped intact soil cores, there was no significant difference among the treatments (Table 10).

Correlations between Bulk Resins and Net Mineralization

There was no significant correlation between treatments between the bulk core resins and net mineralization (Figure 14). The treatment correlation for ammonium varied between $R^2= 0.08$ (wet) and $R^2= 0.47$ (dry) and $R^2= 0.07$ (wet) and $R^2= 0.33$ (wet+fert) for total inorganic N (Figure 14). The treatment correlation for nitrate varied between $R^2= 0.70$ (wet+fert) and $R^2= 0.72$ (dry) (Figure 14).

TABLE 2. Mean bulk density (g cm^{-3}), soil particle size (%) and volumetric water content ($\text{cm}^3 \text{cm}^{-3}$) for the four control (wet) plots by 5 cm increments for the surface 0 to 15 cm layer of mineral soil.

Plot	Treatment	Depth (cm)	Bulk Density (g cm^{-3})	Soil Particle Size			Volumetric Water Content	
				sand %	silt %	clay %	-33 kPa ($\text{cm}^3 \text{cm}^{-3}$)	-1500 kPa ($\text{cm}^3 \text{cm}^{-3}$)
1	wet	0-5	1.21	52.50	38.06	9.44	0.15	0.04
		5-10	1.38	49.65	39.02	11.33	0.13	0.04
		10-15	1.53	42.62	39.73	17.66	0.11	0.07
8	wet	0-5	1.51	52.22	42.75	5.03	0.18	0.05
		5-10	1.50	55.93	37.77	6.30	0.12	0.04
		10-15	1.43	52.25	41.47	6.28	0.12	0.03
11	wet	0-5	1.40	69.21	21.99	8.80	0.12	0.03
		5-10	1.41	62.92	29.54	7.54	0.11	0.03
		10-15	1.47	60.42	32.04	7.54	0.11	0.03
14	wet	0-5	1.49	60.42	32.04	7.54	0.14	0.04
		5-10	1.56	40.61	51.22	8.17	0.12	0.04
		10-15	1.50	40.99	53.99	5.02	0.12	0.05
Mean			1.45 (0.03)	53.31 (2.6)	38.30 (2.56)	8.39 (1.0)	0.13 (0.0)	0.04 (0.0)

±SE of mean enclosed in parentheses.

TABLE 3. Soil pH by treatment type. The pH was averaged using four samples from each of the 16 plots from 0-15 cm. The treatments are: a control plot with no fertilization and no exclusion (wet), no fertilization and exclusion (dry), fertilization with exclusion (dry + fert), and fertilization with no exclusion (wet + fert).

Treatment	Plot	pH	Mean pH
wet	1	4.76	4.86 (0.09)
	8	5.14	
	11	4.73	
	14	4.84	
dry	3	4.59	4.88 (0.14)
	7	4.73	
	10	5.00	
	16	5.22	
dry+fert	4	4.44	4.48 (0.07)
	6	4.30	
	9	4.53	
	13	4.64	
wet+fert	2	5.03	4.91 (0.18)
	5	5.24	
	12	4.98	
	15	4.40	

±SE of mean enclosed in parentheses.

TABLE 4. Statistical summary (probability > F) of treatment and seasonal effects on soil moisture (%) for the bulk and intact core soils from the surface 0 to 15 cm layer of mineral soil for each incubation interval collected May 2013 to September 2014.

(Significant value at $\alpha = 0.1$)

Source	% Soil Moisture					
	Bulk Soil			Intact Core Soil (tube)		
	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>
F	1	12	0.58	1	12.1	0.89
E	1	12	0.02	1	12.1	0.03
F x E	1	12	0.10	1	12.1	0.08
S	6	1605	<.01	6	1438	<.01
F x S	6	1605	0.02	6	1438	0.01
E x S	6	1605	<.01	6	1438	<.01
F x E x S	6	1605	<.01	6	1438	<.01

