PAST, PRESENT, AND FUTURE
SOIL NITROGEN AND PHOSPHORUS DYNAMICS
IN SOUTHERN APPALACHIAN FORESTS

by

KAITLIN JOAN MCLEAN

(Under the Direction of Dr. Jacqueline E. Mohan)

ABSTRACT

Along with climate, nitrogen (N) and phosphorus (P) dynamics in forest ecosystems are critical drivers of forest health, productivity, and carbon (C) balances. In this study, five plots were established at the Coweeta Hydrologic Laboratory in Otto, NC, along a natural elevation, temperature, moisture, and vegetation gradient. These plots established long-term measurements including throughfall, soil nutrients, and soil solution leachate, to better understand the effects of global change on forest biogeochemical cycles. Based on previous measurements in the gradient plots, it was hypothesized that the highest elevation site would receive the most N and P input via throughfall and also the greatest response to increased N and PO_4 deposition, temperature, and moisture dynamics. These hypotheses were supported by throughfall N amounts, N soil transformations, soil P pool fractionation, and quantities of N and P in soil solution leachates in 2010.

INDEX WORDS: nitrogen (N), phosphorus (P), global change, southern Appalachian forests

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B.S. Biology, Salem College, 2007

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2011

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May 2011

DEDICATION

To Brandon Mark McMahan, my future husband, because we are always trying to make the future better through everything we do.

ACKNOWLEDGEMENTS

I would first like to thank all my family and friends for all their support and encouragement. I am eternally grateful to Brandon McMahan for helping me in every way he was able with field work, lab work, editing, and encouragement. I would like to thank and acknowledge my mother for always having faith in me. I would like to express my appreciation to all the folks at the Coweeta Hydrologic Lab for getting me excited about ecological work when I was a summer student, and then encouraging me as I continued the journey to graduate school. I would like to acknowledge my major advisor, Jackie Mohan, and the rest of my committee, Jennifer Knoeep, Paul Hendrix, and Bob Teskey for their continuous feedback and support. I would also like to acknowledge two non-committee members that offered a great deal of feedback, Miguel Cabrera and Dan Markewitz. I would also like to thank my lab group, Katy Bridges, Fern Lehman, Shafkat Khan, Peter Baas, and Megan Machmuller for feedback and cheers. I would also like to thank Corinne Block for commiserating with me on phosphorus fractionations. I would like to acknowledge Jason Love, Jason Meador, Pat Stickney, and Kathy Flowers for help with logistics and field work at the Coweeta Hydrologic Lab research site. I would like to acknowledge the sample handling and processing work done by Cindi Brown, Carol Harper, Sheila Gregory, and Neal Muldoon in the Coweeta wet lab. I would also like to thank those who worked hard on my soil samples at the Whitehall Philips lab and the Ecology analytical lab. Finally, I would like to thank Ted Gragson and the rest of the Coweeta LTER PIs for their funding through the National Science Foundation, and their support and feedback as I completed my project.

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Global climate change is expected to affect temperature, precipitation, nutrient availability, and species distributions (Schlesinger 1997, Iverson & Prasad 1998, Melillo et al. 2002, IPCC 2007). According to the 2007 Intergovernmental Panel on Climate Change (IPCC) report increased levels of atmospheric carbon dioxide (CO_2) is the primary agent behind current and future warming trends, and results from fossil fuel emissions and land-use change (IPCC 2007). Between 1970 and 2004 annual CO_2 emission grew by about 80% and in 2005 atmospheric concentrations of CO_2 reached 379ppm exceeding the natural range over the last 650,000 years (IPCC 2007). Increased levels of atmospheric CO_2 has led to rising average global surface temperatures. 1995 through 2006 were ranked among the twelve warmest years since 1850, when instrumental records began. Unlike temperature, precipitation is not as simple to predict, but what has ben happening over the past 50 years in the southeastern U.s. and what is is projected for the future is increased variability is precipitation (IPCC 2007, Li et al. 2010). According to the United States Global Change Research Program (USGCRP) report from June 2009, the U.S. has experienced a 5% overall increase in precipitation over the last 50 years. This precipitation increase was attributed to more intense storms.

