ABSTRACT

LEGGETT, ZAKIYA HOLMES. Carbon storage and transport in fertilized loblolly pine (*Pinus taeda*) plantations on upland sandy and clayey soils. (Under the direction of Daniel L. Kelting and H. Lee Allen).

Fertilization and soil texture may function independently or interactively to have a positive effect on a forest ecosystem's carbon (C) storage. Fertilization has been identified as an effective management strategy for sequestering additional atmospheric CO_2 by increasing biomass accumulation in loblolly pine plantations. Fertilization may increase soil C sequestration as a beneficial result of enhancing peak leaf area index, which results in increased biomass production and return of litter. The ability of the soil to sequester the additional C fixed is largely dependent on the soil's capacity to retain and protect the C from respiration and leaching loss. Well-drained finer textured soils (clayey soils) have a higher C retention capacity than coarse textured soils (sandy soils).

This study was conducted in 11-year old loblolly pine plantations on sandy and clayey soils with and without the addition of nitrogen and phosphorus fertilization applied at planting. Soil C pools were inventoried prior to planting and soil and forest floor C pools were inventoried 11 years after stand establishment. Tree heights and diameters were used to estimate above- and below-ground biomass. Dissolved organic carbon (DOC) from throughfall and forest floor leachate was measured in the 11th growing season. The chemical composition of DOC from the forest floor leachate was evaluated using liquid state proton nuclear magnetic resonance (^1H NMR).

After 11 years of stand development total ecosystem C increased by 24 Mg/ha on average across both sites (soils). Fertilization increased accretion by 25.3 Mg C/ha with the majority of the increase occurring in the biomass. The clayey site averaged 64% more total ecosystem C than the sandy site. Statistically, the mineral soil C in the surface 20-cm did not change during the 11 years of stand development, except for the significant decrease in soil C within the 10-20cm depth on the control plots of the sandy site.

Fertilization did not have a significant effect on throughfall or forest floor leachate solution volume, DOC concentration, or DOC flux. The yearly flux of DOC that entered the forest floor and soil from throughfall (100 kg/ha/yr) and forest floor leachate (150 kg/ha/yr) was relatively small (6% of the sum of all fluxes evaluated). Based on the ^1H NMR spectrum, fertilization may alter the chemistry of the DOC leaching from the forest floor by increasing the C constituents least resistant to microbial oxidation.

Carbon storage and transport in fertilized loblolly pine (*Pinus taeda*) plantations on upland sandy and clayey soils

by

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To Gillie Carol Shelton Holmes,

my mama, friend, confidant, encourager, supporter, sense of strength and courage…

In Memory of Joedell Erroll Holmes,

my daddy, “running” and riding partner, source of laughter and everlasting support...

BIOGRAPHY

Zakiya Holmes Leggett was born on October 8, 1977 in Memphis, Tennessee to Gillie Holmes and the late Joedell Holmes. She attended elementary and middle school in Memphis before going to a small boarding school called Piney Woods Country Life School in Piney Woods, Mississippi for high school. Piney Woods was founded in 1909 by a man of great faith and perseverance named Dr. Laurence C. Jones. Dr. Jones began Piney Woods by teaching three poor African-American boys to read with his first classroom being outside on a log under a tall cedar tree. Zakiya received enormous support and developed a firm foundation while at Piney Woods and graduated salutatorian of Piney Woods School's class of 1995.

A few weeks before graduating from Piney Woods, Ms. Tina Terrell of the USDA Forest Service visited Piney Woods offering scholarships in forestry. Although few students were interested, Zakiya applied and received the scholarship to attend Tuskegee University with Ms. Terrell as her advisor and liason officer. Tuskegee University was founded in 1881 by Dr. Booker T. Washington. It was at Tuskegee that one of the world's greatest scientists, Dr. George Washington Carver, developed innovative techniques to grow and utilize peanuts, sweet potatoes, among a host of other vegetables. At Tuskegee Zakiya majored in Forest Resources as a Forest Service Initiative Scholar. During the summers she was required to work in South Carolina, Alabama and Louisiana with the USDA Forest Service. The Initiative program was set up as a 3-2 agreement between Tuskegee and several graduate schools.

After attending Tuskegee University for 3 years Zakiya transferred to Duke University's Nicholas School of the Environment where she took graduate courses during her 4th year that would go towards the completion of her Bachelors from Tuskegee and her Masters from Duke. In May 1999 Zakiya graduated Summa Cum Laude (4.0 G.P.A.) with a Bachelors of Science in Forest Resources from Tuskegee University. In the fall of 1999 she went back to Duke for another year and graduated from Duke University with a Masters of Forest Management in May 2000.

Zakiya began pursuing her doctorate degree in forestry at North Carolina State University in August 2000. It was at this time that she met her husband Jacquelle Leggett who was finishing his Masters in Computer Engineering. They were married on May 24, 2003 and currently reside in Raleigh, NC. Zakiya enjoys cooking vegetarian dishes, eating at nice restaurants, traveling, running, and reading novels.

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TABLE OF CONTENTS

LIST OF TABLES viii

LIST OF FIGURES x

CHAPTER 1
Fertilization effects on carbon pools in loblolly pine plantations on upland sandy and clayey soils 1
- ABSTRACT 2
- INTRODUCTION 3
- METHODS 5
- RESULTS 9
- DISCUSSION 13
- REFERENCES 19

CHAPTER 2
Dissolved organic carbon fluxes in 11-year old loblolly pine plantations 32
- ABSTRACT 33
- INTRODUCTION 34
- METHODS 35
- RESULTS 40
- DISCUSSION 43
- REFERENCES 47

CHAPTER 3
^{1}H NMR Analysis of DOC from forest floor leachate in loblolly pine plantations 61
- ABSTRACT 62
- INTRODUCTION 63
- METHODS 64
- RESULTS AND DISCUSSION 67
- REFERENCES 71

APPENDICES 77
- Appendix A. Soil nutrient data for pretreatment (Year 0) soil samples. 78

- Appendix B. Statistical summary (probability > F) of site and fertilization effects on total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil from pretreatment (Year 0) soil samples. 79

- Appendix C. Statistical summary (probability > F) of site and fertilization effects on the resulting difference of Year 11 – Year 0 for total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil. 80

LIST OF TABLES

CHAPTER 1

Table 1. Average DBH, height, volume, basal area, and stand density in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting, and statistical summary of treatment effects. 22

Table 2. Average total C concentration and content for the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil for samples collected in April 1990 prior to stand establishment. 23

Table 3. Statistical summary (probability > *F*) of site and fertilization effects on forest floor mass, and total C concentration and content of the forest floor and fine earth fraction (<2 mm) of the surface 0- to 50-cm of mineral soil in 11-yr-old loblolly pine plantations. 24

Table 4. Average mass and total C concentration and content of the forest floor, and average bulk density and total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 50-cm of mineral soil in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without time-of-planting fertilization. 25

Table 5. Average change in total C concentration and content from year 0 to 11 in the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting, and t-tests evaluating if the change in C was significantly different from zero. 27

Table 6. Statistical summary (Probability > *F*) of site and fertilization effects on estimated ecosystem carbon pools for 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting. 28

Table 7. Average ecosystem carbon pools in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting. 29

CHAPTER 2

Table 1. Stand characteristics in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting. 50

Table 2. Average forest floor mass and carbon in 11-year old loblolly pine plantations with contrasting productivity and statistical summary of site and fertilization effects. 51

Table 3. Average monthly volume, DOC concentration and DOC flux of throughfall and forest floor leachate collected in 11-year old loblolly pine plantations and statistical summary of site, fertilization and month ("seasonal") effects. 52

Table 4. Pearson correlation coefficients and Prob > IrI for monthly throughfall (TF) and forest floor leachate (FF) volume and DOC concentration (DOC [ ]), precipitation, and soil temperature in 11-year old loblolly pine plantations................................. 53

Table 5. Pearson correlation coefficients and Prob > IrI for yearly averages of throughfall (TF) and forest floor leachate (FF) volume, DOC concentration (DOC [ ]), DOC flux, forest floor mass and stand cumulative volume and basal area in 11-year old loblolly pine plantations.. 55

Table 6. Average yearly carbon flux from litterfall, fine roots, and dissolved organic carbon (DOC) in the 11th growing season of loblolly pine plantations. 56

Table 7. Throughfall and forest floor (FF) leachate DOC concentrations (DOC [ ]) and DOC fluxes of DOC for several studies. 57

CHAPTER 3

Table 1. Common types of C examined in ^{1}H NMR and typical examples from loblolly pine litter in order of oxidative resistance.. 73

Table 2. Percentage data from ^{1}H NMR analysis for C constituents of forest floor leachate in 11-year old loblolly pine plantations on contrasting soil textures and/or fertilization levels... 73

Table 3. Mass of the forest floor in 11-year old loblolly pine plantations on contrasting soil textures and/or fertilization levels.. 73

LIST OF FIGURES

CHAPTER 1

Figure 1. Estimated cumulative C inputs from annual litterfall and fine root turnover over 11 years of stand development in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting. Vertical bars represent the standard error (SE), with n=4 for each treatment. 30

Figure 2. Monthly temperature in the surface 18-cm of mineral soil averaged by site during year 11 in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting.. 31

CHAPTER 2

Figure 1. Throughfall (TF) and forest floor leachate (FF) DOC concentration in 11-year old loblolly pine plantations.. 58

Figure 2. Throughfall (TF) DOC flux in 11-year old loblolly pine plantations. 59

Figure 3. Forest floor leachate (FF) DOC flux in 11-year old loblolly pine plantations.. 60

CHAPTER 3

Figure 1 ^{1}H NMR spectrum of DOC samples from control plot on sandy site. (Sanchez et al 2004)... 74

Figure 2 ^{1}H NMR spectrum of DOC samples from control plot on clayey site. (Sanchez et al 2004)... 75

Figure 3 ^{1}H NMR spectrum of DOC samples from fertilized plot on clayey site. (Sanchez et al 2004)... 76

CHAPTER 1

Fertilization effects on carbon pools in loblolly pine plantations on upland sandy and clayey soils

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ABSTRACT

To increase C sequestration in intensively managed forests, fertilization is required on the majority of forest land in the southeastern US to correct widespread nutrient deficiencies. A study was conducted in loblolly pine (*Pinus taeda* L.) plantations on sandy and clayey upland soils, with and without the addition of 250 kg ha^{-1} of diammonium phosphate applied at planting. Soil C pools were inventoried prior to planting and in the 11th year of stand development. Tree inventory data were used to estimate convert stand volume and accumulated biomass. During the 11 years of stand development, total ecosystem C increased by 24.2 Mg ha^{-1} on average across sites, averaging 2.2 Mg C ha^{-1} yr^{-1}. Fertilization increased accretion by 25.3 Mg ha^{-1}, or 2.3 Mg C ha^{-1} yr^{-1}, with the majority of increase (65%) occurring in biomass. The clayey site averaged 64% more total ecosystem C than the sandy site. With the exception of a 13 Mg ha^{-1} loss in mineral soil C for the 10- to 20-cm depth in non-fertilized plots on the sandy site, soil C in the surface 20 cm did not change during the 11 years of stand development. The loss in mineral soil C observed in non-fertilized plots on the sandy site may be explained by this site being inherently less resistant to initial C losses following site preparation, and also less resilient for C recovery owing to higher soil temperatures. Fertilization may have increased resilience on the sandy site in early years by creating a cooler soil as a result of more rapid canopy closure and forest floor accumulation.

INTRODUCTION

The concentration of atmospheric carbon (C) is expected to continue increasing as carbon dioxide (CO_2) released from fossil fuel consumption and changing land-use patterns outpaces the ability of the biosphere to capture C (Schlesinger, 1997). The ability of vegetation and soils to sequester some of this excess atmospheric C is becoming increasingly important, especially in forested ecosystems (Sedjo, 1989; Dixon et al., 1994; Murray et al., 2000).

Intensive forest management is concentrated in the southeastern region of the US, which contains about 33% of the country's fast grown industrial wood plantations (Roise et al., 2000). Loblolly pine is the most commonly planted and intensively managed species in this region (Allen et al., 1990), currently with 13.5 million hectares under management (Roise et al., 2000). Given the large area being managed, understanding the contribution of intensive forest management practices to the source or sink status of this region relative to atmospheric CO_2 is of great importance.

Fertilization has been identified as an effective management strategy for sequestering additional atmospheric CO_2 by increasing above- and belowground biomass accumulation in loblolly pine plantations. Fertilization may increase soil C sequestration as a beneficial result of enhancing peak leaf area index (LAI) which results in increased biomass production and return of litter. Studies investigating loblolly pine plantations in the US South have found LAI to double with fertilization (Albaugh et al., 1998; Lai et al., 2002). In addition, fertilization has been proven to enhance coarse root biomass production (Albaugh et al., 1998; Retzlaff et al., 2001). This large increase in production of foliage and coarse root biomass production increases inputs to the forest floor and mineral soil. As these larger quantities of forest floor and root biomass material decompose, corresponding increases in the level of soil C may be expected.

The ability of the soil to sequester the additional C fixed in a fertilized loblolly pine plantation is largely dependent on the soil's capacity to retain and protect the C from respiration and leaching loss. Retention of C is largely a function of soil texture, mineralogy and drainage class. On well-drained upland sites, finer textured soils (clayey soils) have a higher C retention capacity than coarse textured soils (sandy soils) (Sparks, 1995; Jastrow and Miller, 1998; Hassink et al., 1997; Amelung et al., 1998). Organic matter can be stabilized (turnover time substantially increased) by complexation with clay minerals on charged surfaces and physical protection within very small pores (Oades et al.; 1989). In addition, there may be a greater potential for C storage at greater depths in finer textured soils, with the organic matter potentially being adsorbed by clay minerals in deeper horizons, a beneficial outcome for long-term soil C storage.

Since soils serve as the largest terrestrial reservoir of C (Pennock and van Kessel, 1997; Percival et al., 2000) and forest soils contain 50-63% of all soil C (Kimble et al., 2003), identifying and applying management strategies to intensify the storage of C in this pool could have major impacts on future terrestrial C retention. Fertilization and soil texture are two possible factors that may function independently or in combination to positively affect soil C sequestration via enhanced biomass production and the ability for long-term retention of C, respectively.

This research study was initiated to evaluate the effects of nitrogen (N) + phosphorus (P) fertilization on whole ecosystem C storage and evaluate the effects of soil texture (fine- versus coarse-textured) on soil C storage with N + P fertilization in an 11 year-old loblolly pine plantation. It was hypothesized that fertilization would increase whole ecosystem C storage and the increase in soil C with fertilization would be greater for fine-textured soils.

METHODS

Site Description and Study Layout

Two sites within the Gulf Coastal Plain were identified to evaluate the objectives of this study. The sites were located in Escambia County, Alabama (31°10' N 87°20’ W) and Greene County, Mississippi (31°25’ N 88°27’ W). The climate was similar at both sites with an average growing season (April-September 1990-2001) temperature of 24°C and average growing season rainfall of 780mm (NOAA, 2002).

The site in Alabama was a well-drained clayey soil of the Greenville (fine, kaolinitic, thermic Rhodic Kandiudults) series which was formed in clayey marine sediments. The site in Mississippi was a well-drained sandy soil of the Eustis (siliceous, thermic Psammentic Paleudults) series which was formed in coarse-textured marine or fluvial sediments. Both sites had the potential to be deficient in soil nutrients, such as nitrogen and phosphorus (Appendix A).

The previous stands were 28- and 26-year-old slash pine (*Pinus elliottii* Engelm.) plantations in Alabama and Mississippi, respectively. Both sites were clear-cut harvested in winter of 1989, followed that summer by mechanical site preparation via a three-pass shear, rake, and disk. Following mechanical site preparation, the experiment was installed as a randomized complete block design with 4 blocks. Two 40 m x 40 m treatment plots, with 20 m x 20 m measurement plots centered within each, were established in each block for a total of 8 plots per site. The plots were randomly located within each block with a minimum buffer of 10 m between each plot.

Herbicide (3.5 L Velpar ha^{-1}) was applied to all plots on both sites in April 1990, followed by planting loblolly pine seedlings at a density of 1850 trees per hectare. Two fertilization treatments were randomly assigned to the plots in each block: no fertilization (control) versus fertilization at planting with 45 kg N and 50 kg P per hectare. The fertilizer was applied as a broadcast application of 250 kg ha^{-1} of diammonium phosphate (DAP). No further silvicultural operations were done throughout the duration of this study.

Field Collection

Pre-treatment soil samples, herein referred to as Year 0 soil samples, were collected from the surface 0- to 10-cm and 10- to 20-cm mineral soil depths at 10 random locations within each plot using a 2 cm inside diameter push tube in April 1990. These subsamples were composited at time of collection for one sample per plot, air-dried, and archived by the North Carolina State Forest Nutrition Cooperative in Raleigh, NC.

Eleven years after stand establishment, soil cores (Year 11) were collected at 5 random locations within each plot from the surface 0- to 50-cm of mineral soil using a 6 cm inside diameter Ruark soil coring sampler (Ruark, 1985) in May 2001. These 50 cm cores were divided into five 10 cm increments (i.e. 0- to 10-cm, 10- to 20-cm, etc.).