F, fertilization; E, throughfall exclusion; S, season

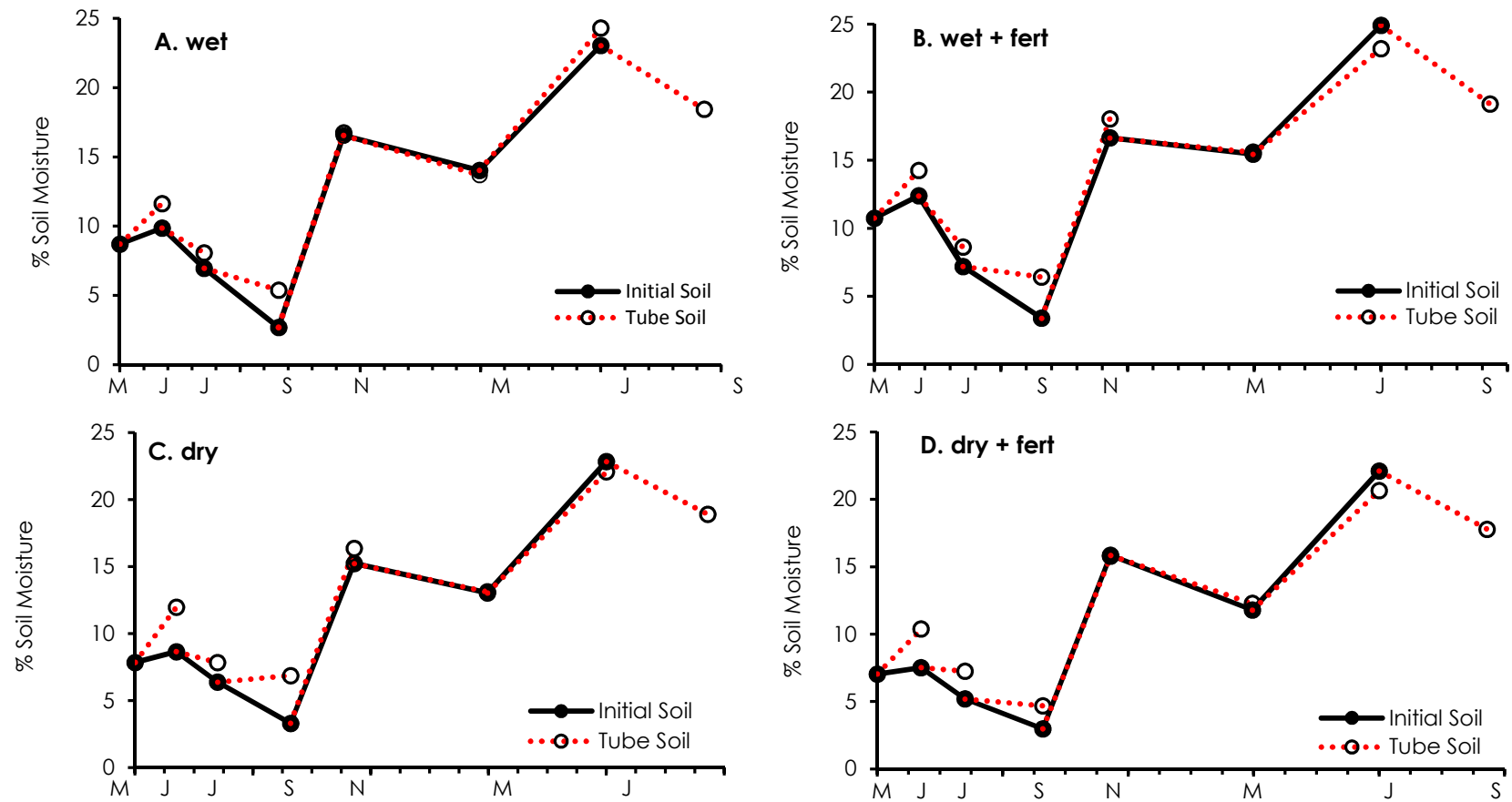


FIGURE 9. Seasonal fluctuations between the soil moisture (%) of bulk soil prior to incubation and the soil moisture (%) within the intact soil (tube) from May 2013 to September 2014. The treatments are wet (A), wet+fert (B), dry (C), and dry+fert (D). The dotted line represents the intact core (tube) soil moisture at the beginning and end of the incubation period.

TABLE 5. Statistical summary (probability > F) of treatment and seasonal effects on bulk soil nitrogen pools in the surface 0 to 15 cm layer of mineral soil for each incubation interval collected May 2013 to September 2014. (P value at $\alpha = 0.1$)

Source	Bulk Soil Pools								
	NH ₄			NO ₃			Total Inorganic N		
	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>
F	1	12.1	0.13	1	12	0.01	1	12.1	0.17
E	1	12.1	0.19	1	12	0.92	1	12.1	0.38
F x E	1	12.1	0.81	1	12	0.23	1	12.1	0.46
S	6	720	<.01	6	708	<.01	6	714	<.01
F x S	6	720	0.02	6	708	<.01	6	714	0.01
E x S	6	720	0.01	6	708	0.63	6	714	0.34
F x E x S	6	720	0.36	6	708	0.70	6	714	0.55

F, fertilization; E, throughfall exclusion; S, season

TABLE 6. Initial soil N pools, net nitrification, net ammonification and net mineralization by season (May 2013 - September 2014).

Incubation Period	Treatment	Initial Soil N Pool ^{1,2}		Initial Soil N Pool ^{1,2}		Initial Soil N Pool ^{1,2}	
		NH ₄ (mg N kg ⁻¹)	Net Ammonification ^{1,2} (mg N kg ⁻¹ day ⁻¹)	NO ₃ (mg N kg ⁻¹)	Net Nitrification ^{1,2} (mg N kg ⁻¹ day ⁻¹)	Total Inorganic N (mg N kg ⁻¹)	Total Net Mineralization ^{1,2} (mg N kg ⁻¹ day ⁻¹)
Late Spring (2013)	wet	6.70 (0.91) ab	-0.11 (0.02) a	2.88 (1.34) a	0.15 (0.02) a	9.58 (1.76) a	0.04 (0.03) ab
	dry	8.75 (0.91) ab	-0.09 (0.02) a	1.51 (1.34) a	0.18 (0.02) a	10.25 (1.76) a	0.09 (0.03) a
	wet + fert	5.57 (0.91) b	-0.11 (0.02) a	8.05 (1.34) b	0.10 (0.02) a	13.62 (1.76) a	-0.01 (0.03) b
	dry + fert	7.90 (0.91) ab	-0.03 (0.02) b	12.41 (1.36) c	0.14 (0.03) a	19.80 (1.76) b	0.09 (0.03) ab
Early Summer (2013)	wet	3.03 (0.91) ab	0.01 (0.02) b	5.17 (1.34) b	0.07 (0.03) a	8.20 (1.76) a	0.07 (0.03) a
	dry	4.60 (0.91) ab	-0.02 (0.02) ab	1.84 (1.34) a	0.15 (0.02) a	6.44 (1.76) a	0.12 (0.03) a
	wet + fert	2.36 (0.92) b	-0.01 (0.02) a	5.35 (1.36) b	0.08 (0.03) ab	7.72 (1.78) a	0.07 (0.03) ab
	dry + fert	4.70 (0.92) a	-0.02 (0.02) ab	5.10 (1.36) b	0.04 (0.03) b	9.78 (1.78) a	0.01 (0.03) b
Late Summer (2013)	wet	2.77 (0.91) a	0.00 (0.02) a	2.99 (1.34) ab	0.04 (0.03) ab	5.75 (1.76) a	0.04 (0.03) a
	dry	3.76 (0.91) a	0.01 (0.02) a	2.29 (1.34) a	0.06 (0.03) a	6.05 (1.76) a	0.06 (0.03) a
	wet + fert	1.91 (0.91) a	0.00 (0.02) a	4.78 (1.34) ab	0.02 (0.03) b	6.69 (1.76) a	0.02 (0.04) b
	dry + fert	3.90 (0.91) a	-0.03 (0.02) a	5.91 (1.34) b	0.03 (0.03) ab	9.82 (1.76) a	0.00 (0.03) ab
Fall (2013)	wet	2.43 (0.91) a	0.08 (0.02) a	0.92 (1.34) a	0.04 (0.03) a	3.36 (1.76) a	0.12 (0.04) a
	dry	3.39 (0.91) a	0.09 (0.02) a	0.93 (1.34) a	0.06 (0.03) a	4.31 (1.76) a	0.16 (0.03) a
	wet + fert	2.09 (0.91) a	0.08 (0.02) a	1.66 (1.36) a	0.07 (0.03) a	3.71 (1.76) a	0.15 (0.03) a
	dry + fert	3.81 (0.91) a	0.06 (0.02) a	3.23 (1.34) a	0.03 (0.03) a	7.04 (1.76) a	0.09 (0.03) a
Winter 2013-14)	wet	10.30 (0.92) a	-0.02 (0.02) a	1.80 (1.36) a	0.01 (0.03) a	12.10 (1.78) a	0.00 (0.03) a
	dry	9.28 (0.91) a	-0.02 (0.02) a	1.20 (1.34) a	0.01 (0.03) a	10.48 (1.76) a	-0.01 (0.03) a
	wet + fert	8.12 (0.91) ab	-0.02 (0.02) a	3.10 (1.34) a	0.00 (0.02) a	11.21 (1.76) a	-0.02 (0.03) a
	dry + fert	6.86 (0.92) b	0.00 (0.02) a	2.76 (1.36) a	0.01 (0.03) a	9.60 (1.78) a	0.00 (0.03) a
Late Spring (2014)	wet	5.49 (0.92) a	0.06 (0.02) a	0.49 (1.36) a	0.05 (0.03) a	5.98 (1.78) a	0.11 (0.03) a
	dry	5.82 (0.92) a	0.06 (0.02) a	0.30 (1.36) a	0.06 (0.03) a	6.13 (1.78) a	0.12 (0.04) a
	wet + fert	5.79 (0.93) a	0.03 (0.02) a	0.85 (1.36) a	0.04 (0.03) a	6.43 (1.78) a	0.08 (0.03) a
	dry + fert	4.74 (0.92) a	0.03 (0.02) a	1.64 (1.36) a	0.07 (0.03) a	6.37 (1.78) a	0.10 (0.04) a
Late Summer (2014)	wet	10.32 (1.00) b	-0.08 (0.02) a	1.70 (1.52) a	0.05 (0.03) b	12.04 (1.99) a	-0.04 (0.04) b
	dry	12.80 (0.97) a	-0.11 (0.03) ab	1.65 (1.47) a	0.04 (0.04) ab	14.50 (1.92) a	-0.07 (0.05) a
	wet + fert	9.00 (0.94) b	-0.07 (0.02) a	3.76 (1.40) a	0.03 (0.03) a	12.74 (1.83) a	-0.04 (0.04) ab
	dry + fert	8.11 (0.97) b	-0.05 (0.03) b	3.87 (1.47) a	0.02 (0.04) ab	11.96 (1.92) a	-0.03 (0.05) a