With increased atmospheric CO_2 concentrations efforts are being focused on potential carbon storage. Forests are being increasingly examined as possible “sinks” for carbon; however, in order to employ forests as carbon sinks we must determine what gives forests the ability to grow and store carbon and, in turn, whether humans can manage these processes (Luyssaert 2008). According to Lafleur et al. (2010) while climate change could potentially lead to species migration, the role of soils will be a crucial determinant of species‟ abilities to recruit and migrate. In addition to the Lafleur et al. (2010) study, previous work at the Harvard Forest LTER has shown that many of the climate warming impacts on tree dynamics are mediated through climatic impacts on soil nutrient processes (Melillo et al., in press).

While there is much climate change research targeting the use of forests as carbon sinks, far less is known about potential effects of soil nitrogen (N) and phosphorus (P) limitations on future forest productivity as a result of climate change (LeBauer and Treseder 2008, Schlesinger 1997). Across ecosystems N and P are both important in organismal growth and thus are important in net primary production (NPP) and carbon sequestration (Schlesinger 1997). A solid understanding of the limitation of N and P in ecosystems is fundamental to understanding overall ecosystem function and forecasting future system function. N and P are common limiting factors in temperate and tropical systems. Past research supports a common N limitation in temperate systems and a P limitation in tropical systems (Vitousek & Howarth 1991, Vitousek et al. 2010, & Walker & Syers 1976), although more current work suggests a global distribution for forest N limitation (LeBauer & Treseder 2008). On highly-weathered soils of the southeastern U.S. and predicted increases in anthropogenic N deposition it is possible that southeastern forests will become P limited or N and P co-limited.

The idea of limitation itself has become more complex with increasing research. A common understanding of limitation comes from Liebig"s Law of the Minimum, which states that if one nutrient is lacking, then plant growth will be poor even if other nutrients are in abundance (Danger et al. 2008). However, this can be complicated by such factors as multiple limitations. which may be common in nutrients with linked biogeochemical cycles such as N and P (Schlesinger 1997, Vitousek et al. 2010, & Walker & Syers 1976). Another complication of limitation is that of species-specific limitation by different environmental resources in multiple species systems such as temperate forests. For example, one tree species may be water limited, while another with deeper tap roots is not. Another example might be where the plant species are limited by a nutrient, but the surrounding soil microbes may be limited by another nutrient. All of these scenarios complicate the generalization of ecosystem limitation. In addition to limitation there may be a close linkage between N and P, and N and P ratios can be used to predict carbon sequestration potential (Parton 1988). Finzi et al. (2011)stresses the need to include N and P cycles in the general circulation models (GCM‟s) that are used to predict future carbon dynamics and climate. The relationship between N and P may be a synergistic, where one may enhance the biological action of the other, while both remain important for forest productivity and carbon storage. Work by Houlton et al. (2008) suggests plant-available N may enhance plant acquisition of P by increasing levels of phosphatase enzymes used by plants to acquire P from the soil. Another model proposed by Perring et al. (2007) suggested that if either plant-available N or plant-available P is limited in a system, the other nutrient will become plant-limited as well. This may occur due to the limitation of one nutrient inhibiting a plant‟s ability to acquire the other nutrient from the soil.

With increased temperatures due to anthropogenic emissions of heat trapping gases including CO_2, the southeastern United States is expected to become warmer with decreased total summer precipitation (USGCRP 2009), increased summer (growing season) precipitation variability, which would include periods of drought and deluge (IPCC 2007, Li et al. 2010). This presents a question as to how southeastern forests, including the traditionally cool and moist southern Appalachian forests, will respond. In addition to temperature and precipitation change as a result of global climate change, nutrient dynamics are expected to change as anthropogenic nitrogen deposition increases in the southeastern United States, particularly as the region becomes increasingly urbanized (atmospheric nitrate (NO_3) is relatively short-lived, and generally deposits near anthropogenic sources) (IPCC 2007, Li et al. 2010).