Forest floor samples were collected in December 2001 using a 35 cm x 35 cm grid at six random locations within each plot. The samples were divided into the Oi (fresh litter or L layer) and Oe+Oa (fragmented litter and humus or F+H layer) layers at the time of collection and composited by plot. Five subsamples of an additional 1 cm of mineral soil were collected and composited from the six random locations beneath the Oe+Oa layer within each plot using a 2 cm inside diameter push tube in December 2001.

Sample preparation and analysis

Soil samples were air-dried and passed through a 2 mm sieve to separate fine- and coarse- fractions. The coarse fractions (roots and rocks) were removed, dried, and weighed to be accounted for in the calculation of bulk density for the fine earth fraction (< 2 mm). Subsamples of the fine earth fractions were ground using a 60 mesh (1 mm) grinder for analysis.

Forest floor samples were dried for 12 hours at 80°C and weighed. Subsamples were ground using a 1 mm grinder for analysis. The loss on ignition procedure (Nelson and Sommers, 1996) was used to correct for mineral soil contamination within the forest floor samples.

All ground subsamples (soil and forest floor) were analyzed for total C using a CHN elemental analyzer (CE Instruments – Model NC2100, CE Elantech Inc., Lakewood, NJ). Bulk density data for pretreatment samples (Year 0) were not available; therefore bulk density was back calculated from the Year 11 samples' bulk densities based on the change in bulk density 12 years after similar site preparation at the Henderson Long-Term Site Productivity Project (Stewart, 1995). Total C concentration data were converted to a content basis (Mg ha^{-1}) using bulk density for soil C and mass for forest floor C. The total C data for the 5 soil cores collected in May 2001 were averaged to yield one value per plot to be compared with pretreatment samples.

Tree Volume and Biomass

Tree diameter at breast height (DBH = 1.3 m) and total height were measured every 2 years at both sites, and volume was estimated using an equation from Smalley and Bower (1968). Allometric equations from the NUTREM 2.0 (Ducey and Allen, 2001) model were used to predict tree biomass components (fine and coarse root biomass, branch biomass, and foliage biomass) over the 11 years of stand development based on total height and DBH measurements. Carbon was estimated as 50% of biomass. NUTREM 2.0 was also used to estimate the 11-year cumulative inputs of litterfall and fine root C to the forest floor and mineral soil.

Soil temperature

Soil temperature was monitored on an hourly basis for a year (April 2001 - April 2002) at an 18 cm depth (approximately 3 cm below the A horizon of at each site) in the soil profile using a data logger (Temperature Data Logger - Model StowAway Tidbit XT, Onset Computer Corporation, Bourne, MA) for recording temperature. One probe was installed in one of the replicated control plots within each site. In addition to the continuous measurements, temperature was also measured at the same soil depth at 3 locations in each plot when the solution samples were collected.

Statistical Analysis

The study was analyzed as a randomized complete block design with replicates nested within sites. Mean values from the four replicated plots within treatments within each site were evaluated for comparisons between treatments and sites after establishing no significant block differences.

An analysis of variance model (ANOVA) was used to evaluate the statistical significance of various effects (i.e. site, fertilization, interactions, etc.) on specific response variables. Effects were considered significant at the 0.10 probability level. The general linear model (GLM) procedure within SAS statistical software (SAS Institute, 2001) software was used for all analysis and mean estimates.

The site effect was evaluated using Type III mean sum of squares (MS) for Rep(Site) as an error term for all models. The treatment effect was referred to as fertilization since there was only one level of fertilization evaluated in this study. The fertilization and site*fertilization effect were evaluated using Type III MS for site*rep*fertilization as an error term for some models.

Since each depth increment was related to the surrounding depth increment(s), it was evaluated as a numeric, continuous variable in the ANOVAs. This was true when evaluating depth interactions as well.

Since pre-treatment soil samples (Year 0 samples) were only collected for the 0-10cm and 10-20cm depths, these were the only depths to be compared with soil samples collected 11 years later (Year 11 samples) in the same plots. In order to evaluate site and treatment effects on soil C over the 11 years of stand development, the difference (soil C Year 11- soil C Year 0) between the means for soil C for each of the 16 plots for Year 11 and Year 0 were compared, and t-tests were used to test if the within treatment change in soil C was significantly different from zero.

RESULTS

Age 11 Stand Yield

Average DBH, total height, volume, and basal area differed significantly between sites at age 11 (Table 1). The clayey site was more productive than the sandy site, averaging 71% greater volume yield at age 11. Fertilization had a significant effect on yield at age 11, with fertilization increasing volume by 44% on average across both sites. There was no statistically significant site by fertilization interaction, indicating that the growth response to fertilization was similar on both sites. However, the fertilization effect on yield was only statistically significant on the clayey site, where fertilization increased volume yield by 65 m^3 ha^{-1}, representing a 49% gain over no fertilization. There were no site or treatment effects on stand density, which averaged 1,729 trees per hectare across both sites and treatments.

Pre-Treatment (Year 0) Soil C

Pretreatment soil samples (Year 0) were evaluated by depth (0-10 cm and 10-20 cm) for any differences that may have existed before study installation. There was a significant ($p<0.10$) effect of site on total C (g kg^{-1}) for the pre-treatment samples (Appendix B), with the clayey site averaging 19.3 Mg ha^{-1} (47%) more total C in the 0- to 20-cm layer (Table 2). When comparing plots that were later grouped into treatments (fertilized and control), they were not statistically different based on ANOVA (Appendix B).

Forest Floor at Year 11

Forest floor mass and total C concentration were significantly different between the sites (Table 3). Averaged across treatments, the clayey site had 1.9 Mg ha^{-1} (17%) greater forest floor mass than the sandy site (Table 4). But, since total C concentration was greater on the sandy site, particularly in the Oe+Oa layer, the total C content was not significantly different statistically between sites. Fertilization did not have a statistically significant effect on forest floor mass or total C concentration or content (Table 3). As expected, mass and total C concentration and content were significantly different between forest floor layers (Table 3), with the Oe+Oa layer containing 4.1 Mg ha^{-1} greater mass and 1.6 Mg ha^{-1} more total C than the Oi layer when averaged across sites (Table 4). Though not statistically significant, the trend was for fertilized plots to have greater mass and total C in the Oe+Oa layer (25% more with fertilization), with the Oi layer showing the same trend but with lower magnitude (10% more with fertilization).

Mineral Soil at Year 11

Total C concentration and content were significantly different between sites across the 0- to 50-cm soil depths, with the depth effect varying by site (Table 3). Fertilization had a significant effect on total C concentration and content. There were no statistically significant fertilization*site, fertilization*depth, or fertilization*site*depth interactions. No statistically significant effects of fertilization on total C concentration or content were observed below the 0- to 10-cm layer (results not shown for depths > 20 cm).

Averaged across both treatments, the clayey site contained 27.5 Mg ha^{-1} (62%) more total C in the 0- to 50-cm of mineral soil compared to the sandy site (Table 4). On an absolute basis, the clayey site contained 22.6 Mg ha^{-1} (72%) more total C in the surface 20 cm of mineral soil, with both sites having similar total C below 20 cm. Both sites had the same distribution of total C on a relative basis, with the surface 0- to 10-cm of mineral soil containing about 50% of the total C content for the 0- to 50-cm layer. The surface 1 cm of mineral soil contained about 10% of the total C content.

Averaged across both sites, fertilization increased total C in the surface 0- to 50-cm of mineral soil by 7.6 Mg ha^{-1}, representing a 14% increase over non-fertilized controls (Table 4). The average increase in the 0- to 10-cm depth was 6.0 Mg C ha^{-1}, or about 80% of the total increase measured with fertilization.

Change in Soil C from Year 0 to 11

There were no statistically significant effects of site, fertilization (treatment), or the site*fertilization interaction on the change in soil C from year 0 to 11 for the surface 0- to 10-

cm and 10- to 20-cm of mineral soil (Appendix C). There was, however, a significant reduction in total C in the 10- to 20-cm depth for the non-fertilized control on the sandy site, where total C decreased by 7.2 g kg^{-1} or 13.0 Mg ha^{-1} (Table 5). Interestingly, though not statistically significant, the trend for change in total C from year 0 to 11 was negative for both sites, with the exception of the 0- to 10-cm depth on the control plots of the clayey site and the fertilized plots of the sandy site.

Ecosystem C Pools

The equations used in NUTREM 2.0 to predict above- and belowground biomass are functions of tree height and DBH, so the treatment and site effects are the same as those described for year 11 yield. Thus, site and fertilization had significant effects on above- and belowground biomass C when examined across sites, with the fertilization effect only being statistically significant on the clayey site (Table 6). Also, site and fertilization had significant effects on mineral soil and total ecosystem carbon. Within site, total ecosystem C was only significantly higher on the clayey site. Interestingly, though fertilization did not have a statistically significant effect on above- and belowground biomass C on the sandy site, fertilization did have a statistically significant effect on mineral soil C on the sandy site.

The clayey site averaged 113.4 Mg ha^{-1} (64%) more total ecosystem C than the sandy site (Table 7). Fertilization increased total ecosystem C by 25.3 Mg ha^{-1} (32%) on average across both sites. On the clayey site, fertilization increased total ecosystem C by 31.7 Mg ha^{-1}, with 80% of the total gain coming from increased above- and belowground biomass, with aboveground biomass alone constituting 63% of the gain. On the sandy site, above- and belowground biomass accounted for 49% of the gain in total ecosystem C with fertilization, while 50% of the gain was in the mineral soil. Averaged across sites, the soil contained the largest percentage of total ecosystem C at 65% of the total, followed by aboveground biomass at 24% of the total.

Litterfall and Fine Root C Inputs

Estimated cumulative C inputs from litterfall and fine root turnover averaged 10.5 Mg ha^{-1} averaged for control plots on both sites (Fig. 1). Fertilization increased cumulative C inputs by 4.9 Mg ha^{-1} on average across both sites, with the increase coming from greater litterfall. The fertilization effect on cumulative C inputs was greater on the clayey site, where fertilization increased inputs by 6.3 Mg C ha^{-1}, representing a 59% gain over the non-fertilized control. The cumulative litterfall inputs represent 135% of the forest floor that has accumulated on control plots and 233% of the forest floor that has accumulated on fertilized plots (see Table 7). The gain in C inputs with fertilization represents 100% of the absolute gain in the forest floor plus mineral soil C pools for the clayey site, and 268% of the absolute gain in these pools for the sandy site.

Soil Temperature

Temperature in the surface 18-cm of mineral soil varied seasonally (Fig. 2), showing a statistically significant ($p<0.10$) site by month interaction. There were no statistically significant treatment effects on soil temperature ($p>0.10$). Soil on the sandy site warmed up more rapidly in the spring and averaged 2 ^{o}C higher than the clayey site during the summer. Both sites had similar soil temperatures in winter.

DISCUSSION

The 12.2 m^{3} ha^{-1} yr^{-1} annualized growth rate for control plots on the clayey site is within the 9 to 14 m^{3} ha^{-1} yr^{-1} range reported for similarly treated loblolly pine plantations also growing on well drained, fine textured, soils (Nilsson and Allen, 2003). Annualized growth for control plots on the sandy site was considerably lower at 7.4 m^3 ha^{-1} yr^{-1}, but is consistent with values reported for loblolly pine growing on excessively well drained sands (Albaugh et al., 1998).

The large growth response to fertilization implies that both sites are N and P deficient (Tables 1 and 7). In fact, the 5.9 m^3 ha^{-1} yr^{-1} annualized growth gain with fertilization on the clayey site is consistent with growth responses for severely P-deficient sites (Allen et al., 2001). The smaller annualized growth response to fertilization of 2.9 m^3 ha^{-1} yr^{-1} on the sandy site is probably a function of several limiting factors (e.g. low available water, N, and micronutrients), as repeated fertilization with a combination of macro- and micronutrients on excessively drained sands has resulted in loblolly pine growth gains in excess of 10 m^3 ha^{-1} yr^{-1} (Albaugh et al., 1998).

Neither site is achieving its carbon storage potential, as the fertilization effect on stand growth was probably nearly gone by age 11. Evidence for this can be seen in the forest floor, where there was no fertilization effect on the mass of the Oi layer. The similarity in Oi layers is a good indication that control and fertilized plots are producing similar amounts of leaf area, which is also supported by visual observation of individual tree crowns in the field. Since leaf area is strongly related to current productivity (Albaugh et al., 1998), the trees on both control and fertilized plots are now probably growing at similar rates. In order to maintain high growth rates it is necessary to carry out repeated fertilizations (Allen et al., 2001). With repeated fertilizations in combination with other silvicultural tools, growth rates exceeding 25 m^3 ha^{-1} yr^{-1} are The year 11 mineral soil C results showed that fertilization increased soil C storage by 7.6 Mg ha^{-1} (14%). Based on the increases in growth measured with fertilization, it would be convenient to say that the change in soil C is explained by increased C inputs with higher productivity. But, soil C was only significantly higher with fertilization on the sandy site, where volume yield wasn't significantly changed with fertilization.

The increase in soil C with fertilization cannot be explained by the forest floor and fine root inputs on either site, as C inputs to the forest floor and soil were equal to the change in soil C on the clayey site and much less than the C inputs on the sandy site. In fact, the analysis of the change in soil C from year 0 to 11 showed that there were no significant changes in soil C in the first 11 years of stand development, with the exception of the non-fertilized control on the sandy site which actually lost 13 Mg C ha^{-1}.

Our results for mineral soil C are consistent with the findings of Harding and Jokela (1994), who reported no change in soil C 25 years after fertilization at planting even though fertilized plots had 110% greater biomass accumulation. Canary et al. (2000) also found no significant changes in mineral soil C with multiple applications of urea over a sixteen year period in Douglas-fir (*Pseudotsuga menziesii*) stands that did exhibit significant increases in biomass C. In their meta-analysis of fertilization effects on soil C, Johnson and Curtis (2001) found that fertilization in general increased soil C, but some studies in the analysis showed no response.

The lack of change in mineral soil C with fertilization found in our study and reported by others may be explained by rapid decomposition of C inputs. Richter et al. (1999) found that of the 38 Mg C ha^{-1} estimated to have been input to the mineral soil over 40 years of development of a loblolly pine plantation, only 1.45 Mg C ha^{-1} (4%) had accumulated in the mineral soil, demonstrating rapid turnover of C inputs. Rapid turnover of C inputs may explain why studies have found soil C to remain stable over long periods in forest ecosystems (e.g. Richter et al., 1995; Trettin et al., 1999). So, given the likelihood of rapid turnover of C inputs, the potential to increase the size of the mineral soil C pool with intensive management appears to be relatively low.

An interesting result was the loss of mineral soil C from non-fertilized control plots on the sandy site. In fact, it was this loss that made it appear that fertilization increased mineral soil C at year 11. The loss in mineral soil C is consistent with the model of change in soil C over time following harvest presented by Henderson (1995), wherein soil C declines for a period of time following harvest as C outputs via respiration exceed C inputs in young stands. The pattern of initial C loss followed by accumulation was shown empirically by Richter et al. (1999), who tracked soil C over 40 years of stand development in a loblolly pine plantation. In their study, the surface 0- to 7.5-cm layer of mineral soil lost C for at least the first 6 years, and it was 15 to 20 years before mineral soil C was back at the stand establishment level. Why was significant C loss not observed above the 10- to 20-cm layer on the sandy site in our study? The 0- to 10-cm layer probably did show significant C loss early on, but this is also the zone where root activity and forest floor C transfer to mineral soil would be greatest, allowing more rapid recovery of C in this layer.

The significant loss of mineral soil C from year 0 to 11 in control plots on the sandy site may be attributed to site and treatment effects on soil resistance and resilience to C loss. Both sites were prepared by raking off all surface debris followed by disking. Since the debris was raked off of the sites, organic matter was not incorporated into the mineral soil with disking. Thus, all plots would have experienced C loss from the mineral soil for some period following site preparation. The clayey site was probably more resistant to initial C loss, as physical protection of C within microaggregates would have slowed C release (Buyanovsky et al., 1994). Soil C probably also recovered more rapidly (high resilience) on the clayey site, as this inherently more productive site (71% greater stand volume at age 11 compared to the sandy site) would have had more rapid canopy closer and forest floor accumulation, resulting in a cooler soil and lower decomposition rates. No doubt, the magnitude of difference in surface soil temperature in the earlier years was probably even greater than the $2^{o}C$ difference measured between the sites during the summer in year 11. The lack of physical protection of soil C in microaggregates on the sandy site made this site less resistant to initial C loss, and higher soil temperatures made the sandy site less resilient for C recovery. Fertilization increased resilience on the sandy site in earlier years by creating a cooler soil as a result of more rapid canopy closure and forest floor accumulation. This effect of fertilization on soil temperature and mineral soil C loss was documented for loblolly pine plantations growing on a similar soil (Maier and Kress, 2000), where fertilization resulted in lower soil temperature, correspondingly lower heterotrophic soil respiration, and positive net ecosystem productivity: non-fertilized plots had higher soil temperature, correspondingly higher heterotrophic soil respiration, and negative net ecosystem productivity.

Tree biomass is the most significant pool in terms of opportunity to increase C sequestration with fertilization. The majority of the aboveground pool will be exported from the site through thinning and final harvest, leaving the belowground pool behind. At year 11, the belowground pool ranged from 3.5 to 10.6 Mg C ha^{-1} depending on site and treatment. This pool will continue to accrue with time, as studies in older loblolly pine plantations have reported belowground C pools ranging from 12.8 to 17.0 Mg ha^{-1} (Johnson and Lindberg, 1992; Richter et al., 1995). Thus, the fate of the belowground C pool has important implications for longer term sequestration. In a chronosequence study of loblolly pine root systems, Ludovici et al. (2002) found that large roots persisted for 35 to 60 years following harvest. With such low decomposition rates, and considering that plantations are managed on a 25 year rotation, several cohorts of large roots could be present in the soil profile, contributing significantly to long term C sequestration.