¹ Results were based on soil gravimetric dry weights.

² SE of mean enclosed in parentheses. Treatment means followed by the same letter are not significantly different in a given incubation interval.

TABLE 7. Statistical summary (probability > F) of treatment and seasonal effects on nitrogen accumulation on the bulk resins within the surface 0 to 15 cm layer of mineral soil for each incubation interval collected May 2013 to September 2014. (P value at $\alpha = 0.1$)

Source	Bulk Resin Nitrogen Concentration								
	NH ₄			NO ₃			Total Inorganic N		
	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>
F	1	12.1	0.69	1	12.1	0.02	1	12.1	0.38
E	1	12.1	0.95	1	12.1	0.14	1	12.1	0.81
F x E	1	12.1	0.73	1	12.1	0.51	1	12.1	0.40
S	6	613	<.01	6	487	<.01	6	617	<.01
F x S	6	613	0.23	6	487	0.11	6	617	0.40
E x S	6	613	0.44	6	487	0.13	6	617	0.29
F x E x S	6	613	0.89	6	487	0.98	6	617	0.79

F, fertilization; E, throughfall exclusion; S, season

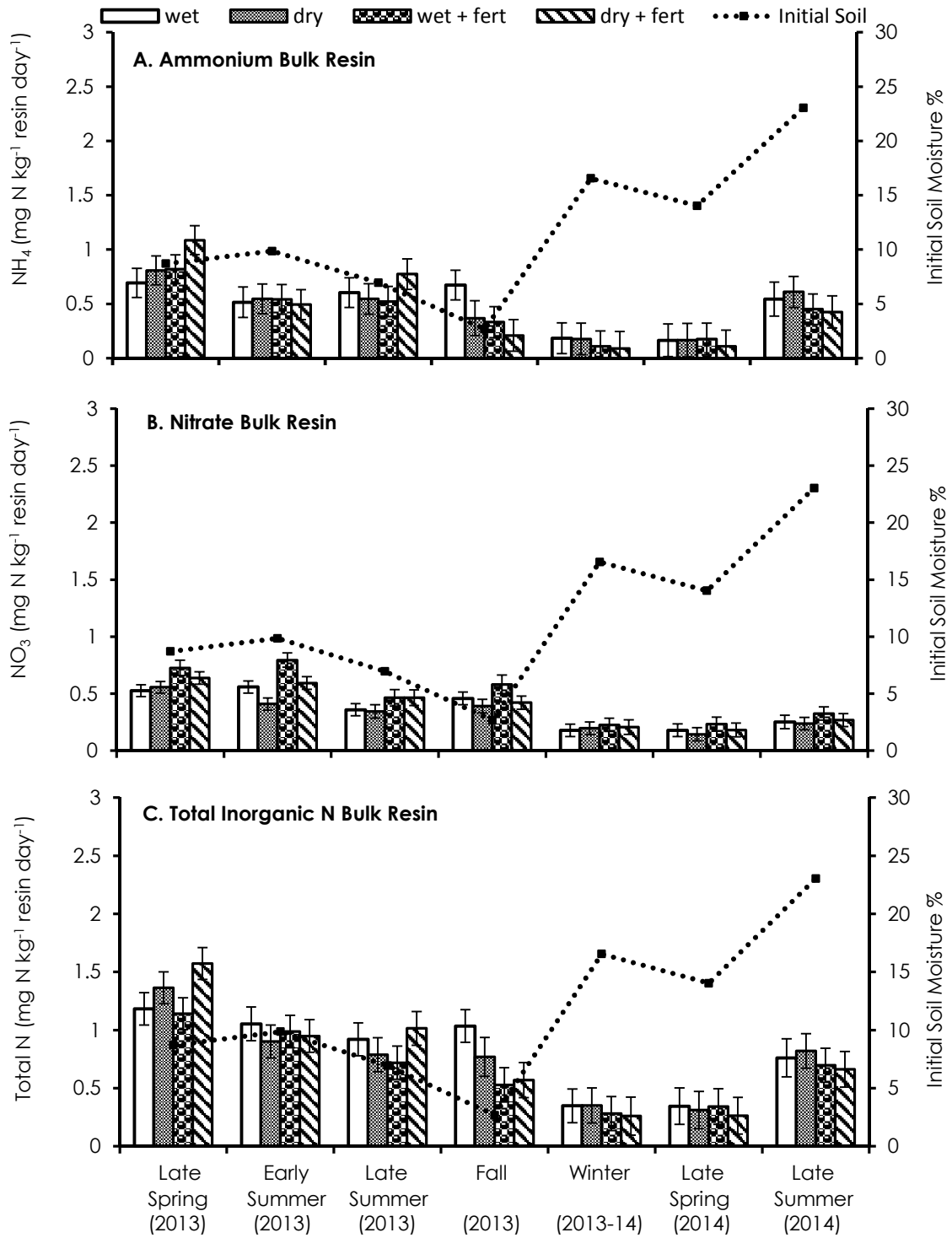


FIGURE 10. Mean initial soil moisture (%), ammonium (A), and nitrate (B) and total inorganic N accumulation on the bulk resins ($\text{mg N kg}^{-1} \text{ resin day}^{-1}$) by different seasons (May 2013-September 2014). Values represent mean values (\pm SE).