REFERENCES

Albaugh, T.J., H.L. Allen, P.M. Dougherty, L.W. Kress, and J.S. King. 1998. Leaf area and above- and belowground growth responses of loblolly pine to nutrient and water additions. For. Sci. 44:317-328.

Allen, H.L., P.M. Dougherty, and R.G. Campbell. 1990. Manipulation of water and nutrients-practice and opportunity in southern U.S. pine forests. For. Ecol. Manage. 30:437-453.

Allen, H.L., D.L. Kelting, and T.J. Albaugh. 2001. Nutrient management concepts and practices in southern pine plantations. p. 27-31. *In* C.R. Bamsey (ed.) Enhanced Forest Management: Fertilization and Economics. Clear Lake Ltd., Edmonton, Alberta, Canada.

Amelung, W., W. Zech, X. Zhang, R. F. Follett, H. Tiessen, E. Knox, and K.W. Flach. 1998. Carbon, nitrogen, and sulfur pools in particle-size fractions as influenced by climate. Soil Sci. Soc. Am. J. 62:172-181.

Buyanovsky, G.A., M. Aslam, and G.H. Wagner. 1994. Carbon turnover in soil physical fractions. Soil Sci. Soc. Am. J. 58:1167-1173.

Canary, J.D., R.B. Harrison, J.E. Compton, and H.N. Chappell. 2000. Additional carbon sequestration following repeated urea fertilization of second-growth Douglas-fir stands in western Washington. For. Ecol. Manage. 138:225-232.

Dixon, R.K., S. Brown, R.A. Houghton, A.M. Solomon, M.C. Trexler, and J. Wisniewski. 1994. Carbon pools and flux of global forest ecosystems. Science 263:185-190.

Ducey, M., and H.L. Allen. 2001. Nutrient supply and fertilization efficiency in midrotation loblolly pine plantations: a modeling analysis. For. Sci. 47:96-102.

Harding, R.B., and E.J. Jokela. 1994. Long-term effects of forest fertilization on site organic matter and nutrients. Soil Sci. Soc. Am. J. 58:216-221.

Hassink, J., A.P. Whitmore, and J. Kubat. 1997. Size and density fractionation of soil organic matter and the physical capacity of soils to protect organic matter. Eur. J. Agron. 7:189-199.

Henderson, G.S. 1995. Soil organic matter: a link between forest management and productivity. p. 419-436. *In* W.W. McFee and J.M. Kelly (ed.) Carbon Forms and Functions in Forest Soils. SSSA, Madison, WI.

Jastrow, J.D., and R.M. Miller. 1998. Soil aggregate stabilization and carbon sequestration: feedbacks through organomineral associations. p. 207-223. *In* R. Lal, J.M. Kimble, R.F. Follett, and B.A. Stewart (ed.) Soil Processes and the Carbon Cycle. CRC Press, Boca Raton, FL.

Johnson, D.W., and P.S. Curtis. 2001. Effects of forest management on soil C and N storage: meta analysis. For. Ecol. Manage. 140:227-238.

Johnson, D.W., and S.E. Lindberg. 1992. Atmospheric Deposition and Forest Nutrient Cycling. Ecological Studies 91. Springer-Verlag, New York, NY.

Kimble, J.M., R.A. Birdsey, R. Lal, and L.S. Heath. 2003. Introduction and general description of U.S. forests. p. 3-14. *In* J.M Kimble, L.S. Heath, R.A. Birdsey, and R. Lal (ed.) The Potential of U.S. Forest Soils to Sequester Carbon and Mitigate the Greenhouse Effect. CRC Press, New York, NY.

Lai, C.T., G. Katul, J. Butnor, M. Siqueira, D. Ellsworth, C. Maier, K. Johnsen, S. McKeand, and R. Oren. 2002. Modelling the limits on the response of net carbon exchange to fertilization in a south-eastern pine forest. Plant Cell Environ. 25:1095-1119.

Ludovici, K.H., S.J. Zarnoch, and D.D. Richter. 2002. Modeling in-situ pine root decomposition using data from a 60-year chronosequence. Can. J. For. Res. 32:1675-1684.

Maier, C.A., and L.W. Kress. 2000. Soil CO_2 evolution and root respiration in 11 year-old loblolly pine (*Pinus taeda*) plantations as affected by moisture and availability. Can. J. For. Res. 30:347-359.

Murray, B.C., S.P. Prisley, R.A. Birdsey, and R.N. Sampson. 2000. Carbon sinks in the Kyoto protocol. J. For. 98 (9):6-11.

National Oceanic and Atmospheric Administration. 2002. National climatic data center: Weather station locator [Online]. Available at http://lwf.ncdc.noaa.gov/oa/climate/stationlocator.html (verified 25 June 2003).

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3 Chemical Methods. SSSA, Madison, WI.

Nilsson, U., and H.L. Allen. 2003. Short- and long-term effects of site preparation, fertilization and vegetation control on growth and stand development of planted loblolly pine. For. Ecol. Manage. 175:367-377.

Oades, J.M., G.P. Gillman, and G. Uehara. 1989. Interactions of soil organic matter and variable charge clays. p. 69-95. *In* D.C. Coleman, J.M. Oades, and G. Uehara (ed.) Dynamics of soil organic matter in tropical ecosystems. Department of Agronomy and Soil Science, Univ. Hawaii, Honolulu.

Pennock, D.J., and C. van Kessel. 1997. Effects of agriculture and of clear-cut forest harvest on landscape-scale soil organic carbon storage in Saskatchewan. Can. J. Soil Sci, 77:211-218.

Percival, H.J., R.L. Parfitt, and N.A. Scott. 2000. Factors controlling soil carbon levels in New Zealand grasslands: Is clay content important? Soil Sci. Soc. Am. J. 64:1623-1630.

Retzlaff, W.A., J.A. Handset, D.M. O'Malley, S.E. McKeand, and M.A. Topa. 2001. Whole-tree biomass and carbon allocation of juvenile trees of loblolly pine (*Pinus taeda*): influence of genetics and fertilization. Can. J. For. Res. 31:960-970.

Roise J.P., F.W. Cubbage, R.C. Abt, and J.P. Siry. 2000. Regulation of timber yield for sustainable management of industrial forest plantations- theory and practice. p. 217-255. *In* K. von Gadow, T. Pakkula, and M. Tomé (ed.) Sustainable Forest Management. Kluwer Academic Publishers, The Netherlands.

Richter, D.D., D. Markewitz, S.E. Trumbore, and C.G. Wells. 1999. Rapid accumulation and turnover of soil carbon in a re-establishing forest. Nature 400:56-58.

Richter, D.D., D. Markewitz, C.G. Wells, H.L. Allen, J.K. Dunscombe, K. Harrison, P.R. Heine, A. Stuanes, B. Urrego, and G. Bonani. 1995. Carbon cycling in a loblolly pine forest: implications for the missing carbon sink and for the concept of soil. p. 233-252. *In* W.W. McFee and J.M. Kelly (ed.) Carbon Forms and Functions in Forest Soils. SSSA, Madison, WI.

Ruark, G.A. 1985. A refined soil coring system. Soil Sci. Soc. Am. J. 49:278-281.

SAS Institute. 2001. The SAS system for Windows. Release 8.20. SAS Inst., Cary, NC.

Schlesinger, W.H. 1997. Biogeochemistry: An Analysis of Global Change. 2nd Edition. Academic Press Inc., New York, NY.

Sedjo, R.A. 1989. Forests to offset the greenhouse effect. J. For. 87(7):12-15.

Smalley, G.W., and D.R. Bower. 1968. Volume tables and point sampling factors for loblolly pine plantations on abundant fields in Tennessee, Alabama, and Georgia Highlands. USDA Forest Service Southern Forest Experiment Station. Research Paper SO-32.

Sparks, D.L. 1995. Environmental soil chemistry. Academic Press Inc., San Diego, CA.

Stewart, C.C. 1995. Harvesting and site preparation effects on soil physical properties 12 years after establishment of a loblolly pine plantation. M.S. Thesis. Dept. of Forestry. North Carolina State Univ., Raleigh, NC. 41pp.

Trettin, C.C., D.W. Johnson, and D.E. Todd, Jr. 1999. Forest nutrient and carbon pools at Walker Branch Watershed: Changes during a 21-year period. Soil Sci. Soc. Am. J. 63:1436-1448.

Table 1. Average DBH, height, volume, basal area, and stand density in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting, and statistical summary of treatment effects.

Subsoil Texture (Site)	Treatment	DBH†	Height	Volume	Basal Area	Stand Density
		- cm -	- m -	- m^3 ha^{-1} -	- m^2 ha^{-1} -	- trees ha^{-1} -
Clayey (AL)	Control	13.0 (0.6)‡	10.5 (0.3)	134 (9)	24 (1)	1792 (58)
	Fertilized	15.1 (0.4)	12.0 (0.3)	199 (20)	32 (3)	1736 (80)
Sandy (MS)	Control	10.8 (0.4)	8.9 (0.3)	81 (7)	17 (1)	1730 (60)
	Fertilized	12.5 (0.7)	9.9 (1.3)	113 (25)	21 (2)	1656 (27)
Comparison	Effect	- Probability > *F* - - - - - - - - - - - - - - - - - - -				
Across Sites	Site	0.002	0.038	0.003	0.002	0.369
	Fertilization	0.022	0.125	0.047	0.044	0.157
	Site*Fertilization	0.740	0.749	0.427	0.464	0.825
Within Clayey Site	Fertilization	0.066	0.092	0.089	0.113	0.502
Within Sandy Site	Fertilization	0.184	0.481	0.346	0.278	0.114

† DBH is tree Diameter at Breast Height (1.3 m).

‡ Numbers in parentheses indicate the standard error (SE), where n=4 for each treatment.

Table 2. Average total C concentration and content for the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil for samples collected in April 1990 prior to stand establishment.

Subsoil Texture (Site)	Treatment	Depth	Total Carbon	
		- cm -	- - g kg^{-1} - -	- - Mg ha^{-1} - -
Clayey (AL)	Control	0-10	27.6 (6.7)†	32.6 (7.9)
		10-20	15.8 (2.2)	23.5 (3.9)
		0-20	--	56.1 (11.9)
	Fertilized	0-10	29.5 (4.7)	33.0 (3.7)
		10-20	20.2 (2.2)	31.9 (3.7)
		0-20	--	64.9 (5.2)
Sandy (MS)	Control	0-10	15.2 (0.3)	19.9 (1.1)
		10-20	12.7 (1.4)	21.1 (2.0)
		0-20	--	41.0 (2.3)
	Fertilized	0-10	15.4 (3.0)	20.0 (3.3)
		10-20	12.8 (3.5)	21.5 (5.6)
		0-20	--	41.5 (8.9)

† Numbers in parentheses indicate the standard error (SE), where n=4 for each treatment.

Table 3. Statistical summary (probability > *F*) of site and fertilization effects on forest floor mass, and total C concentration and content of the forest floor and fine earth fraction (<2 mm) of the surface 0- to 50-cm of mineral soil in 11-yr-old loblolly pine plantations.

Comparison	Effect	Total Carbon		Mass
		- g kg^{-1} -	- Mg ha^{-1} -	
- Forest Floor -				
Across Layers	Site	0.048	0.213	0.094
	Fertilization	0.368	0.288	0.184
	Site*Fertilization	0.821	0.470	0.525
	Layer	0.001	0.001	0.001
	Layer*Site	0.248	0.563	0.280
	Layer*Fertilization	0.401	0.287	0.160
	Layer*Site*Fertilization	0.121	0.439	0.626
- Mineral Soil -				
Across Depths	Site	0.003	0.004	--
	Fertilization	0.020	0.011	--
	Site*Fertilization	0.652	0.534	--
	Depth	0.001	0.001	--
	Depth*Site	0.001	0.001	--
	Depth*Fertilization	0.176	0.150	--
	Depth*Site*Fertilization	0.885	0.818	--
Within 0- to 10-cm depth	Site	0.050	0.040	--
	Fertilization	0.035	0.046	--
	Site*Fertilization	0.761	0.740	--
Within 10- to 20-cm depth	Site	0.023	0.036	--
	Fertilization	0.347	0.143	--
	Site*Fertilization	0.258	0.273	--
Within 0- to 1-cm depth	Site	0.051	0.124	--
	Fertilization	0.018	0.093	--
	Site*Fertilization	0.186	0.552	--

Table 4. Average mass and total C concentration and content of the forest floor, and average bulk density and total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 50-cm of mineral soil in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without time-of-planting fertilization.

Subsoil Texture (Site)	Treatment	Depth	Mass	Bulk Density	Total Carbon	
		- layer or cm -	- Mg ha^{-1} -	- g cm^{-3} -	- g kg^{-1} -	- Mg ha^{-1} -
Clayey (AL)	Control	Oi	3.3 (0.3)†	--	489 (7.4)	1.6 (0.1)
		Oe + Oa	7.4 (0.8)	--	446 (8.6)	3.3 (0.4)
		Oi + Oe + Oa	10.7 (0.9)	--	--	4.9 (0.5)
		0-1	--	--	48.0 (4.4)	6.3 (0.5)‡
		0-10	--	1.33 (0.05)	25.1 (4.0)	32.5 (4.6)
		10-20	--	1.40 (0.04)	13.5 (2.2)	18.8 (3.5)
		20-30	--	1.55 (0.07)	5.2 (1.1)	7.7 (1.2)
		30-40	--	1.56 (0.05)	3.6 (0.9)	5.5 (1.2)
		40-50	--	1.46 (0.11)	3.4 (1.5)	4.5 (1.5)
		0-50	--	--	--	69.0 (5.8)
	Fertilized	Oi	3.4 (0.4)	--	495 (3.3)	1.7 (0.2)
		Oe + Oa	8.4 (0.8)	--	417 (2.5)	3.5 (0.4)
		Oi + Oe + Oa	11.8 (1.1)	--	--	5.2 (0.6)
		0-1	--	--	58.0 (3.0)	7.5 (0.2)
		0-10	--	1.30 (0.08)	29.4 (3.4)	37.7 (2.4)
		10-20	--	1.51 (0.01)	13.3 (2.3)	19.3 (3.2)
		20-30	--	1.62 (0.04)	5.4 (1.3)	8.5 (1.9)
		30-40	--	1.52 (0.04)	3.5 (0.7)	5.3 (1.0)
		40-50	--	1.56 (0.03)	2.6 (0.6)	4.1 (0.8)
		0-50	--	--	--	74.9 (6.1)

Table 4. Continued

Subsoil Texture (Site)	Treatment	Depth	Mass	Bulk Density	Total Carbon	
Sandy (MS)	Control	Oi	2.6 (0.2)	--	509 (7.0)	1.3 (0.1)
		Oe + Oa	5.3 (1.0)	--	459 (7.0)	2.5 (0.5)
		Oi + Oe + Oa	7.9 (1.2)	--	--	3.8 (0.5)
		0-1	--	--	39.6 (3.8)	5.8 (0.5)
		0-10	--	1.48 (0.06)	12.8 (1.6)	18.6 (2.8)
		10-20	--	1.60 (0.06)	5.5 (0.8)	8.1 (0.8)
		20-30	--	1.61 (0.04)	3.6 (0.6)	5.4 (0.8)
		30-40	--	1.57 (0.06)	2.8 (0.4)	4.3 (0.4)
		40-50	--	1.55 (0.04)	2.2 (0.2)	3.4 (0.3)
		0-50	--	--	--	39.8 (3.4)
	Fertilized	Oi	3.1 (0.3)	--	496 (3.0)	1.5 (0.1)
		Oe + Oa	7.6 (1.2)	--	457 (3.2)	3.5 (0.5)
		Oi + Oe + Oa	10.7 (1.3)	--	--	5.0 (0.6)
		0-1	--	--	43.2 (3.4)	6.4 (0.4)
		0-10	--	1.50 (0.05)	18.2 (4.8)	25.4 (5.2)
		10-20	--	1.62 (0.04)	6.9 (1.3)	11.0 (1.9)
		20-30	--	1.66 (0.03)	3.1 (0.2)	5.1 (0.2)
		30-40	--	1.62 (0.02)	2.5 (0.2)	4.1 (0.3)
		40-50	--	1.56 (0.03)	2.3 (0.1)	3.6 (0.1)
		0-50	--	--	--	49.2 (6.8)

† Numbers in parentheses indicate the standard error (SE), where n=4 for each treatment.

‡ Total C content for the 0-1 cm depth was estimated using the bulk density from 0-10 cm.

Table 5. Average change in total C concentration and content from year 0 to 11 in the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting, and t-tests evaluating if the change in C was significantly different from zero.

Subsoil Texture (Site)	Treatment	Depth	Change in Total C		g kg^{-1}	Mg ha^{-1}
		- cm -	g kg^{-1}	Mg ha^{-1}	Probability > |t|	
Clayey (AL)	Control	0-10	-0.8	2.3	0.913	0.744
		10-20	-2.3	-4.7	0.360	0.329
	Fertilized	0-10	-0.1	4.7	0.986	0.347
		10-20	-6.8	-12.5	0.207	0.171
Sandy (MS)	Control	0-10	-2.4	-1.3	0.226	0.718
		10-20	-7.2	-13.0	0.003	0.002
	Fertilized	0-10	2.8	5.4	0.500	0.278
		10-20	-5.9	-10.5	0.134	0.122

Table 6. Statistical summary (Probability > *F*) of site and fertilization effects on estimated ecosystem carbon pools for 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting.