TABLE 8. Statistical summary (probability > F) of treatment and seasonal effects on net nitrogen mineralization in the surface 0 to 15 cm layer of mineral soil for each incubation interval collected May 2013 to September 2014. (P value at $\alpha = 0.1$)

Source	Nitrogen Mineralization								
	Ammonification			Nitrification			Net Mineralization		
	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>
F	1	693	0.92	1	689	0.03	1	697	0.09
E	1	693	0.71	1	689	0.30	1	697	0.36
F x E	1	693	0.45	1	689	0.27	1	697	0.65
S	6	693	<.01	6	689	<.01	6	697	<.01
F x S	6	693	0.21	6	689	0.69	6	697	0.85
E x S	6	693	0.15	6	689	0.90	6	697	0.47
F x E x S	6	693	0.50	6	689	0.49	6	697	0.43

F, fertilization; E, throughfall exclusion; S, season

TABLE 9. Statistical summary (probability > F) of treatment and seasonal effects on nitrogen accumulation on the intact core resins within the surface 0 to 15 cm layer of mineral soil for each incubation interval collected May 2013 to September 2014. (P value at $\alpha = 0.1$)

Source	Core Resin Nitrogen Concentration								
	NH ₄			NO ₃			Total Inorganic N		
	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>	Num df	Den df	<i>P</i> > <i>F</i>
F	1	12.1	0.09	1	12.1	0.11	1	12.1	0.06
E	1	12.1	0.80	1	12.1	0.46	1	12.1	0.41
F x E	1	12.1	0.49	1	12.1	0.89	1	12.1	0.79
S	6	613	<.01	6	487	<.01	6	617	<.01
F x S	6	613	<.01	6	487	<.01	6	617	<.01
E x S	6	613	0.70	6	487	0.50	6	617	0.56
F x E x S	6	613	0.07	6	487	0.34	6	617	0.51

F, fertilization; E, throughfall exclusion; S, season

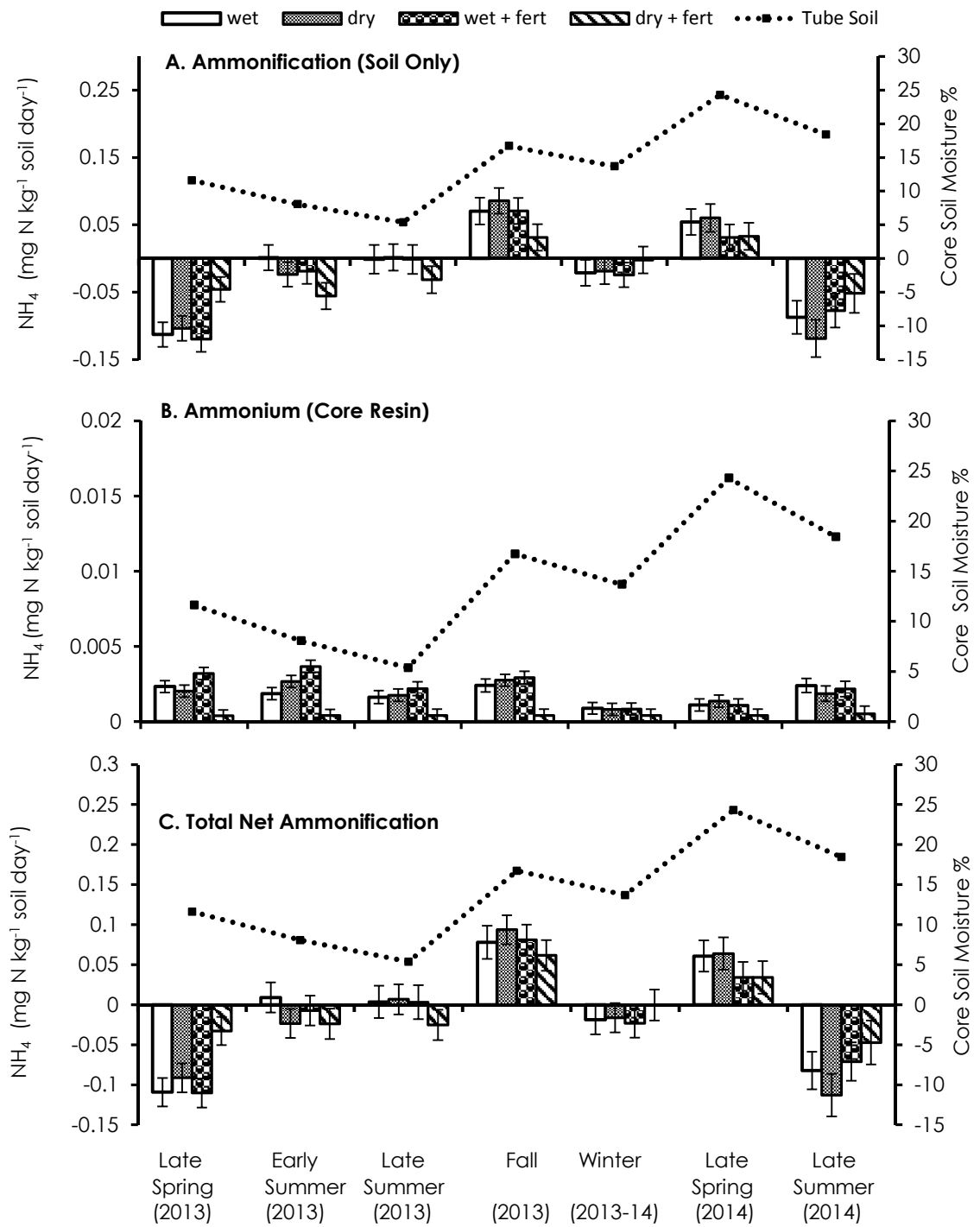


FIGURE 11. Mean core soil moisture (%) compared to ammonification (soil only) (A), ammonium accumulation on the core resins (B), and (C) total net ammonification (mg N kg⁻¹ soil day⁻¹) by different seasons. Values represent mean values (\pm SE).