Comparison	Effect	Aboveground Biomass	Belowground Biomass	Forest Floor	Mineral Soil	Total
Across Sites	Site	0.001	0.001	0.347	0.009	0.001
	Fertilization	0.015	0.013	0.672	0.068	0.008
	Site*Fertilization	0.182	0.138	0.711	0.616	0.364
Within Clayey Site	Fertilization	0.030	0.028	0.569	0.381	0.020
Within Sandy Site	Fertilization	0.321	0.332	0.973	0.092	0.181

Table 7. Average ecosystem carbon pools in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting.

Subsoil Texture (Site)	Treatment	Pool	Total C	% of Total Ecosystem C	Total C Gain with Fertilization	
					Absolute Gain	% of Total Gain
			- Mg ha^{-1} -		- Mg ha^{-1} -	
Clayey (AL)	Control	Aboveground Biomass	18.4 (2.4)†	19	--	--
		Belowground Biomass	5.3 (0.6)	5	--	--
		Forest Floor	4.8 (0.4)	5	--	--
		Mineral Soil (0-50 cm)	69.1 (5.8)	71	--	--
		Total Ecosystem	97.6 (5.7)	--	--	--
	Fertilized	Aboveground Biomass	38.5 (3.4)	30	20.1*	63
		Belowground Biomass	10.6 (0.9)	8	5.3*	17
		Forest Floor	5.3 (0.6)	4	0.5	2
		Mineral Soil (0-50 cm)	74.9 (6.1)	58	5.8	18
		Total Ecosystem	129.3 (8.4)	--	31.7*	100
Sandy (MS)	Control	Aboveground Biomass	12.0 (2.4)	20	--	--
		Belowground Biomass	3.5 (0.6)	6	--	--
		Forest Floor	4.4 (0.4)	7	--	--
		Mineral Soil (0-50 cm)	39.8 (3.4)	67	--	--
		Total Ecosystem	59.7 (3.6)	--	--	--
	Fertilized	Aboveground Biomass	19.7 (4.3)	25	7.6	40
		Belowground Biomass	5.3 (1.0)	7	1.8	9
		Forest Floor	4.4 (0.8)	6	0.0	1
		Mineral Soil (0-50 cm)	49.2 (6.8)	63	9.4*	50
		Total Ecosystem	78.6 (9.7)	--	18.8	100

† Numbers in parentheses indicate the standard error (SE), where n=4 for each treatment.

* Gain found to be significant at 0.10 probability level.

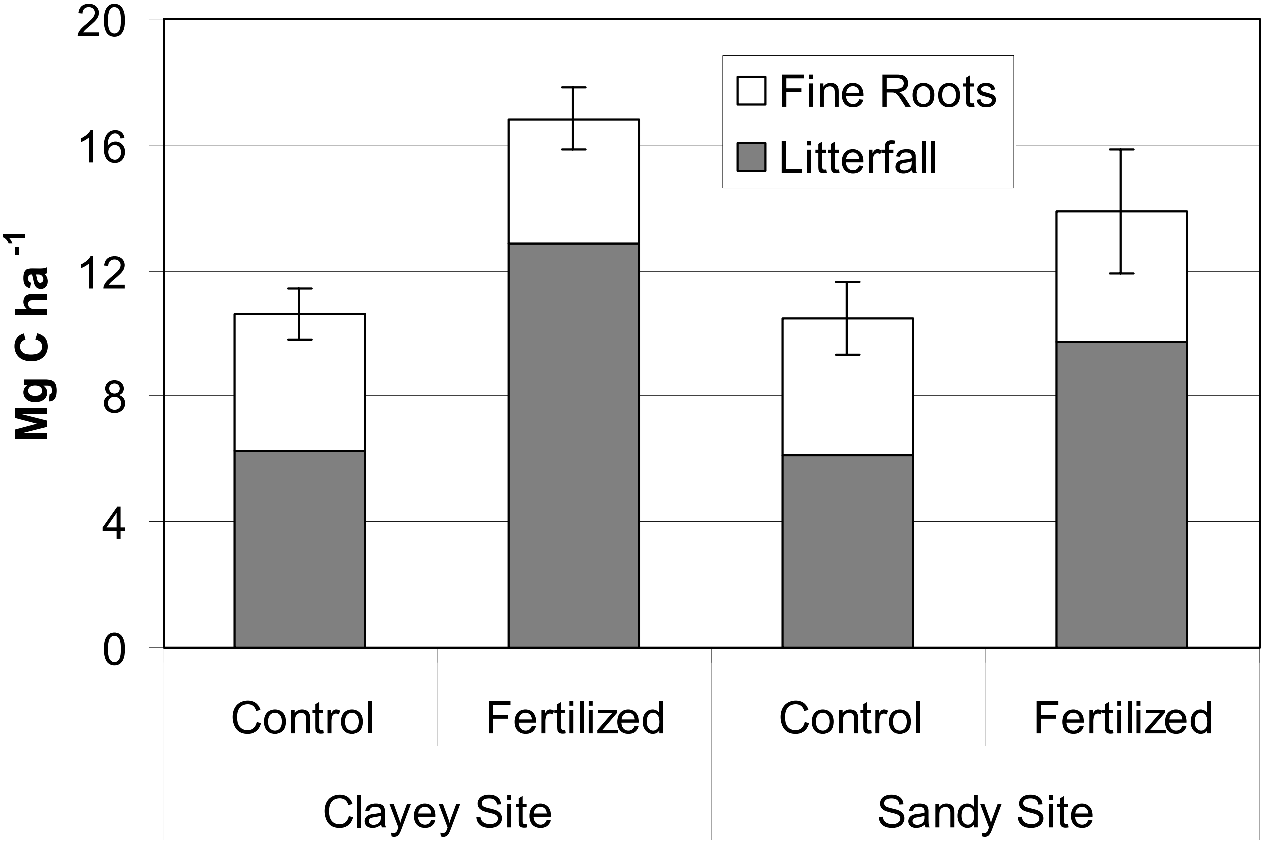

Figure 1. Estimated cumulative C inputs from annual litterfall and fine root turnover over 11 years of stand development in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting. Vertical bars represent the standard error (SE), with n=4 for each treatment.

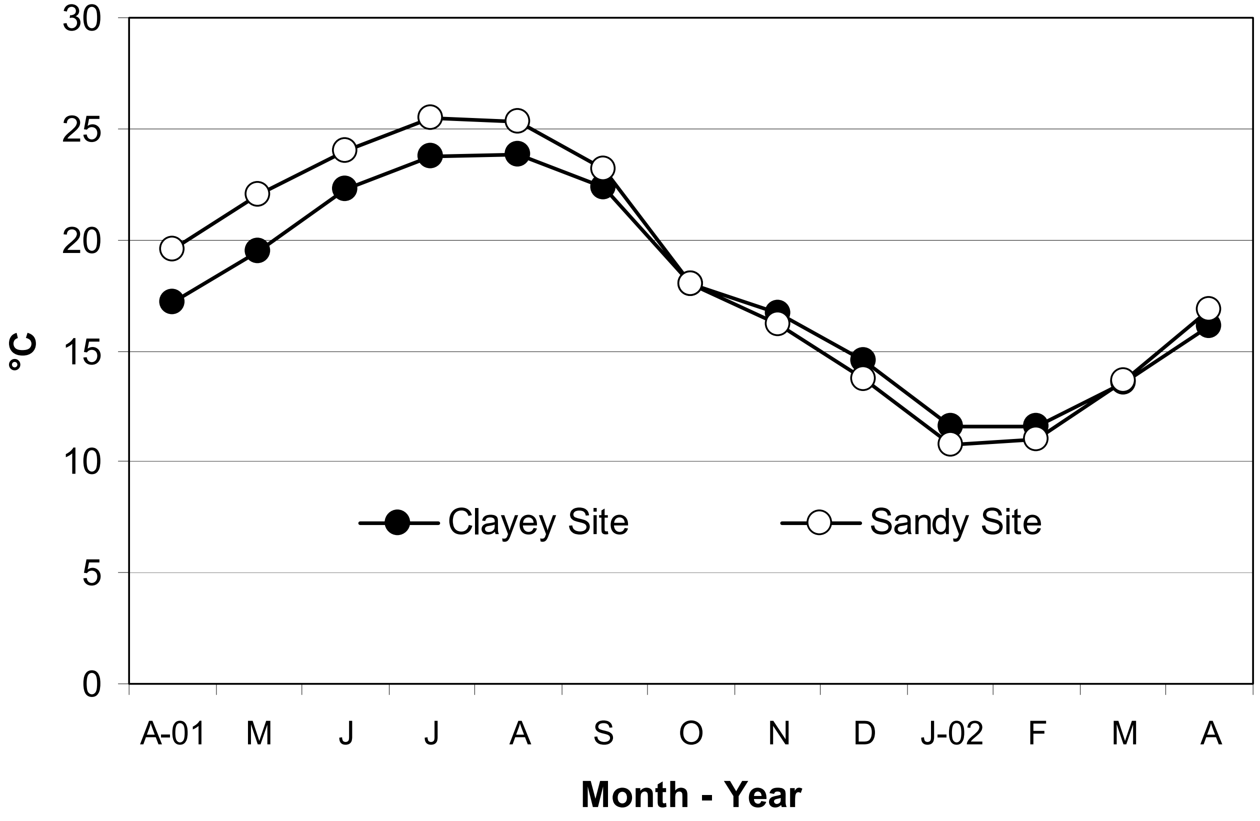

Figure 2. Monthly temperature in the surface 18-cm of mineral soil averaged by site during year 11 in loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting.

CHAPTER 2

Dissolved organic carbon fluxes in 11-year old loblolly pine plantations

Zakiya H. Leggett, Daniel L. Kelting, H. Lee Allen

ABSTRACT

Dissolved organic carbon (DOC) plays an important role in carbon cycling and nutrient availability in forest ecosystems. Fertilization may influence the magnitude of DOC in throughfall and forest floor leachate by increasing the leaf area and the amount of foliage returned to the forest floor. This study was conducted in 11-year old loblolly pine plantations with and without nitrogen and phosphorus fertilization. Throughfall and forest floor leachate samples were collected on a monthly basis and DOC concentration was measured and used to calculate DOC flux (kg/ha/mo and kg/ha/yr). Fertilization did not have a significant effect on throughfall or forest floor leachate solution volume, DOC concentration, or DOC flux. Both solution volumes were positively correlated with precipitation. The volume of solution collected as throughfall was negatively correlated with tree volume and basal area. The yearly flux of DOC that entered the forest floor and soil from throughfall (100 kg/ha/yr) and forest floor leachate (152 kg/ha/yr) was relatively small (6% of the sum of all fluxes evaluated) compared to the yearly fluxes of C estimated as being contributed from litterfall and fine roots in these 11-year old loblolly pine plantations.

INTRODUCTION

Dissolved organic carbon (DOC) plays a key role in C cycling, chemistry and nutrient availability of soil ecosystems (Moore and Matos, 1999). When considering the fluxes of C into the soil ecosystem, the DOC flux is often considered minor as far as magnitude but has the potential to be important as far as its ecological influence and significance (Liu and Sheu, 2003). The DOC leaching from forest canopies (throughfall) and through the forest floor have been found to be high in carbohydrates and/or consisting of carbon of low molecular weight (McDowell and Likens, 1988; Lichter et al., 2000). These fluxes can therefore serve as a major energy source for microbial communities, which can often influence the mineralization and release of nutrients.

Loblolly pine is the most commonly planted and intensively managed forest species in the southeastern US (Allen et al., 1990; Roise et al., 2000). Fertilization, which is a common management practice within loblolly pine plantations, has been proven to increase foliage and stemwood biomass production (Allen et al., 2001; Albaugh et al., 1998). This increase in foliage production translates into increased litterfall inputs to the forest floor and may result in an increase in the magnitude of DOC in throughfall and forest floor leachate.

Throughfall and forest floor leachate compositions are governed by a complex interaction of hydrological, biological and chemical processes (Moreno et al., 2001). In order to better understand these fluxes of C entering the soil ecosystem, it is important to understand what influences or controls their variability. The major controls on the extent of soluble DOC are based on temperature and precipitation frequency due primarily to effects on microbial activity and leaching patterns (Godde et al., 1996; Liu and Sheu, 2003). Dissolved organic carbon has been found to increase exponentially with temperature (Christ and David, 1996). As decomposition proceeds, C is solubilized and available for leaching by the next precipitation event (Godde et al., 1996). Precipitation chemistry (Puckett, 1991) and amount (Switzer at al., 1988; Liu and Sheu, 2003; Zarnoch et al., 2002; Abrahamson et al., 1988) can be major factors in determining the variability of throughfall composition, which in turn influences forest floor leachate composition.

This research study was initiated to determine the effects of fertilization on dissolved organic carbon at two different levels (throughfall and forest floor leachate) within two 11-year old loblolly pine plantations. An additional objective was to determine what factors explain the variability in these DOC concentrations and fluxes. It was hypothesized that fertilization would result in greater DOC concentration and flux. In addition, it was expected that temperature and amount of precipitation would influence the variability in solution volume and DOC at both levels.

METHODS

Site Description and Study Layout

Two sites in the Gulf Coastal Plain were identified to evaluate the DOC fluxes. The sites were located in Escambia County, Alabama (31°10' N 87°20’ W) and Greene County, Mississippi (31°25’ N 88°27’ W). The Alabama site was on a well-drained clayey soil of the Greenville (fine, kaolinitic, thermic Rhodic Kandiudults) series and the Mississippi site was on a well-drained sandy soil of the Eustis (siliceous, thermic Psammentic Paleudults) series. Both sites have the potential to be deficient in soil nutrients, such as nitrogen and phosphorus (Appendix A). The climate was similar at both sites with mean annual temperature and precipitation of 19°C and 1613 mm from 1990 through 2001 (NOAA, 2002). The mean monthly precipitation was 118 mm at the Alabama site and 129 mm at the Mississippi site during the sampling period (NOAA, 2002).

The experiment was installed as a randomized complete block design with 4 blocks per site. Two 40 m x 40 m treatment plots, with 20 m x 20 m measurement plots centered within each, were established in each block for a total of 8 plots per site. The plots were randomly located within each block with a minimum buffer of 10 m between each treatment plot. After being planted with loblolly pine seedlings in April 1990, two fertilization treatments were randomly assigned to plots at each site: no fertilization (control) versus fertilization at planting with 45 kg N and 50 kg P per hectare applied as a broadcast application of 250 kg ha^{-1} of diammonium phosphate (DAP).

Stand Characteristics

The two sites differed in productivity with the site in Alabama being more productive than the site in Mississippi and averaging 71% and 47% greater volume yield and basal area, respectively, at age 11 (Table 1). Details about stand measurements and biomass can be found in Leggett and Kelting (2004). For the purposes of this paper the Alabama site will be referred to as the high productivity (HP) site and the Mississippi site will be referred to as the low productivity (LP) site.

Sample and Data Collection

Forest floor samples were collected in December 2001 using a 35 cm x 35 cm metal square at six random locations within each plot and composited by plot at the time of collection. The samples were also divided into the Oi layer (fresh litter or L layer) and Oe+Oa (fragmented litter and humus or F+H layer) layers at the time of collection.

Throughfall (rainwater leaching from the forest canopy) and forest floor leachate were collected on a monthly basis during a 12-month period starting in November 2001 and continuing through October 2002. There were no samples collected in February 2002 resulting in 11 months of collection.

Throughfall was collected below the canopy in three collectors per plot that consisted of a 14 cm diameter polyethylene funnel inserted in a 3.78 L polyethylene jug and mounted about 50 cm above the ground. Acid washed polyfil was inserted in the funnel opening to keep leaves, small branches, insects and other large objects from entering the jug. The polyfil was replaced and the funnels were cleaned after each collection. Volume of throughfall was measured with a graduated cylinder and samples were composited by plot at time of collection.

Three tension-free lysimeters (25 cm x 9 cm) as described by Markewitz et al. (1998) made from PVC (polyvinyl chloride plastic) were installed at the interface of the bottom of the forest floor (specifically Oa horizon/ humus layer) and the surface mineral soil within each plot. Forest floor leachate was collected in amber glass bottles buried 45-cm below the soil surface adjacent to the lysimeters with polyurethane tubing connecting the lysimeter and collection bottle. Samples were composited by plot at time of collection. Volume of forest floor leachate was estimated as 95% of throughfall volume (Helvey and Patric, 1965)

Soil temperature was monitored on an hourly basis for one year (April 2001 - April 2002) at an 18 cm depth in the soil profile using a data logger (Temperature Data

Logger - Model StowAway Tidbit XT, Onset Computer Corporation, Bourne, MA) for recording temperature. One probe was installed in one of the replicated control plots within each site. The data were averaged on a monthly basis for comparison between sites. Precipitation data was gathered from National Oceanic and Atmospheric Administration (2002) on a monthly basis for comparison between sites.

Sample preparation and analysis

Forest floor samples were dried for 12 hours at 80°C and weighed to obtain dry mass. The loss on ignition procedure (Nelson and Sommers, 1996) was used to correct for mineral soil contamination within the forest floor samples. Subsamples were ground using a 1 mm grinder and analyzed for total C using a CHN elemental analyzer (CE Instruments – Model NC2100, CE Elantech Inc., Lakewood, NJ). Values were converted to mass or C per unit area (kg/ha) using the 0.1225 m^2 area of the grid used for collection.

Solution samples were filtered through glass fiber filters (0.22 µm) within 48 hours of collection and stored at 4 °C until further analyses (usually within 48 hours). Dissolved organic carbon (DOC) concentration was determined using a dissolved organic carbon analyzer (Shimadzu TOC Analyzer- Model 9300C, Columbia, MD). Concentration data were converted to flux data (kg/ha/mo) using the corresponding volume and area of collector.

Statistical Analysis

Forest floor

The forest floor (Oi and Oe+Oa) layers were analyzed separately in a randomized complete block design with replicate plots nested within sites. Mean values from the four replicated plots within treatments within site were evaluated for comparisons between treatments and sites.

An analysis of variance model (ANOVA) was used to evaluate the statistical significance of various effects (i.e. site, fertilization, site*fertilization interaction) on forest floor mass, C concentration, and C content. The general linear model (PROC GLM) procedure within SAS statistical software (SAS Institute, 2001) was used for this analysis.

The site effect was evaluated using Type III mean sum of squares (MS) for Rep(Site) as an error term for all models. The treatment effect was referred to as fertilization since there was only one level of fertilization evaluated in this study.

Throughfall and forest floor leachate

Throughfall and forest floor leachate were analyzed separately in a randomized complete block design with replicate plots nested within sites. Mean values from the four replicated plots within treatments within each site were evaluated as monthly repeating measures for comparisons between treatments and sites.

A mixed model accounting for repeated measures was used to evaluate the statistical significance of various effects (i.e. site, fertilization, month, and various interactions) on solution volume, DOC concentration, and DOC flux. The mixed model (PROC MIXED) procedure within SAS statistical software (SAS Institute, 2001) was used for this analysis. The replicates nested within sites and the interaction of site*replicates*fertilization were defined as random effects.

Monthly correlations

The correlation between monthly averages for throughfall and forest floor leachate solution volume and DOC concentration with each other and with monthly precipitation and monthly soil temperature were evaluated using Pearson correlation coefficients. This analysis was done for each site at the month level (n=11; 11 months of collection = 11 averages per variable evaluated) using the correlations (PROC CORR) procedure within SAS statistical software (SAS Institute, 2001).

Eleventh year correlations

The correlation between the 11th year monthly average of throughfall and forest floor leachate solution volume, DOC concentration, and DOC flux with each other and with the 11th year averages for forest floor mass, stem volume, and basal area were measured using Pearson correlation coefficients. This analysis was done with both sites together at the plot level (n=16; 16 plots = 16 eleventh year values for each variable evaluated) using the correlations (PROC CORR) procedure within SAS statistical software (SAS Institute, 2001). For all analyses, effects or correlations were considered significant at the 0.10 probability level.

RESULTS

Forest Floor Mass

Total forest floor mass was significantly different between the sites with the high productivity (HP) site having 20% greater mass than the low productivity (LP) site (Table 2). However, the LP site had approximately 2% greater C concentration across both layers. Since C concentration was greater on the LP site, the C content was not significantly different between sites. Fertilization did not have a statistically significant effect on forest floor mass, C concentration, or C content.

Throughfall (TF) and forest floor leachate

The average monthly solution volume collected for throughfall and forest floor leachate was 41% greater on the low productivity (LP) than the high productivity (HP) site (Table 3). Although there was a site effect on monthly solution volume, there was no site effect on DOC concentration or DOC flux of throughfall or forest floor leachate. Fertilization did not have a significant effect on monthly solution volume, DOC concentration or DOC flux for either site.

Forest floor leachate had 2 times the DOC concentration of throughfall for both sites (Table 3). There was greater (2 kg/ha/mo and 7 kg/ha/mo for the HP and LP site, respectively) DOC flux from forest floor leachate than from throughfall for both sites.

As expected, there was a significant difference between months of collection for all three variables (solution volume, DOC concentration, and DOC flux) for both throughfall and forest floor leachate (Table 3). In addition, the month effect varied by site for all three variables for both throughfall and forest floor leachate.

Throughfall DOC concentration ranged from 4-31 mg/L with the overall monthly dynamics being similar for the two sites with the exception of a pulse of 19 mg/L in March 2002 for the LP site as compared to 6 mg/L for the HP site (Figure 1). Both sites reached their peak (23 mg/L and 31 mg/L for the LP and HP sites, respectively) in throughfall DOC concentration in December 2001.

Dissolved organic carbon concentration for forest floor leachate ranged from 5-36 mg/L with the overall monthly dynamics being similar for the two sites with the exception of a low of 5 mg/L in March 2002 for the HP site compared to 18 mg/L for the LP site and a peak of 36 mg/L in June 2002 for the LP site compared to 20 mg/L for the HP site (Figure 1). The HP site reached its highest DOC concentration (28 mg/L) in May 2002 and the LP site reached its highest DOC concentration (36 mg/L) in June 2002.

Throughfall DOC flux ranged from 2-26 kg/ha/mo. The monthly dynamics for throughfall DOC flux are almost identical to the dynamics seen for its DOC concentration with a pulse in March 2002 for the LP site and peaks (approximately 24 kg/ha) in December 2001 for both sites (Figure 2). However, there were peaks in DOC flux in July 2002 and September 2002 for the HP site.

The DOC flux of forest floor leachate was more dynamic over the collection year than its corresponding DOC concentration (Figure 3). The DOC flux ranged from 3-31 kg/ha/mo for the forest floor leachate.

Correlations

When evaluating correlations for monthly averages of throughfall and forest floor leachate there was a positive correlation (0.90 and 0.62 for HP and LP sites, respectively) between precipitation and solution volume for both sites (Table 4). The monthly throughfall DOC flux was most positively correlated with its volume for the HP site and most positively with its DOC concentration for the LP site. The monthly forest floor flux was most positively correlated with its volume for both sites. Soil temperature was not found to be correlated with any solution measurements for either site.

When evaluating correlations for the 11th year monthly averages of throughfall and forest floor leachate with each other and with forest floor mass, stem volume and basal area (which are “cumulative” data) across both sites, throughfall volume was negatively correlated with stem volume (-0.67) and basal area (-0.69) (Table 5). Forest floor leachate volume was not significantly correlated (Prob > |r| = 0.108) with the mass of the forest floor although there was a negative trend (-0.42). Mass of Oi layer, mass of Oe+Oa layer, and total forest floor mass were positively correlated with stem volume and basal area.

DISCUSSION

Although the stem volume and basal area data revealed significant site and fertilization effects, the same was not true for DOC concentration or flux. Stem volume and basal area are cumulative measures that reflect the accumulation of tree growth in diameter and height over the 11 years of this plantation's development. However, the DOC measures in this study were ephemeral or for one year of the 11 years of this plantation's development. In order to understand why there were no significant differences in DOC concentration and flux, some of the variables that might directly affect this measure were evaluated.

It was expected that leaf area and forest floor mass would have direct effects on throughfall and forest floor leachate solution volume, DOC concentration, and in turn DOC flux. Leaf area is an index of canopy cover which will determine the level of interception of rainfall. Greater leaf area will result in greater interception and therefore should be inversely related to the amount of throughfall solution collected.

Although leaf area was not measured in this study, stem volume growth is linearly and positively related to leaf area index (Vose and Allen, 1998). In addition, basal area provides a logical expression of stand density by representing the cross-sectional area of all stems and is highly correlated with tree volume (Avery and Burkhart, 1994).

Throughfall volume was negatively correlated stem volume, revealing the potential effects of leaf area on this measure. Additionally, there was significantly greater throughfall volume on the low productivity (LP) site (Table 3) which was found to have significantly lower stem volume and basal area (Table 1). Other studies found that stand characteristics such as accelerated canopy growth (Lichter et al., 2000) as well as leaf area index and basal area (Abrahamson et al. 1988) were paralleled with decreasing trends in throughfall volume.

Total forest floor mass (Oi and Oe+Oa layers) differed between sites but revealed no significant fertilization effect (Table 2). Since forest floor mass reflects the density and level of forest floor development, it is expected to influence DOC concentration of forest floor leachate. This can explain the fact that there was no fertilization effect on these variables for forest floor leachate (Table 3).

Similar to other studies (Liu and Sheu, 2003; Lichter et al., 2000; Currie et al., 1996), there was a significant effect of time (month). This effect differed between sites and levels (Table 3). As found in this study and others, the amount of monthly precipitation had a strong positive influence on the dynamics of throughfall volume (Switzer at al., 1988; Liu and Sheu, 2003; Zarnoch et al., 2002; Abrahamson et al., 1988).

Temperature has been predicted to have a strong effect on leaching patterns (Liu and Sheu 2003). Monthly soil temperature was measured and was not found to be correlated with monthly solution volume, DOC concentration or flux.

The yearly flux of DOC that entered the forest floor and soil from throughfall and forest floor leachate in these 11-year old loblolly pine plantations was relatively small (6% of the sum of all fluxes evaluated) compared to the yearly fluxes of C estimated as being contributed from litterfall and fine roots (Table 6). This relative flux size does not necessarily indicate or reflect that these pools are less important or influential on C and nutrient cycling in these pools.

Similar DOC concentrations and fluxes for throughfall have been observed in other studies (Table 7). The DOC concentrations for forest floor leachate in this study were also found to be similar to other studies although it was in the lower end of the range of concentrations found in other studies. The DOC flux for forest floor leachate was found to be much lower than data from other studies and was not within the range of these other studies. This is the result of the lower DOC concentration for the forest floor leachate in this study and possibly the young age and lower productivity of these stands as compared with those of other studies.

Stemflow is another possible important flux that was not evaluated in this study. Other studies in loblolly plantations found that the amount of stemflow solution collected was considerably less that that of throughfall: Switzer et al. (1988), Hoover (1953), and Swank et al. (1972) found that 72%, 74%, and 71%, respectively, of incident precipitation was collected as throughfall and 21%, 8% and 19%, respectively, was collected as stemflow while the remaining precipitation was intercepted. However, stemflow solution has been found to have a higher DOC concentration as compared to throughfall (Liu and Sheu, 2003). Although the concentration may be higher for stemflow solution, its relative flux size is limited by the small amount of this solution expected to enter the forest floor and soil ecosystem. Its importance to and influence on the forest ecosystem’s C and nutrient cycling may be based on its DOC “quality” as compared to flux.

Fertilization was not found to have an effect on throughfall or forest floor leachate DOC for this 11-year old loblolly pine plantation. However, the difference in the productivity between the two sites was still important in governing DOC dynamics. There are several variables, factors, and/or processes within this forest ecosystem that influence the variability in the volume of solution entering the ecosystem, DOC concentrations, and DOC fluxes for the two levels (throughfall and forest floor) evaluated. Although precipitation and tree productivity were found to have the greatest correlations with these measures, other factors not investigated such as stand spatial variability, various biological processes, and precipitation chemistry could also be quite influential on the results found. In addition, data collection extended longer than one year time may reveal and/or confirm trends and stronger correlations to better explain the dynamics of DOC in this loblolly pine ecosystem.

REFERENCES

Abrahamson, D.A., P.M. Dougherty, and S.J. Zarnoch. 1998. Hydrological components of a young loblolly pine plantation on a sandy soil with estimates of water use and loss. Water Resources Research 34: 3503-3513.

Albaugh, T.J., H.L. Allen, P.M. Dougherty, L.W. Kress, and J.S. King. 1998. Leaf area and above- and belowground growth responses of loblolly pine to nutrient and water additions. Forest Science 44:317-328.

Allen, H.L., P.M. Dougherty, and R.G. Campbell. 1990. Manipulation of water and nutrients-practice and opportunity in southern U.S. pine forests. Forest Ecology and Management 30:437-453.

Allen, H.L., D.L. Kelting, and T.J. Albaugh. 2001. Nutrient Management Concepts and Practices in Southern Pine Plantations. Pgs 27- 31, In: C. Bamsey (ed.), Enhanced Forest Management: Fertilization and Economics. Clear Lake Ltd. Edmonton, Canada. 169pp.

Avery, T.E. and H.E. Burkhart. 1994. Forest measurements. McGraw Hill. Boston, MA.

Borken, W., Y.J. Xu, R. Brumme, and N. Lamersdorf. 1999. A climate change scenario for carbon dioxide and dissolved organic carbon fluxes from a temperate forest soil: drought and rewetting effects. Soil Science Society of America Journal 63:1848-1855.

Christ, M.J. and M.B. David. 1996. Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol. Soil Biology and Biochemistry 28:1191-1199.

Currie, W.S., J.D. Aber, W.H. McDowell, R.D. Boone, and A.H. Magill. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry 35:471-505.

Ducey, M., and H.L. Allen. 2001. Nutrient supply and fertilization efficiency in midrotation loblolly pine plantations: a modeling analysis. For. Sci. 47:96-102.

Godde, M., M.B. David, M.J. Christ, M. Kaupenjohann, and G.F. Vance. 1996. Carbon mobilization from the forest floor under red spruce in the Northeastern U.S.A. Soil Biology and Biochemistry 28:1181-1189.

Helvey, J.D. and J.H. Patric. 1965. Canopy and litter interception of rainfall by hardwoods of eastern United States. Water Resources Research 1: 193-206.

Hoover, M.D. 1953. Interception of rainfall in a young loblolly pine plantation. Station paper no. 21. Southeastern Forest Experiment Station, U.S. Dept. of Agriculture, Forest Service.

Laclau, J., J. Ranger, J. Nzila, J. Bouillet, P. Deleporte. 2003. Nutrient cycling in a clonal stand of Eucalyptus and an adjacent savanna ecosystem in Congo: 2. Chemical composition of soil solutions. Forest Ecology and Management 180:527-544.

Leggett, Z. H. and D.L. Kelting. 2004. Fertilization effects on carbon pools in loblolly pine plantations on upland sandy and clayey soils. Soil Science Society of America Journal (submitted)

Lichter, J., M. Lavine, K.A. Mace, D.D. Richter, and W.H. Schlesinger. 2000. Throughfall chemistry in a loblolly pine plantation under elevated atmospheric CO2 concentrations. Biogeochemistry 50:73-93.

Liu, C.P. and B.H. Sheu. 2003. Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. Forest Ecology and Management 172:315-325.

McDowell, W.H. and G.E. Likens. 1988. Origin, composition and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs 58:177-195.

Markewitz, D., D.D. Richter, H.L. Allen, J. B. Urrego. 1998. Three decades of observed soil acidification in the Calhoun Experimental Forest: Has acid rain made a difference? Soil Science Society of America Journal 62: 1428-1439

Michalzik, B. and E. Matzner. 1999. Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem. European Journal of Soil Science 50:579-590.

Moore, T.R. and L. Matos. 1999. The influence of source on the sorption of dissolved organic carbon by soils. Canadian Journal of Soil Science 79:321-324.

Moreno, G., J.F. Gallardo, and F. Bussotti. 2001. Canopy modification of atmospheric deposition in oligotrophic Quercus pyrenaica forests of an unpolluted region (central-western Spain). Forest Ecology and Management 149:47-60.

National Oceanic and Atmospheric Administration. 2002. National climatic data center: Weather station locator [Online]. Available at http://lwf.ncdc.noaa.gov/oa/climate/stationlocator.html (verified 24 October 2003).

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3 Chemical Methods. SSSA, Madison, WI.

Puckett, L.J. 1991. Spatial variability and collector requirements for sampling throughfall volume and chemistry under a mixed-hardwood canopy. Canadian Journal of Forest Research 21:1581-1588.

Qualls, R.G. and B.L. Haines. 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Science Society of America Journal 56:578-586.

Qualls, R.G., B.L. Haines, W.T. Swank, and S.W. Tyler. 2000. Soluble organic and inorganic nutrient fluxes in clearcut and mature deciduous forests. Soil Science Society of America Journal 64:1068-1077.

Qualls, R.G., B.L. Haines, W.T. Swank, and S.W. Tyler. 2002. Retention of soluble organic nutrients by a forested ecosystem. Biogeochemistry 61:135-171.

Richter, D.D., D. Markewitz, S.E. Trumbore, and C.G. Wells. 1999. Rapid accumulation and turnover of soil carbon in a re-establishing forest. Nature 400:56-58.

Richter, D.D., D. Markewitz, C.G. Wells, H.L. Allen, J.K. Dunscombe, K. Harrison, P.R. Heine, A. Stuanes, B. Urrego, and G. Bonani. 1995. Carbon cycling in a loblolly pine forest: implications for the missing carbon sink and for the concept of soil. p. 233-252. *In* W.W. McFee and J.M. Kelly (ed.) Carbon Forms and Functions in Forest Soils. SSSA, Madison, WI.

Roise J.P., F.W. Cubbage, R.C. Abt, and J.P. Siry. 2000. Regulation of timber yield for sustainable management of industrial forest plantations- theory and practice. p. 217-255. *In* K. von Gadow, T. Pakkula, and M. Tomé (ed.) Sustainable Forest Management. Kluwer Academic Publishers, The Netherlands.

SAS Institute. 2001. The SAS system for Windows. Release 8.20. SAS Inst., Cary, NC.