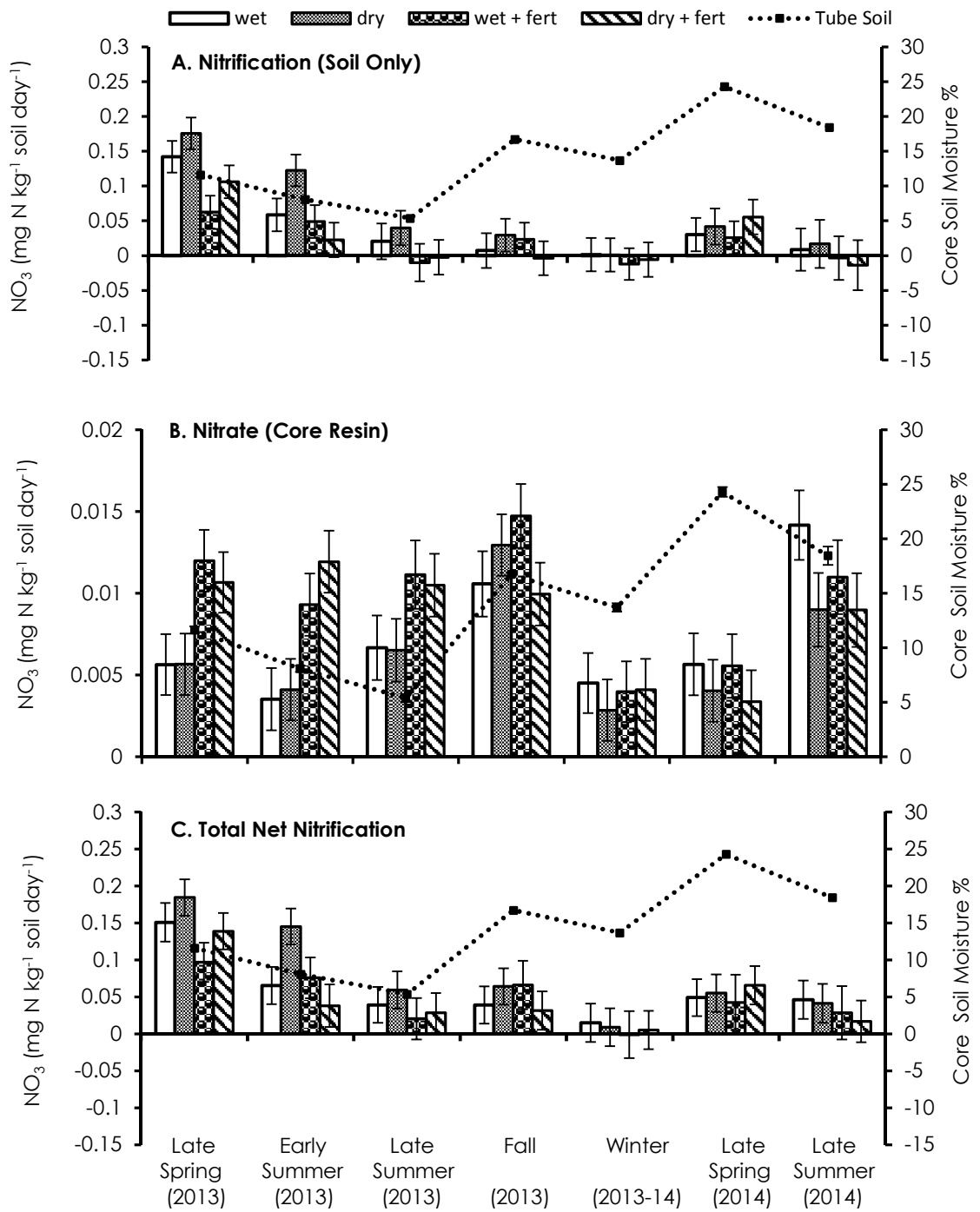


FIGURE 12. Mean core soil moisture (%) compared to nitrification (soil only) (A), nitrate accumulation on the core resins (B), and (C) total net nitrification (mg N kg^{-1} soil day^{-1}) by different seasons. Values represent mean values (\pm SE)