Solinger, S., K. Kalbitz, and E. Matzner. 2001. Controls on the dynamics of dissolved organic carbon and nitrogen in a Central European deciduous forest. Biogeochemistry 55: 347-349.

Swank, W.T., N.B. Goebel, J.D. Helvey. 1972. Interception loss in loblolly pine stands of the South Carolina Piedmont. Journal of Soil and Water Conservation 27: 160-164.

Switzer,G.L., L.E. Nelson, and M.G. Shelton. 1988. Influence of the canopy of loblolly pine plantations on the disposition and chemistry of precipitation. Technical Bulletin 154. Mississippi State, Mississippi: The Station.

Vose, J.M. and H.L. Allen. 1988. Leaf area, stemwood growth and nutrition relationships in loblolly pine. Forest Science 34:547-563.

Zarnoch, S.J., D.A. Abrahamson, and P.M. Dougherty. 2002. Sampling throughfall and stemflow in young loblolly pine plantations. Research Paper SRS-27. Asheville, NC: U.S. Department of Agriculture, Forest Service, Southern Research Station. 6 p.

Table 1. Stand characteristics in 11-yr-old loblolly pine plantations on contrasting subsoil textures with and without fertilization at planting.

Site	Treatment	DBH†	Height	Volume‡	Basal Area	Trees ha^{-1}
		------ cm ------	------ m ------	--- m^3 ha^{-1} ---	--- m^2 ha^{-1} ---	
High Productivity (HP) Clayey (AL)	Control	13.0 (0.59)*	10.5 (0.31)	134 (9)	24 (1)	1792 (58)
	Fertilized	15.1 (0.39)	12.0 (0.30)	199 (20)	32 (3)	1736 (80)
Low Productivity (LP) Sandy (MS)	Control	10.8 (0.37)	8.9 (0.25)	81 (7)	17 (1)	1730 (60)
	Fertilized	12.5 (0.71)	9.9 (1.29)	113 (25)	21 (2)	1656 (27)

†DBH= Diameter at Breast Height (1.3m)

‡Stem volume estimated using Smalley and Bower (1968) formula

*Numbers in parentheses indicate the standard error (SE).

Table 2. Average forest floor mass and carbon in 11-year old loblolly pine plantations with contrasting productivity and statistical summary of site and fertilization effects.

Site[†]	Layer[‡]	Mass	Carbon	
		----- kg ha^{-1} ----	------- % ------	----- kg ha^{-1} ----
HP (AL)	Oi	3313 (236)[‡]	49.24 (0.39)	1634 (122)
	Oe + Oa	7919 (550)	43.16 (1.35)	3424 (269)
	Total Forest Floor	11232 (688)		5058 (361)
LP (MS)	Oi	2854 (203)	50.22 (0.42)	1430 (96)
	Oe + Oa	6478 (831)	45.82 (0.57)	2973 (391)
	Total Forest Floor	9331 (962)		4404 (444)
Comparison	*Effect*	-------------- Probability > F --------------		
Oi	Site	0.108	0.074	0.155
	Fertilization	0.454	0.597	0.483
	Site*Fertilization	0.596	0.195	0.685
Oe + Oa	Site	0.182	0.122	0.360
	Fertilization	0.143	0.327	0.254
	Site*Fertilization	0.522	0.378	0.421

[†] HP = High productivity; LP = Low productivity

[‡] Numbers in parentheses indicate the standard error (SE).

Table 3. Average monthly volume, DOC concentration and DOC flux of throughfall and forest floor leachate collected in 11-year old loblolly pine plantations and statistical summary of site, fertilization and month ("seasonal") effects.

Level	Site[†]	Volume	DOC concentration	DOC flux
		------ L/ha/mo[‡] -----	---- mg L^{-1} ----	------ kg/ha/mo -----
Throughfall	HP (AL)	732.06 (50.61)*	10.36 (0.95)	7.97 (1.11)
	LP (MS)	1038.98 (67.56)	9.65 (0.87)	8.32 (0.81)
Forest floor leachate	HP (AL)	539.88 (42.81)	18.65 (1.23)	10.03 (1.21)
	LP (MS)	757.84 (49.93)	22.07 (1.00)	15.64 (1.15)
Comparison	*Effect*		------------------- Probability > F -------------------	
Throughfall	Site	0.038	0.637	0.369
	Fertilization	0.245	0.527	0.690
	Site*Fertilization	0.974	0.396	0.277
	Month	<0.0001	<0.0001	<0.0001
	Month*Site	<0.0001	<0.0001	0.0002
Forest floor leachate	Site	0.044	0.633	0.242
	Fertilization	0.153	0.896	0.675
	Site*Fertilization	0.804	0.161	0.087
	Month	<0.0001	<0.0001	<0.0001
	Month*Site	<0.0001	<0.0001	<0.0001

[†] HP = High productivity; LP = Low productivity

[‡] Volume values divided by 1000.

[*] Numbers in parentheses indicate the standard error (SE).

Table 4. Pearson correlation coefficients and Prob > IrI for monthly throughfall (TF) and forest floor leachate (FF) volume and DOC concentration (DOC [ ]), precipitation, and soil temperature in 11-year old loblolly pine plantations.

Site[†]	Variable	TF Volume	TF DOC [ ]	TF Flux	FF Volume	FF DOC [ ]	FF Flux	Precipitation	Soil Temperature
HP (AL)	TF Volume	-----	-0.176	0.726	1.000	-0.143	0.751	0.896	0.403
		-----	0.604	0.011	<0.0001	0.675	0.008	0.0002	0.282
	TF DOC [ ]		-----	0.532	-0.172	0.353	0.008	-0.325	-0.036
			-----	0.092	0.613	0.287	0.981	0.330	0.927
	TF Flux			-----	0.727	0.568	0.568	0.527	0.297
				-----	0.011	0.068	0.068	0.096	0.437
	FF Volume				-----	-0.134	0.759	0.899	0.400
					-----	0.694	0.007	0.0002	0.286
	FF DOC [ ]					-----	0.446	-0.036	0.348
						-----	0.169	0.916	0.359
	FF Flux						-----	0.692	0.530
							-----	0.018	0.142
	Precipitation							-----	0.397
								-----	0.291
	Soil Temperature								-----

Table 4. Continued

Site[†]	Variable	TF Volume	TF DOC [ ]	TF Flux	FF Volume	FF DOC [ ]	FF Flux	Precipitation	Soil Temperature
LP (MS)	TF Volume	-----	-0.429	0.273	1.000	-0.399	0.971	0.622	0.124
		-----	0.188	0.416	<0.0001	0.224	<0.0001	0.041	0.733
	TF DOC [ ]		-----	0.736	-0.437	0.077	-0.436	-0.214	-0.295
			-----	0.010	0.179	0.822	0.180	0.528	0.408
	TF Flux			-----	0.267	-0.266	0.241	0.203	-0.332
				-----	0.428	0.429	0.475	0.549	0.349
	FF Volume				-----	-0.391	0.972	0.619	0.124
					-----	0.235	<0.0001	0.042	0.734
	FF DOC [ ]					-----	-0.218	-0.113	0.292
						-----	0.520	0.742	0.414
	FF Flux						-----	0.712	0.191
							-----	0.014	0.598
	Precipitation							-----	0.092
								-----	0.800
	Soil Temperature								-----

[†] HP = High productivity; LP = Low productivity

Table 5. Pearson correlation coefficients and Prob > IrI for yearly averages of throughfall (TF) and forest floor leachate (FF) volume, DOC concentration (DOC [ ]), DOC flux, forest floor mass and stand cumulative volume and basal area in 11-year old loblolly pine plantations.

Variable†	TF Volume	TF DOC [ ]	TF Flux	FF Volume	FF DOC [ ]	FF Flux	Forest Floor Mass	Oi Mass	Oe+Oa Mass	Stem Volume	Basal Area
TF Volume	-----	-0.101	0.353	0.879	-0.024	0.307	-0.452	-0.343	-0.437	-0.673	-0.693
	-----	0.710	0.180	<0.0001	0.929	0.247	0.079	0.194	0.091	0.004	0.003
TF DOC [ ]		-----	0.846	-0.020	0.328	0.291	0.200	0.255	0.161	0.243	0.210
		-----	<.0001	0.942	0.215	0.275	0.458	0.340	0.551	0.365	0.435
TF Flux			-----	0.350	0.172	0.298	-0.051	0.077	-0.085	-0.065	-0.093
			-----	0.184	0.525	0.262	0.852	0.778	0.754	0.811	0.731
FF Volume				-----	0.226	0.565	-0.417	-0.334	-0.398	-0.798	-0.898
				-----	0.400	0.0225	0.108	0.206	0.127	0.0002	<0.0001
FF DOC [ ]					-----	0.919	0.107	0.083	0.103	-0.095	-0.169
					-----	<0.0001	0.693	0.761	0.704	0.726	0.533
FF Flux						-----	-0.040	-0.004	-0.047	-0.372	-0.444
						-----	0.882	0.989	0.861	0.156	0.085
Forest Floor Mass							-----	0.728	0.977	0.715	0.685
							-----	0.001	<.0001	0.002	0.003
Oi Mass								-----	0.564	0.514	0.459
								-----	0.023	0.042	0.074
Oe+Oa Mass									-----	0.701	0.682
									-----	0.003	0.004
Stem Volume										-----	0.980
										-----	<.0001
Basal Area											-----
											-----

†Oi = "fresh" litter; Oe + Oa = fragmented and humus

Table 6. Average yearly carbon flux from litterfall, fine roots, and dissolved organic carbon (DOC) into the forest floor and mineral soil in the 11th growing season of loblolly pine plantations.

Carbon Flux	kg/ha/yr[‡]	% of Sum
Litterfall[†]	2521 (298)*	63
Fine Roots[†]	1260 (149)	31
DOC-Throughfall	100 (7)	2
DOC-Forest Floor Leachate	152 (15)	4

†Estimated using NUTREM 2.0 model (Ducey and Allen 2001)

[‡] Data averaged across sites (high productivity-AL and low productivity-MS)

[*] Numbers in parentheses indicate the standard error (SE).

Table 7. Throughfall and forest floor (FF) leachate DOC concentrations (DOC [ ]) and DOC fluxes of DOC for several studies.

Location	Climate†	Age	Vegetation	Productivity‡	FF C	Throughfall		FF Leachate		Reference
		yrs			kg C/ha	DOC [ ] mg L^{-1}	DOC flux kg/ha/yr	DOC [ ] mg L^{-1}	DOC flux kg/ha/yr	
Escambia County, AL, USA	1613 mm, 19°C	11	Loblolly pine	AG = 28 Mg C/ha	5058	10	109	19	132	This study
Greene County, MS, USA	1613 mm, 19°C	11	Loblolly pine	AG = 16 Mg C/ha	4403	10	91	22	172	This study
Calhoun Experimental Forest, SC, USA	1170 mm, 16°C	30 - 40	Loblolly pine	AG = 124 Mg C/ha	32800	8	80	34	320	Richter et al. 1995; Richter et al. 1999
Hubbard Brook Experimental Forest, NH, USA	1310 mm	65 - 75	Hardwood	AG = 69 Mg C/ha	23200	12	47	28 - 38	263	McDowell and Likens 1988
Germany	1100 mm, 5°C	140	Norway spruce	---	132300	15	84	36 - 38	443	Michalzik and Matzner, 1999
Southern Appalachains, NC, USA	1770 mm	---	Hardwood	---	5725*	9	130	33	402	Qualls et al. 2002; Qualls et al. 1991
Harvard Forest, MA, USA	1000 mm	50 - 66	Red pine	---	---	13 - 37	139	14 - 75	398	Currie et al. 1996
			Hardwood			11 - 60	117	6 - 45	225	
Taiwan	2300 - 2700 mm, 10°C - 22°C	---	Chinese fir	---	---	7	167	---	---	Liu and Sheu 2003
			Hardwood			8 - 10	189 - 231	---	---	
Germany	775 mm, 8°C	130	Hardwood	BA = 30 m^2/ha	12000	12 - 16	---	28 - 78	---	Solinger et al. 2001
Congo	1400 mm, 25°C	6 - 8	Eucalyptus	Vol = 158 m^3/ha	---	---	---	43	---	Laclau et al. 2003
Germany	1090 mm, 6°C	65	Norway spruce	BA = 50 m^2/ha	---	---	93 - 106	---	---	Borken et al. 1999
Duke University FACE plots, NC, USA	---	13 - 16	Loblolly pine	---	---	---	90	---	---	Lichter et al. 2000

†Annual precipitation, mean annual temperature

‡AG = Aboveground biomass; BA = Basal area; Vol = Stem volume

* Assuming biomass is 50% C

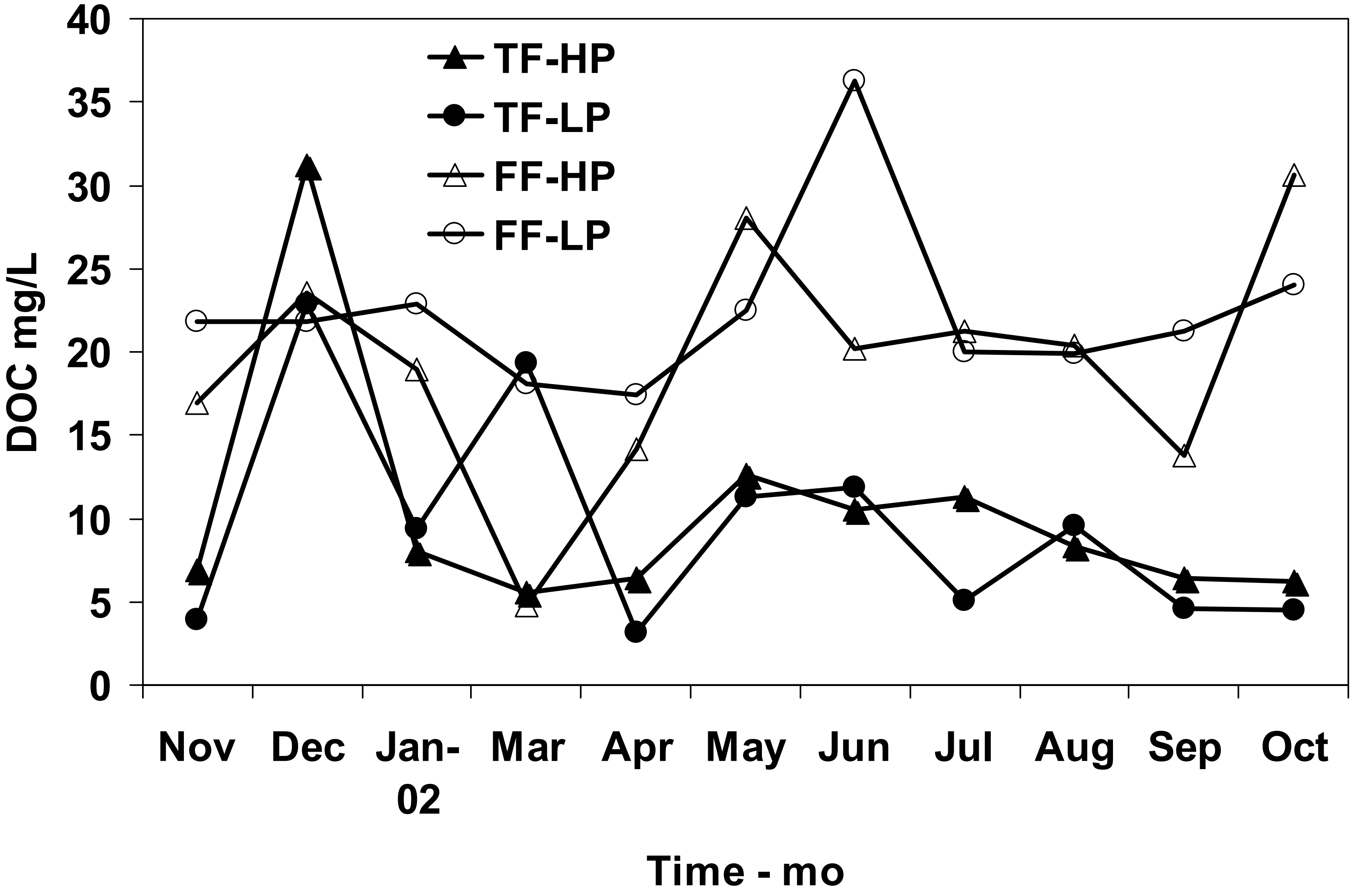

Figure 1. Throughfall (TF) and forest floor leachate (FF) DOC concentration in 11-year old loblolly pine plantations.

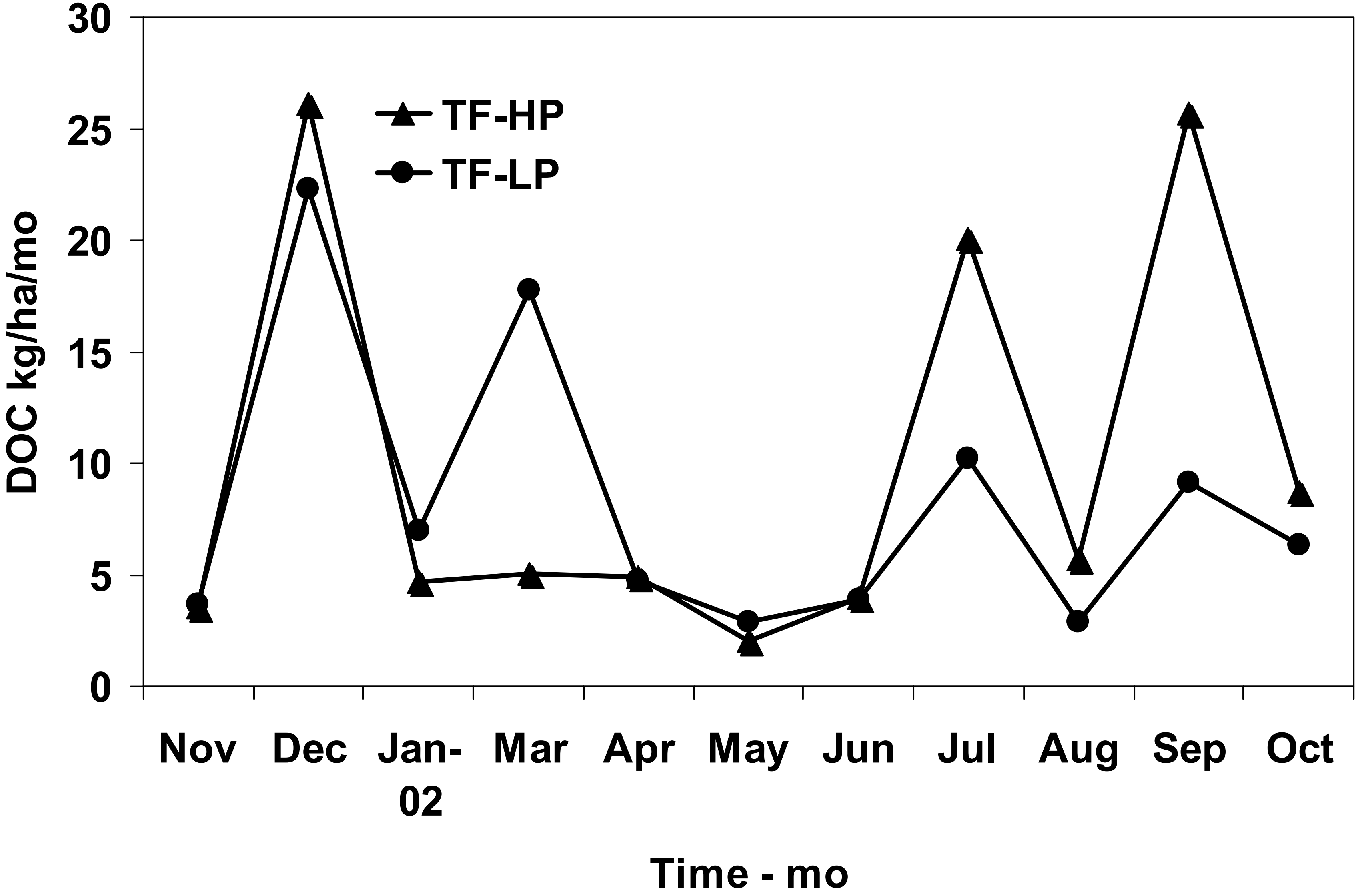

Figure 2. Throughfall (TF) DOC flux in 11-year old loblolly pine plantations.

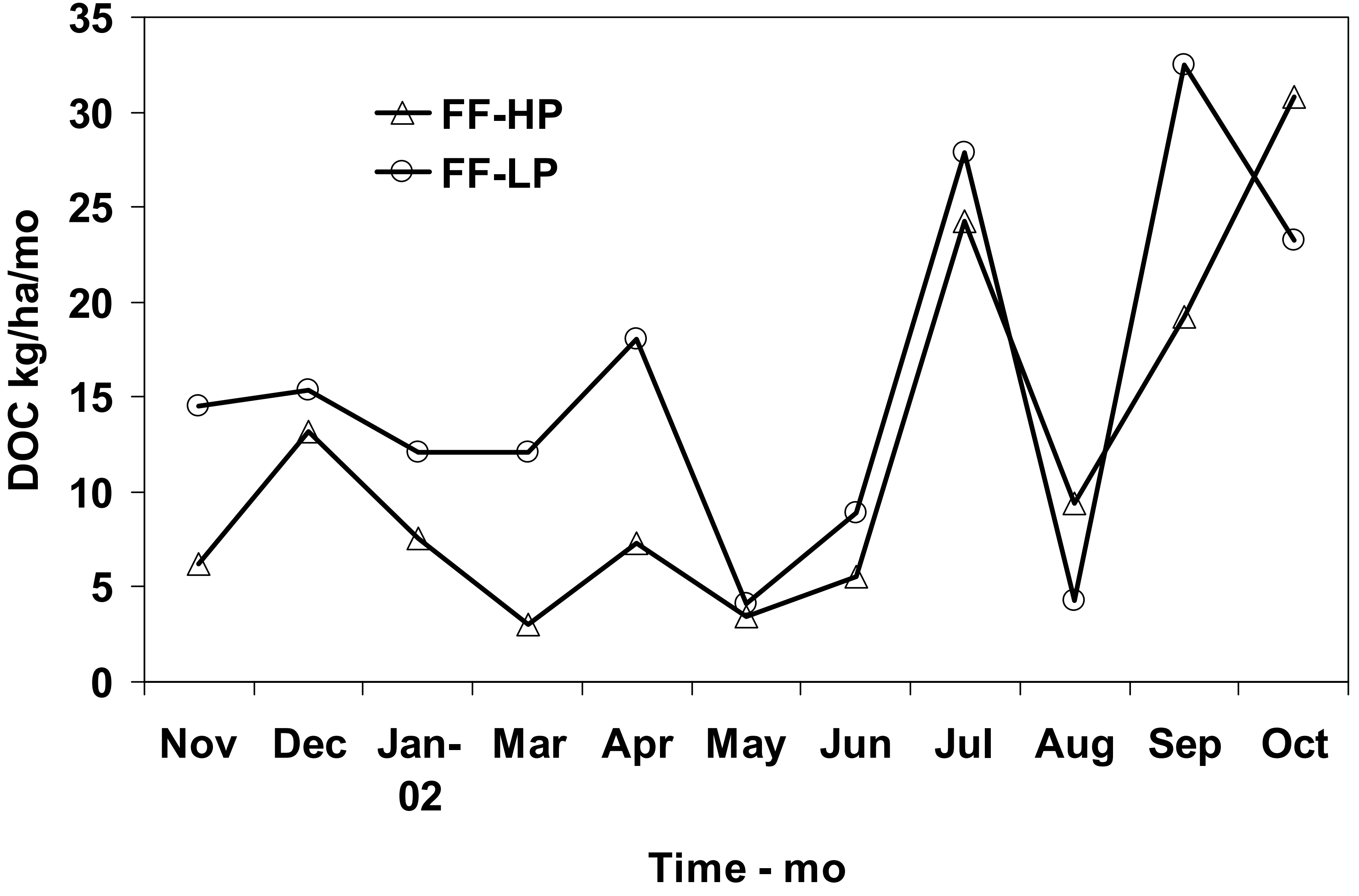

Figure 3. Forest floor leachate (FF) DOC flux in 11-year old loblolly pine plantations.

CHAPTER 3

^{1}H NMR Analysis of DOC from forest floor leachate in loblolly pine plantations

Zakiya H. Leggett and Felipe G. Sanchez

ABSTRACT

The forest floor is a major reservoir of organic matter and nutrients for forest ecosystems. Water soluble organics leaching from the forest floor play an important role in carbon and nutrient turnover and microbial activity. Fertilization may influence the chemistry of dissolved organic carbon (DOC) of forest floor leachate by increasing the labile fraction of carbon (C). Forest floor leachate samples from loblolly pine plantations with contrasting soil textures and/or fertilization regimes were analyzed by liquid state proton nuclear magnetic resonance (^{1}H NMR). The ^{1}H NMR spectrum of the sample from the sandy site revealed the presence of an abundance of alkyl C (83%) with some inclusions of O-alkyl and aromatic C. The sample from the clayey site having received no fertilization had very little presence of alkyl C and was dominated by O-alkyl C (75%) while the sample from the clayey sites that received fertilization had mainly alkyl C (80%) with no presence of aromatic C. Under different environmental conditions resulting from contrasting soil textures, leachate from the same type of forest floor material may vary in its chemical composition. Fertilization may alter the chemistry of the DOC leaching from the forest floor

INTRODUCTION

Investigations into dissolved organic carbon (DOC) dynamics in forested ecosystems have become quite common, especially those studies related to C cycling and storage. Examination of the retention and turnover of DOC is useful in characterizing and quantifying the C storage capacity of forest soils (McCracken et al., 2002).

The forest floor is a major reservoir of organic matter and nutrients for the ecosystem and as such it influences or regulates most of the functional processes occurring throughout the ecosystem (Gosz et al., 1976). With DOC being one of the main transports of C from the forest floor (Andersson and Nilsson 2001) into the soil, it is important to understand the composition of this flux of C. Soluble organic compounds released from organic forest floor layers comprise decomposition products that cover a wide range of chemical structures and molecular weights (Kaiser et al., 2002).

When considering the fluxes of C into the soil ecosystem, the DOC flux is often considered minor as far as magnitude but is important in terms of its ecological influence and significance (Liu and Sheu, 2003). The DOC leaching through the forest floor has been found to be high in carbohydrates and/or consisting of carbon of low molecular weight (McDowell and Likens, 1988; Lichter et al., 2000). These fluxes serve as a major energy source for microbial communities *(*Travnik, 1992), which in turn often influence the mineralization and release of nutrients.

Dissolved organic carbon originating from forest floor leachate may consist of C components of varying resistance to microbial oxidation. In addition, management practices such as fertilization may alter the stability of the C in this forest floor material. Both Janzen et al. (1992) and Nyborg et al. (1999) found that fertilization increased the labile fraction of C in agricultural soils and grasslands, respectively. Sanchez (2001) found that loblolly pine (*Pinus taeda* L.) litter on fertilized plots decomposed at a faster rate as compared with control plots. This alteration in fertilized forest ecosystems may be evident when evaluating the leachate of the forest floor material.

Solid state ^{13}C NMR has been used successfully in numerous studies to characterize changes in the chemistry of decomposing forest organic materials (Baldock and Preston 1995). Liquid state ^{1}H NMR has been used to evaluate changes in solution chemistry of forest floor leachate (Kaiser et al., 2002, Sanchez et al., 2004).

This study was initiated to evaluate variation in the quantity and composition of C constituents in forest floor leachate samples from contrasting soil textures and/or fertilization regimes. It is hypothesized that fertilization will have an influence on the constituent composition and the relative abundance of these constituents in DOC originating from the forest floor.

METHODS

Site Description

Forest floor leachate samples were collected from two sites located in Escambia County, Alabama (31°10' N 87°20’ W) and Greene County, Mississippi (31°25’ N 88°27’ W). The climate was similar at both sites with a mean annual temperature and precipitation of 19 ºC and 1250 mm. The site in Alabama was a well-drained clayey soil of the Greenville (fine, kaolinitic, thermic Rhodic Kandiudults) series and the site in Mississippi was a well-drained sandy soil of the Eustis (siliceous, thermic Psammentic

Paleudults) series. Both sites had the potential to be deficient in soil nutrients, such as nitrogen and phosphorus (Appendix A).

The experiment was installed as a randomized complete block design replicated on 4 blocks. Two fertilization treatments were randomly assigned to the plots in each block: no fertilization (control) versus fertilization at planting with 45 kg N and 50 kg P per hectare. A complete description of the site and experimental design is provided elsewhere (Leggett and Kelting 2004).

Sample and data collection

Zero tension lysimeters made with PVC materials were installed at the interface of the bottom of the forest floor (specifically Oa horizon/ fragmented layer) and the surface mineral soil within each plot. Forest floor leachate was collected in amber glass bottles (45 cm below soil surface) adjacent to the lysimeters. Samples were filtered through glass fiber filters (0.22 microns) within at least 48 hours of collection and stored at 4 °C until further analyses. The samples selected for this study were collected from a control plot on the sandy site in July 2002 and both a control and fertilized plot on the clayey site in August 2002. Only three samples were analyzed in this study because the original purpose of the analysis was to conduct a preliminary examination of carbon chemistry for the DOC samples obtained from the different soil texture and fertilization regimes. To achieve this goal, this study utilized a new method developed by Sanchez et al. (2004) to quantitatively analyze water soluble compounds.

Forest floor samples were collected in December 2001 using a 35 cm x 35 cm grid at six random locations within each plot and composited by plot at the time of collection. The samples were also divided into the Oi (fresh litter or L layer) and Oe+Oa (fragmented litter and humus or F+H layer) layers at the time of collection. Forest floor samples were dried for 12 hours at 80°C and weighed to obtain dry mass. The loss on ignition procedure (Nelson and Sommers, 1996) was used to correct for mineral soil contamination within the forest floor samples.

Sample preparation and analyses

The leachate samples were placed on a hotplate and evaporated down to approximately 5 mL. The samples were then placed in 10 mL test tubes and evaporated to dryness, in a SVC 100H Speed Vac Concentrator (Savant Instruments, Holbrook, NY). Samples were derivatized with trifloroacetic anhydride (TFAA) and dissolved in deuterated chloroform ($CDCl_3$) following the procedures outlined in Sanchez et al. (2004) and analyzed by ^1H NMR.

The ^1H NMR experiments were performed on a Mercury VX 400 Spectrometer (Varian, Inc., Palo Alto, CA) at an operating ^1H frequency of 400.137 MHz by means of a 5 mm 4NUC probe equipped with additional coils for z-gradients. Sixty four scans were collected with a spectral width of 5200 Hz using a pulse width of 7 μsec and a pulse delay of 1 sec. The free induction decays were multiplied by an exponential line broadening function of 0.5 Hz prior to Fourier transformation to improve the signal/noise ratio of the spectra. All chemical shifts are reported relative to trimethylsilane which was used as an external standard. A consistent feature in each spectrum will be a single peak at 7.27 ppm due to the presence of trace amounts of $CHCl_3$ in the solvent. The percentage of the C constituents was obtained from calculating the area under the peaks using Origin Pro 7.0 (OriginLab Corporation, Northampton, MA).

RESULTS AND DISCUSSION

Dissolved organic carbon originating from forest floor leachate consists of several carbon compounds varying in stability and ^{1}H NMR analysis reveals the various carbon constituents that exist in these samples. These constituents can be ranked as far as their resistance to microbial oxidation and grouped by common components of loblolly pine litter and humus material (Table 1).

Results from ^{1}H NMR striking differences for the DOC collected from the different soil texture and treatment combinations. The spectrum of the leachate sample from the control plot on the sandy site (Figure 1) reveals the presence of an abundance (83%, Table 2) of alkyl C (0 – 2.0 ppm) with some inclusions of O-alkyl (1.8 – 5.0 ppm) and aromatic C (6 – 9 ppm). In sharp contrast, the spectrum of the leachate sample from the control plot on the clayey site (Figure 2) had very little presence of alkyl C and was dominated (75%, Table 2) by O-alkyl C with small percentages of aromatic and alkyl C. It is unlikely that the sharp peak at 3.9 ppm in Figure 2 is carbohydrate since carbohydrates tend to produce a mulitplet in this region (Sanchez et al. 2004). Consequently due to its chemical shift, shape and origin, the signal at 3.9 ppm is probably due to simple peptides or amino acids. The spectrum of the leachate sample from the fertilized plot on the clayey site (Figure 3) revealed mainly (80%, Table 2) the presence of alkyl C.

Baldock and Preston (1995) performed ^{13}C NMR analyses on original fresh pine litter and monitored litterbag samples periodically to monitor changes in chemical composition as decomposition proceeds. They found that in progressing from living needles to well-decomposed organic materials, there was a loss of O-alkyl C and an accumulation of alkyl, aromatic and carbonyl C. This trend is also evident based on the results from this study and others (Zech et al. 1992).

Since the Oe+Oa layer is more dominant as far as forest floor mass (Table 3) and potentially influence in the forest floor on these sites, it is predicted that this more decomposed material is contributing the most DOC leaching from the forest floor. This is evidenced in the fact that there is very little O-alkyl C in two of the three samples with a "build-up" of alkyl C which is more resistant to oxidation. This suggests that there is preferential utilization of carbohydrate structures by the microbial communities and accumulation of the more recalcitrant waxes, resins, and cutin. Zech et al. (1992) found that the main features of humification in the investigated forest humus profiles evaluated were preferential mineralization of carbohydrates and accumulation of refractory alkyl components. In addition, Qualls and Haines (1992) found that freshly fallen dead litter contained a large portion of biodegradable DOC and this biodegradability decreased as it percolated downward through the forest floor. Much of the labile soluble organic matter, largely carbohydrates, appeared to decompose before being leached from the litter in their study. This was evident by the forest floor leachate in their study shortly after litterfall containing far less of the labile fraction of soluble organic matter than the freshly fallen litter (Qualls and Haines, 1992).

Based on these results, the control plot on the sandy site seems to be quite diverse as far as its ^{1}H NMR spectrum and overall chemistry. This could result from the fact that this site had a higher soil temperature (Chapter 1) and less developed forest floor as compared to the clayey site (Table 3). These environmental conditions may contribute to a less active microbial community as compared to the other site, especially in comparison to the fertilized plot on the clayey site. Decomposition processes can be influenced by environmental parameters such as temperature, nutrient status, and water content (Baldock and Preston 1995).