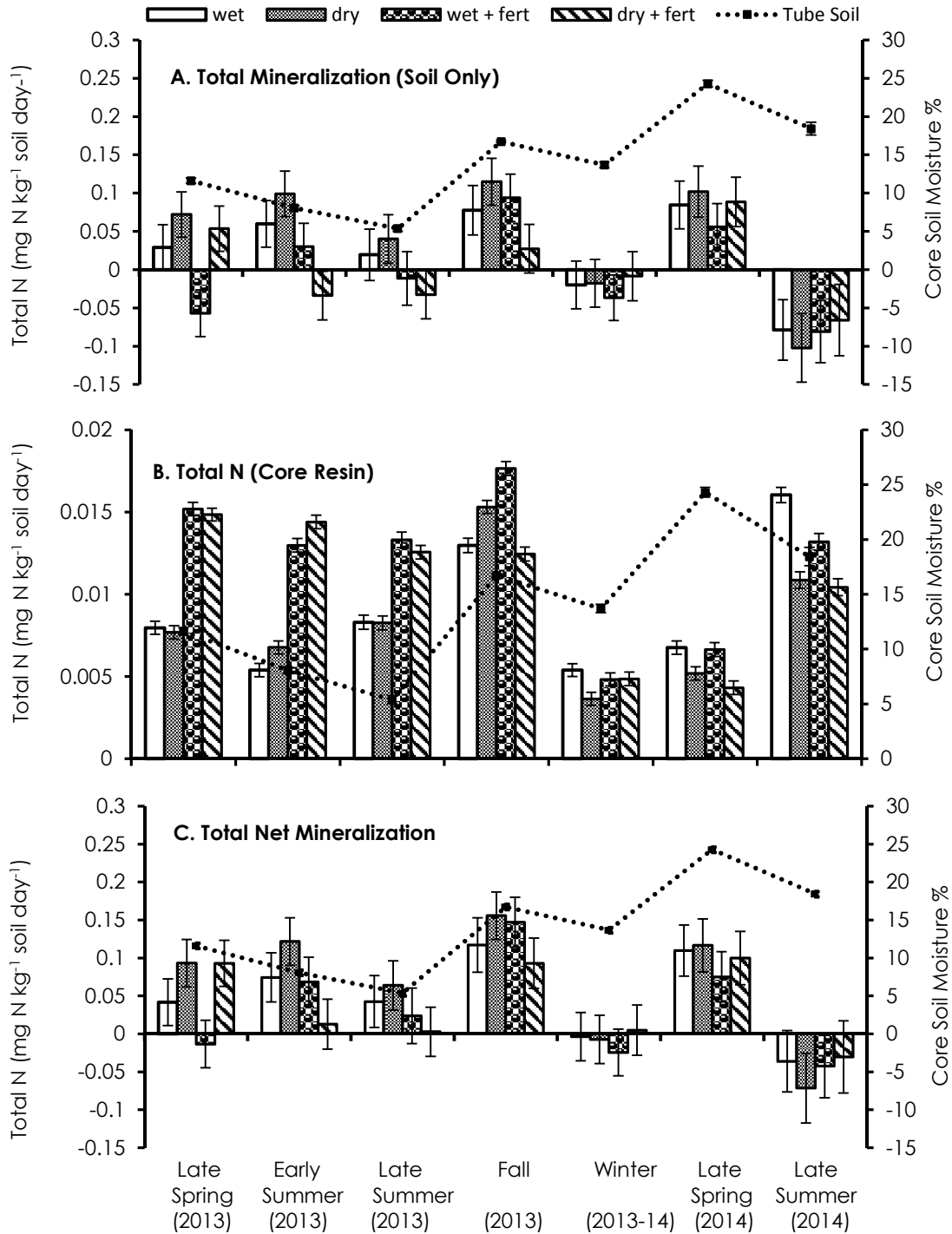


FIGURE 13. Mean core soil moisture (%) compared to mineralization (soil only) (A), and total N accumulation on the core resins (B), and (C) total net mineralization (mg N kg⁻¹ soil day⁻¹) by different seasons. Values represent mean values (\pm SE).

TABLE 10. Mean values and statistical summary (probability > F) of treatment effects on % soil moisture between the open and capped intact soil cores for each incubation interval collected May 2013 to September 2014. Values represent mean values (\pm SE).

Treatment	Intact Soil Cores		P Value ¹
	Mean Percent Soil Moisture		
	Open	Capped	
wet	14.15	12.87	0.70
dry	13.85	12.29	0.60
wet+fert	15.23	13.54	0.59
dry+fert	12.61	10.89	0.60
Mean	13.9 (0.54)	12.21 (0.56)	

¹ P value at $\alpha = 0.1$.

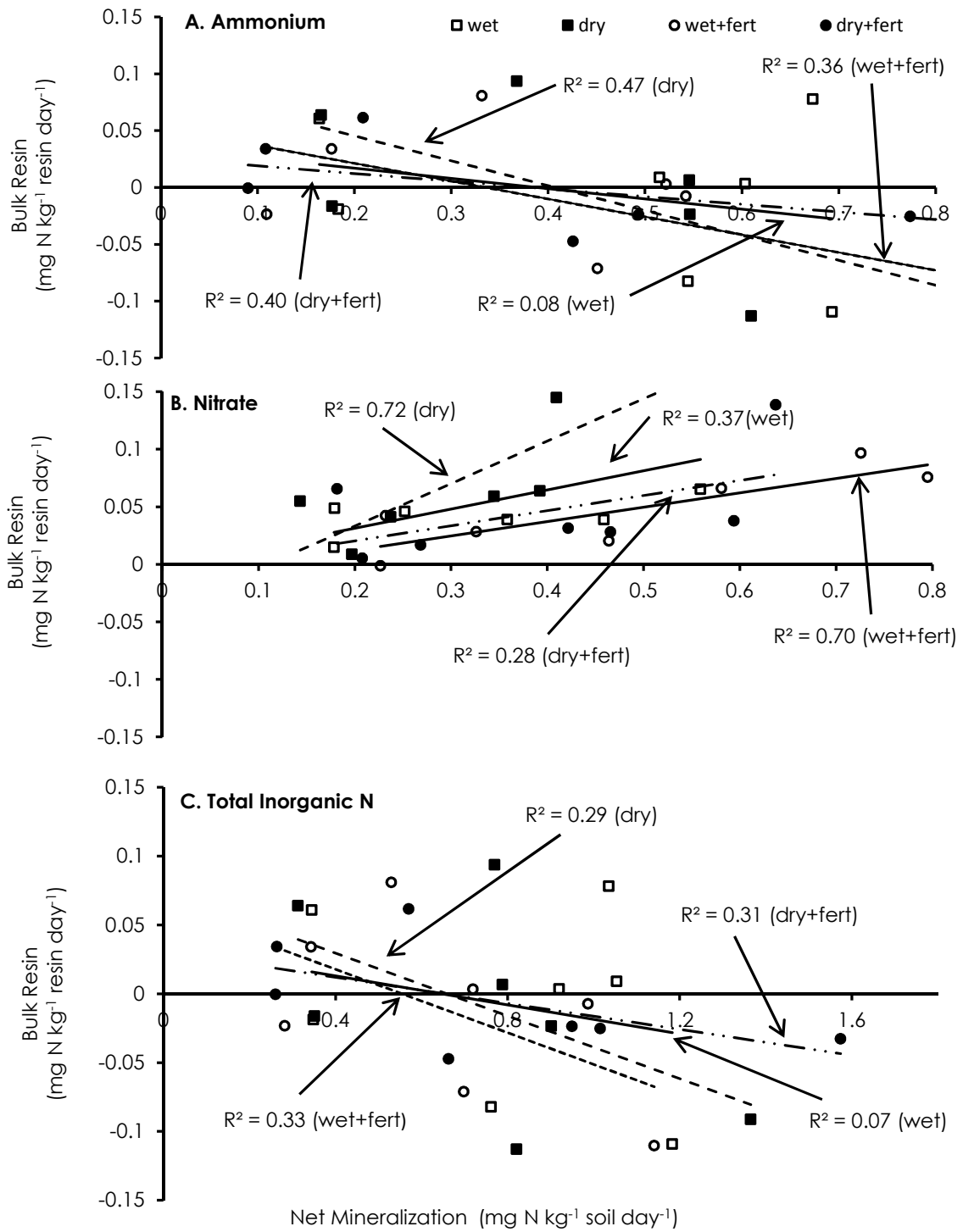


FIGURE 14. Correlation between the bulk resin concentrations and mineralization for ammonium (A), nitrate (B) and (C) total inorganic N. Treatments are wet, dry, wet+fert, and dry+fert. (Significance at $p < 0.10$).

CHAPTER V

DISCUSSION

Nitrogen Accumulation on Resin Bags

The objective of this study was to evaluate the effect of soil moisture and fertilization on nutrient availability in a loblolly pine plantation by examining their influence on N mineralization rates. Previous studies have shown that using IER bags to index nutrient availability can be very effective when differentiating between fertilized and unfertilized sites (e.g., Binkley and Matson, 1983; Hart and Binkley, 1985) and we expected similar results here. Our results supported these previous studies with nitrate, showing a significant difference existing between fertilized and unfertilized treatments using the bulk IERs. This was as expected, since a leaf area index (LAI) study at this site indicated a moderate response (+ 20%) in the foliage to the treatments (unpublished data), showing a positive response with fertilization and a negative response to the throughfall exclusion and therefore we anticipated a similar response with fertilization reflected in our results. The conversion from NH_4 to NO_3 would be stimulated with the application of N fertilizers (Sehy et al., 2003; Subbarao, et al., 2009) resulting in increased mineralization rates (Schröder et al., 2000; Chen et al., 2011; Loecke et al., 2012).