When comparing the treatment plots within the clayey site, it can be inferred that the forest floor on the fertilized plot consists of more labile material. The minor presence of O-alkyl C indicates that most of this C as well as the aromatic C (which was non-existent in the ^{1}H NMR spectrum) have been oxidized by the microbial communities in this forested ecosystem. The temperature and the well developed forest floor on this site are favorable environments for this type of activity to take place.

Oades et al. (1988) and Baldock et al. (1992) observed an accumulation of aromatic C during the initial stages of decomposition of organic materials. There is very little (clayey control) or no (clayey fertilized) aromatic presence for the other two plots, relative to the leachate from the sandy control plot. However, there is still some aromatic C found in the forest floor leachate for the sandy control plot which indicates that the forest floor may still be in the initial stages of decomposition. In addition, the fact that there is no aromatic C in the leachate for the clayey fertilized plot could indicate that the forest floor material that has been leached on this plot has progressed past the initial stages of decomposition and therefore further along in this process; indicating that this material may have consisted of mainly labile C constituents that are oxidized quite rapidly. Whether or not aromatic C accumulates during decomposition is thought to be a function of the relationships between the chemical nature of the litter, the composition of the decomposer community, and the environmental conditions (temperature, nutrient status and water content) (Baldock and Preston 1995).

Although this study is limited by its lack of replication, the results imply that under slightly different environmental conditions, decomposition of the same type of forest material may result in different chemical composition of the resultant DOC. In addition, fertilization not only increases the “quantity” of forest floor material but may alter the chemistry of the DOC leaching from the forest floor by increasing the C components least resistant to microbial oxidation.

REFERENCES

Andersson, S. and S.I. Nilsson. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. Soil Biology and Biochemistry. 33:1181-1191.

Baldock, J.A., J.M. Oades, A.G. Waters, X. Peng, A.M. Vassallo, and M.A. Wilson. 1992. Aspects of the chemical structure of soil organic materials as revealed by solid-state ^{13}C NMR spectroscopy. Biogeochemistry 16:1-42.

Baldock, J.A. and C.M. Preston. 1995. Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. *In* W.W. McFee and J.M. Kelly (ed.) Carbon forms and functions in forest soils. Soil Science Society of America, Inc. Madison, WI.

Gosz, J.R., G.E. Likens and F.H. Bormann. 1976. Organic matter and nutrient dynamics of the forest and forest floor in the Hubbard Brook forest. Oecologia. 22:305-320.

Janzen, H.H., C.A. Campbell, S.A. Brandt, G.P. Lafond and L. Townley-Smith. 1992. Light-fraction organic matter in soils from long-term crop rotations. Soil Science Society of America. 56:1799-1806.

Leggett, Z.H. and D.L. Kelting. 2004. Fertilization effects on carbon pools in loblolly pine plantations on upland sandy and clayey soils. Soil Science Society of America Journal. (submitted)

Lichter, J., M. Lavine, K.A. Mace, D.D. Richter, and W.H. Schlesinger. 2000. Throughfall chemistry in a loblolly pine plantation under elevated atmospheric CO2 concentrations. Biogeochemistry. 50:73-93.

Liu, C.P. and B.H. Sheu. 2003. Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. Forest Ecology and Management. 172:315-325.

McCracken, K.L., W.H.McDowell, R.D. Harter, and C.V. Evans. Dissolved organic carbon retention in soils: comparison of solution and soil measurements. Soil Science Society of America Journal. 66:563-568.

McDowell, W.H. and G.E. Likens. 1988. Origin, composition and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs. 58:177-195.

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961-1010. *In* D.L. Sparks (ed.) Methods of Soil Analysis. Part 3 Chemical Methods. SSSA, Madison, WI.

Nyborg, M., S.S. Malhi, E.D. Solberg, and R.C. Izaurralde. 1999. Carbon storage and light fraction C in a grassland Dark Chernozem soil as influenced by N and S fertilization. Canadian Journal of Soil Science. 79:317-320.

Oades, J.M., A.G. Waters, A.M. Vassallo, M.A. Wilson, and G.P. Jones. 1988. Influence of management on the composition of organic matter in red-brown earth as shown by ^{13}C nuclear magnetic resonance. Australian Journal of Soil Research. 26:289-299.

Qualls, R.G. and B.L. Haines 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and stream water. Soil Science Society of America Journal. 56:578-586.

Sanchez, F.G. 2001. Loblolly Pine Needle Decomposition As Affected by Irrigation, Fertilization, and Substrate Quality. Forest Ecology and Management. 152: 85-96.

Sanchez, F.G., Z.H. Leggett and S. Sankar. 2004. Analyzing water soluble soil organics as trifluoroacetyl derivatives by ^{1}H NMR. Communications in Soil Science and Plant Analysis (submitted)

Travnik, L.R. 1992. Allochthonous dissolved organic matter as an energy source for pelagic bacteria and the concept of the microbial loop. Hydrobiologia. 229:107-114.

Zech, W., F. Ziegler, I. Kogel-Knabner, and L. Haumaier. 1992. Humic substances distribution and transformation in forest soils. The science of the total environment. 117/118:155-174.

Table 1. Common types of C examined in ^{1}H NMR and typical examples from loblolly pine litter in order of approximate oxidative resistance.

Order from least to most resistance to microbial oxidation	C constituent	Example from loblolly pine litter and/or humus
1	Carbonyls	Organic acids
2	O-alkyls	Carbohydrates and/or amino acids
3	Aromatics and phenolics	Lignin and tannins
4	Alkyl	Cutin, waxes and lipids

†Table adapted from Zech et al. 1992

Table 2. Percentage data from ^{1}H NMR analysis for C constituents of forest floor leachate in 11-year old loblolly pine plantations on contrasting soil textures and/or fertilization levels.

	Percentage of each type of C		
Site - treatment	O-alkyl	Aromatic	Alkyl
Sandy-control	14	3	83
Clayey-control	75	10	15
Clayey-fertilized	20	-	80

Table 3. Mass of the forest floor in 11-year old loblolly pine plantations on contrasting soil textures and/or fertilization levels.

Site - treatment	Forest Floor Layer	Mass
Sandy-control	Oi	2351
	Oe+Oa	5039
Clayey-control	Oi	3251
	Oe+Oa	7526
Clayey-fertilized	Oi	3776
	Oe+Oa	10793

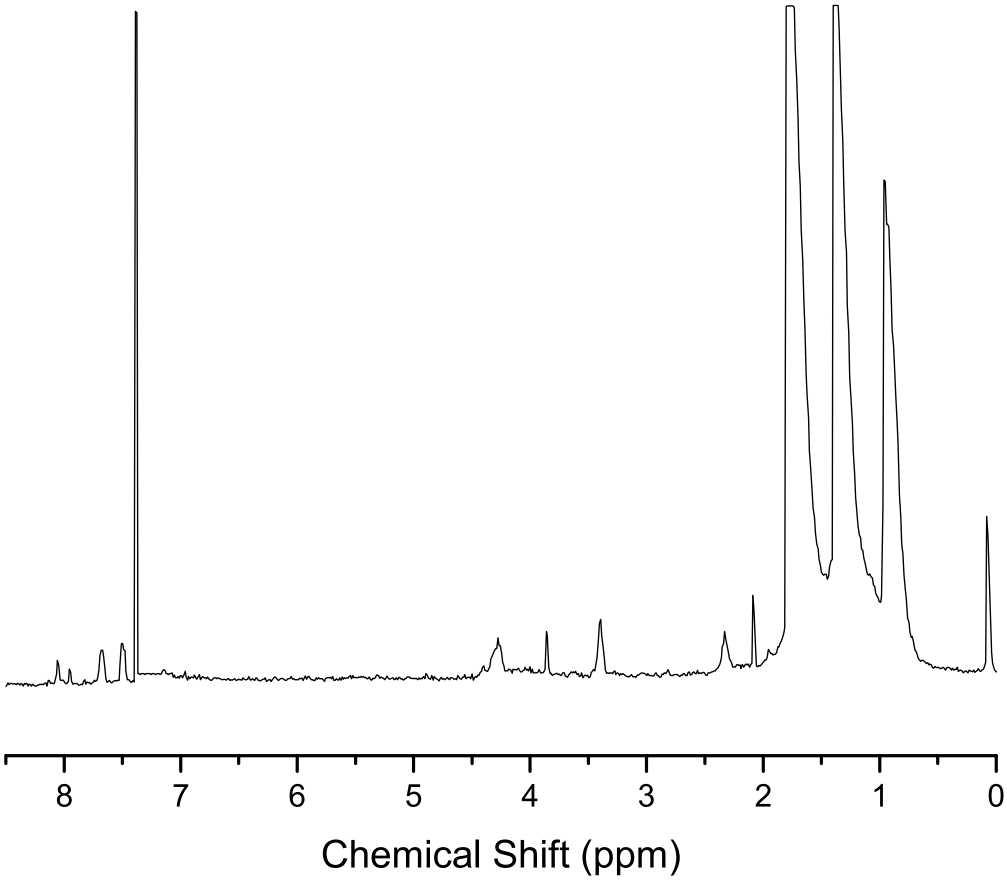

Figure 1 ^{1}H NMR spectrum of DOC samples from control plot on sandy site (Sanchez et al 2004).

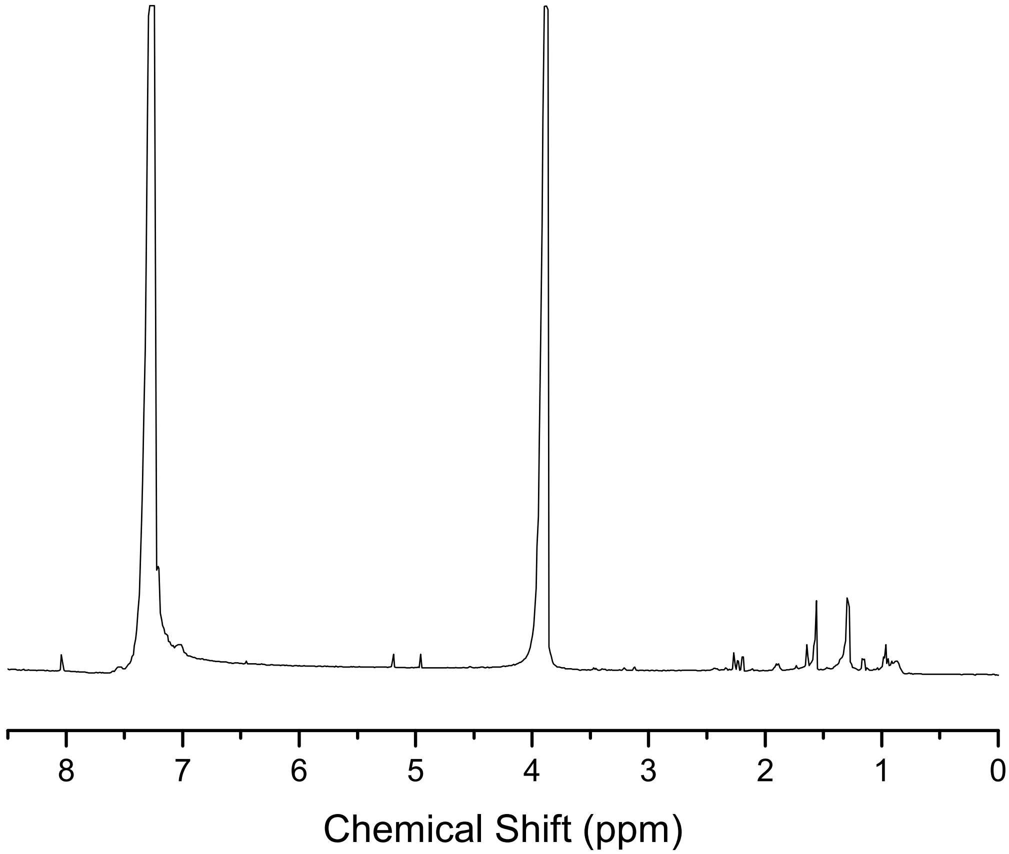

Figure 2 ^{1}H NMR spectrum of DOC samples from control plot on clayey site (Sanchez et al 2004).

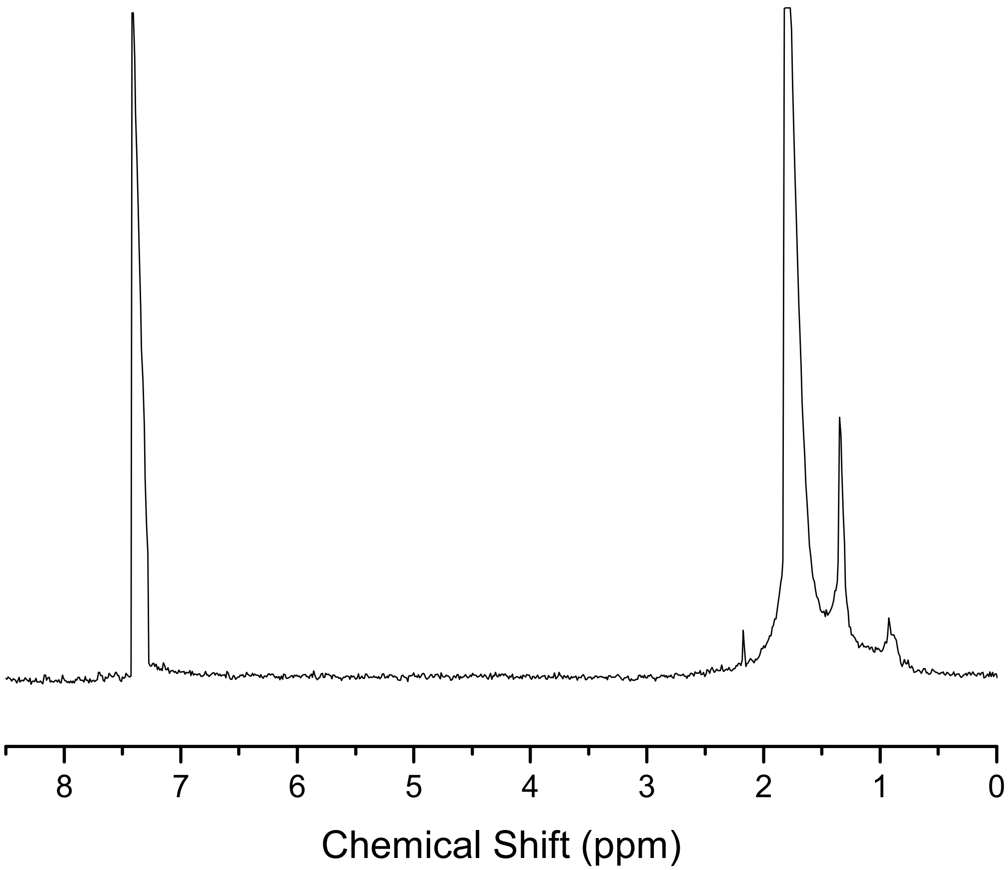

Figure 3 ^{1}H NMR spectrum of DOC samples from fertilized plot on clayey site. (Sanchez et al 2004).

APPENDICES

Appendix A. Soil nutrient data for pretreatment (Year 0) soil samples.

Site	Treatment	Depth	P (%)	N (%)	P (kg/ha)	N (kg/ha)
Clayey (AL)	Control	0-10cm	0.0002	0.103	2.02	1220.32
Clayey (AL)	Control	10-20cm	0.0001	0.063	1.81	938.43
Clayey (AL)	Later Fertilized	0-10cm	0.0002	0.108	2.30	1205.00
Clayey (AL)	Later Fertilized	10-20cm	0.0001	0.070	1.58	1110.41
Sandy (MS)	Control	0-10cm	0.0002	0.052	1.98	681.59
Sandy (MS)	Control	10-20cm	0.0002	0.047	2.51	783.88
Sandy (MS)	Later Fertilized	0-10cm	0.0002	0.054	2.30	699.37
Sandy (MS)	Later Fertilized	10-20cm	0.0002	0.044	2.93	734.50

Appendix B. Statistical summary (probability > F) of site and fertilization effects on total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil from pretreatment (Year 0) soil samples.

Comparison	Effect	Total Carbon	
		- g kg^{-1} -	- Mg ha^{-1} -
Across Depths	Site	0.065	0.114
	Plots later grouped by Treatment	0.992	0.723
	Depth	0.005	0.346
	Depth*Site	0.005	0.132
Within 0- to 10-cm depth	Site	0.039	0.037
	Replicate(Site)	0.085	0.164
	Plots later grouped by Treatment	0.760	0.917
Within 10- to 20-cm depth	Site	0.189	0.205
	Replicate(Site)	0.191	0.277
	Plots later grouped by Treatment	0.291	0.254

Appendix C. Statistical summary (probability > F) of site and fertilization effects on the resulting difference of Year 11 – Year 0 for total C concentration and content of the fine earth fraction (<2 mm) of the surface 0- to 20-cm of mineral soil.

Comparison	Effect	Total Carbon	
		- g kg^{-1} -	- Mg ha^{-1} -
Across Depths	Site	0.577	0.926
	Fertilization	0.217	0.158
	Site* Fertilization	0.823	0.926
	Depth	0.089	0.006
Within 0- to 10-cm depth	Site	0.874	0.771
	Fertilization	0.466	0.367
	Site* Fertilization	0.578	0.661
Within 10- to 20-cm depth	Site	0.486	0.479
	Fertilization	0.574	0.547
	Site* Fertilization	0.319	0.251