Past studies have shown high variability both within and between sites when evaluating multiple methods to determine indices for nutrient availability (e.g., Binkley and Matson, 1983; Hart and Binkley, 1985, Vitousek and Matson, 1985, Knoepp and Swank, 1995). Soil moisture

plays an important part in this when examining N accumulation on IERs (Binkley, 1984; Binkley et al., 1986; Hart and Firestone, 1989). Soil water content influences ion mobility and some ions, such as NO_3 , will be taken up in greater quantities on IERs than NH_4 , which is much more dependent on water percolation (Binkley et al., 1986; Fisher and Binkley, 2000). Intact soil cores will generally have higher moisture content than that of the bulk soil. This has been attributed to the differences in texture between the soil and resin within the core which can delay the wetting front and impede water movement as well as the lack of root interception (Hart and Firestone, 1989). In our study, the only periods where the soil moisture within the cores was higher than the bulk soil was spring of 2013 and 2014, and fall which should have allowed for higher N accumulation on the core resins during those incubations due to leaching, but that was not observed here.

When comparing bulk resin and intact soil cores N availability indices, previous studies have shown that indices for NO_3 correlated better than ammonium or total N (e.g., Vitousek and Matson, 1985; Binkley et al., 1986; Hart and Firestone, 1989). This was only supported in our study in the dry ($R^2= 0.72$) and wet+fert ($R^2= 0.70$) treatments. On the bulk resins, variation in nitrate production between the treatments was dependent on season, and as soil moisture increased from 5 to 20% the nitrate accumulation dropped from approximately 0.70 to 0.30 mg N kg^{-1} resin day^{-1} and 0.14 to 0.30 mg kg^{-1} resin day^{-1} . This could be attributed to lateral flow and tree uptake. With nothing present to impede water fluctuations across treatments, the transfer of nutrients within and to outside the measurement plot may occur. Therefore, lateral flow working in tandem with root interception could decrease what was available for sorption on the bulk resins. While there was little difference overall between ammonium and nitrate concentrations, the patterns for total N accumulation on the bulk resins appeared to be influenced by a slightly higher NH_4 concentration, with decreasing N accumulation from spring 2013 to winter and increasing by summer 2014 and no treatment of significance.

Comparing the resins within the intact cores to the bulk resin method there was two to three times higher nitrate production within the cores, and while not significant there was a greater differentiation between the fertilized and unfertilized treatments on the core resins from spring 2013 to fall. This is likely due to the lack of root interception, which is inhibited by the cores, allowing NO₃ production within the tube to more likely become adsorbed to the resins due to ion mobility as opposed to being freely taken up by the tree in the bulk soil. Unlike the bulk resins, total N was influenced more by nitrate production than ammonium, which remained at a constant low concentration. The influence of soil moisture within the cores did not appear to affect the core resin sorption, as the highest total N and nitrate concentrations occurred during both high and low moisture levels.

Net N Mineralization Soil Dynamics

From the 1960's to 1970's, mineralization rates have been studied *in situ* to obtain reliable indices of mineralization rates (e.g., Eno, 1960; Remacle, 1977; Rapp et al., 1979). Mineralization rates were generally lower in forests than in agricultural soils. Literature from studies in loblolly pine plantations produced net total N estimates ranging from 31.7 - 42.9 mg N kg⁻¹ soil (10 months) (Hart and Firestone, 1989), 22.4 - 96.4 kg N ha⁻¹ soil yr⁻¹ (Gurlevik et al., 2004), and 16.3 - 143.2 kg N ha⁻¹ soil (10 months) (Li et al., 2003). In our study there was considerable variation in N_{min} rates. The mean values for each treatment ranged from 37.84 (wet), 51.71 (dry), 25.59 (wet+fert), and 30.22 (dry+fert) kg N ha⁻¹ soil yr⁻¹.

The only significant effect for net mineralization was for nitrate and total inorganic N_{min} in the fertilized treatments however, the most notable aspect of this study was the mineralization patterns. In general, net N mineralization rates will steadily increase at the beginning of the growing season from spring through the late summer as the soil temperature rises, and then

decline as the season ebbs through late fall and winter (e.g., Hart and Firestone, 1989; Li et al., 2003; Gurlevik et al., 2004). In our study, total N mineralization decreased both years when there should have been a steady increase moving from spring to late summer. The highest concentrations for total inorganic N occurred in fall and spring 2014, which correspond to the greatest increases in soil moisture within the cores.

Net (total inorganic N) mineralization is not only a product of ammonification and nitrification rates, but is also influenced by the processes of immobilization, leaching and plant uptake. In spring 2013, there was negative ammonification and high net nitrification. The soil N reservoir prior to core incubation had NH_4 5.6 - 8.8 mg N kg⁻¹ soil day⁻¹ and 1.5 - 12.4 mg N kg⁻¹ soil day⁻¹ NO_3 . Examining the amount of N extracted from the resins within the cores, less than 0.005 NH_4 and 0.009 NO_3 mg N kg⁻¹ soil day⁻¹ was captured. This suggests that both immobilization and nitrification was occurring at the same time during this period since the initial soil N pools should have remained sufficient enough to result in higher N concentrations after incubation. In contrast with the same period the following year, where soil NH_4 and NO_3 pools averaged 5.5 and 0.82 mg N kg⁻¹ soil day⁻¹, respectively, there was positive ammonification and half of the previous nitrification rate. Since a negligible amount of NH_4 was captured on the resins within the core, it implies what was extracted was from the initial pools and rapid immobilization may have both been inhibiting sorption to core resin and further nitrate conversion. It is possible the differences in soil moisture within the cores during these intervals had some influence on ammonification during 2014 and the subsequent nitrification.

Early and late summer 2013, an increase in nitrification should have been apparent, however the opposite effect occurred and mineralization rates decreased within all treatments. Ammonification measured between -0.03 and 0.009 mg N kg⁻¹ soil day⁻¹ while only 0.0004 to 0.003 mg kg⁻¹ was held on the resins during both incubation intervals. Nitrate extracted from the core resins increased from spring to fall 2013 and spring to summer 2014, and correlated better to

N fluctuations experienced in past studies (e.g., Hart and Firestone, 1989; Li et al., 2003; Gurlevik et al., 2004). In addition, higher levels of nitrate (0.004 to 0.012 mg kg⁻¹) were adsorbed to the core resins, particularly in the fertilized treatments, lending some support to H2. Even though beginning substrate for both ammonium and nitrate remained high, nitrate accumulation still declined.

Loblolly pine will generally have lower levels of soil extractable NO₃ (Piatek and Allen, 1999; Gurlevik et al., 2004), which has been attributed to the preference of microbes to the more energy efficient NH₄. In undisturbed sites, a constant carbon input from organic matter will induce immobilization of ammonium and reduce nitrification (Davidson et al., 1992; Hart et al., 1994; Zerpa et al., 2010), and it may be possible the organic carbon within the cores remained sufficient to support this. Negative N transformations may also be the result of an oscillating nitrifying population influenced by soil moisture as illustrated by the trends in N availability observed here.

Moisture Effects on Net Nitrification and N Mineralization

Based on previous studies, we expected to see significantly higher mineralization rates on the wet (control) plots, and the highest with the wet+fert treatment (Samuelson et al., 2004, 2008; Tang et al., 2004; Albaugh et al., 2006; Campoe et al., 2013). In contrast, a study by Coyle et al., (2008) found no measurable response with either irrigation alone or fertilization plus irrigation. Unexpectedly, while our study showed some seasonally significant excluder treatment differences, it did not appear to follow the conventional patterns. In many cases the unfertilized and dry plots had the highest rates, which seem to contradict a previous study on this site that examined LAI (unpublished data) that found a positive response with fertilization and a negative response to the throughfall exclusion. We had expected to find this reflected in our study because

in N limited forests aboveground biomass, including LAI, is highly correlated to N availability (Shumway and Atkinson, 1978; Agren, 1983; Pastor et al., 1984; Birk and Vitousek, 1986). This is due to a positive relationship existing between aboveground productivity and soil microbial activity (Myrold et al., 1989).

Maximum N_{min} occurs when soil moisture is close to field capacity (Stanford and Epstein, 1974; Cassman and Munns, 1980; Goncalves and Carlyle, 1994). It has been suggested that with increasing moisture N immobilization rates can become faster than mineralization rates (e.g., Miller and Johnson, 1964; Stanford and Epstein, 1974). This may help explain what is occurring with the N_{min} rates of 2014 compared to the beginning of 2013. In addition to the immobilization of NH_4 , the environmental conditions within the cores may be satisfactory for denitrification, since the substrate provided a sufficient initial nitrate source and highly soluble organic matter. The mean volumetric water content for the bulk soil was close to the field capacity average ($0.381 \text{ cm}^3 \text{ cm}^{-3}$) in spring 2014 at $35.25 \text{ cm}^3 \text{ cm}^{-3}$ (WFPS 77.84%) and $33.42 \text{ cm}^3 \text{ cm}^{-3}$ (WFPS 73.80%) within the intact core by the end of the incubation interval. This would have increased the likelihood of denitrification from advancing anaerobic conditions occurring within the cores during this incubation, and explain the reason for the lower N rates in 2014.

Limitations of Experimental Approach

Due to the nature of this study, there are a number of conditions that could influence the net mineralization rates we observed. Microbial turnover in soils is rapid can influence differences in N_{min} rates, depending on the season and length of incubation interval (Pansu et al., 2005; Wang et al., 2006). Given the size of the measurement plots differences in the substrate quality may also occur, even at the same data point within the plot. Mineralization of litter settling on top of a core may provide additional N to the core environment. However, a previous study has indicated that

concern may be of little consequence to available N in mid-rotation loblolly pine plantations (Piatek and Allen, 2001).

Incubation intervals need to be long enough to provide significant changes in mineralized N, but not so long as to induce nitrification or denitrification in systems where it would not normally be significant (Knowles, 1981; Firestone, 1982; Raison et al., 1986; Smethurst and Nambiar, 1989). In our study, an attempt was made to keep the incubation intervals at the beginning of the growing season to approximately 4 weeks, however environmental conditions on site prevented the insertion of new cores during and resulted in longer incubations.

In precipitation manipulation experiments such as this, short-term studies become a challenge. Inter- and intra- annual variability and environmental extremes have a greater influence on long-term ramifications (Fay et al., 2011; Beier et al., 2012). Precipitation intensity and timing may change within the measurement plots at a single event, altering what was received by the plot (Beier et al., 2012). The throughfall excluders may also contribute to differences in light and wind, shifting evapotranspiration levels. In addition, fluctuating water levels in the profile could promote nitrogen from beneath the core level to become sorbed to the core resins, influencing final estimates (Smethurst and Nambiar, 1989; Gurlevik et al., 2004).

The time of day *in situ* samples are taken could also influence final estimates as studies have indicated mineralization rates are tied to temperature (e.g., Cassman and Munns, 1980; Adams et al., 1989; Ellert and Bettany, 1992; Goncalves and Carlyle, 1994; Franklin and Wigge, 2014). This would have been most influential during the summers, when the air temperatures ranged between 22.0°C and 38.6°C.

Conclusions

The primary objective of this study was to examine the links between fertilization and drought on N mineralization rates. Previous studies have shown N_{min} rates to be highly seasonal along with fluctuating nitrification (Nadelhoffer et al., 1983, 1984; Pastor et al., 1984). We had hypothesized that fertilization will increase N mineralization rates; however it will be slightly lower in the excluded plots, due to the influence of additional N inputs and water requirements on microbial communities. In this study, fertilization was shown to increase mineralization rates, particularly for nitrate. We had also hypothesized that as soil moisture decreased net mineralization rates would also decline, however the addition of fertilizer combined with decreased moisture would result in mineralization rates higher than the unfertilized treatment. There were also indications of this for nitrification, but they were not significant. The second interesting aspect of this study was the mineralization patterns, which did not appear to follow that from previous studies.

In summary, I recommend the following for further study:

- a) Evaluate the buried-bag method (Eno, 1960) as well as the intact soil cores at this site to examine N mineralization differences between the two techniques.
- b) Shorten the incubation intervals to 15 days (growing season) and 30 days (the remaining time) to better trace seasonal changes in ammonification and nitrification fluctuations and lengthen the total time of the study.
- c) Perform laboratory aerobic incubations to serve as a comparison to field evaluations
- d) Repeat this study concurrently at a second location, ideally with similar soil type, soil organic matter, pH, stand age, climate and topography.
- e) Evaluate the gross N mineralization rates using ^{15}N , as a study by Hart et al. (1994) found that gross mineralization does not significantly correlate to net mineralization rates due to differences between productive and consumptive N processes.

f) Evaluate fluctuations in microbial communities while repeating incubations.

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