In addition to increased atmospheric $CO_{2,}$ atmospheric N has also increased with increased fossil fuel use and large scale land use change toward food production. From 1980 to 2020 N deposition in North America is predicted to increase more than 50% (Galloway et al. 1994, Galloway et al. 2008). A study by Aber et al. (1989) found that with increased N deposition a previously N limited forest became saturated with N, which led to declines in productivity as well as acidification of forest soils and streams and forests becoming a source of N rather than a sink (Galloway et al. 1994, Galloway et al. 2008, Goulding et al. 1998, Van Miegroet and Jandl 2007).

In addition to N deposition, the anthropogenic deposition of particulate P is increasing, although natural atmospheric sources of gaseous P are extremely rare (Schlesinger 1997). At study by Mahowald et al. (2008) examined sources of P deposition and found that phosphorus in areas influenced by industrialization or biomass burning, such as the southeastern United States, as much as 50% of total P deposition can be contributed to anthropogenic influence (2008). This suggests that P deposition dynamics may also be increasing.

Further, southern Appalachian tree species distribution is expected to change, which in turn may affect both forest carbon sequestration and nutrient availability (Iverson & Prasad 1998). Understanding biogeochemical dynamics and nutrient limitation(s) in southern Appalachian forests under global climate is critical for predicting how these forests will look and function in the next century and beyond. Thus the issue of global change increases the urgency of learning more about the biogeochemistry of N and P in forest systems, particularly in southern Appalachian forests which serves as a global hotspot for temperate tree species diversity.

The temperate forests of the southern Appalachian Mountains have traditionally been considered to be N-limited systems (Knoepp et al. 2008, Knoepp and Vose 2008). The potential of N limitation for forest productivity and species composition is especially important, given that upper elevations in the southern Appalachians currently receive high levels of anthropogenic N deposition from industrial and agricultural sources (Knoepp et al. 2008). Future deposition rates will depend in part on the continuing exacerbation and development of the southern Appalachian regions. With increased N deposition it is possible that another factor, such as P, will become limiting in southern Appalachian forests. If southern Appalachian forests prove to be limited by N and not P, rates of productivity and carbon storage in these ecosystems may continue to be enhanced through N deposition (LeBauer and Treseder 2008). Conversely, if P limitation is important in these forests and is not alleviated by increases in N availability, anthropogenic N deposition, which is projected to increase in the future, will not enhance productivity and carbon storage by southern Appalachian forest ecosystems and the importance of P for these forests becomes even more critical.

In order to better understand temperature, precipitation, nutrient availability, and species distributions in southern Appalachian forest ecosystems, gradient plots were established in 1991 as a part of the Coweeta Long-term Ecological Research (LTER) project, funded by the National Science foundation (Knoepp and Swank 1998). The gradient plots were established for intensive measurement purposes such as throughfall chemistry, soil nitrogen transformations, soil solution chemistry, and above ground vegetation productivity (Clark et al. 1998, Knoepp et al. 2008). The plots were placed along a natural elevation, temperature, moisture, vegetation gradient at Coweeta and were representative of four southern Appalachian forest types: mixed-oak pine (OP), cove hardwoods (CH), low elevation mesic mixed oak (MO-L), high elevation mesic mixed oak (MO-H), and northern hardwoods (NH) (Clark et al. 1998, Knoepp et al. 2000, Knoepp and Vose 2007, Knoepp et al. 2008).

Knoepp et al. (2008) took throughfall measurements examining nutrients coming into the systems and found that throughfall NO_3 concentrations were greatest at the mixed oak sites, while throughfall ammonium (NH_4) concentrations were greatest at the high elevation sites, the MO-H and NH forests. This suggests that species composition and canopy-precipitation interactions may be just as important as nutrient deposition for nutrients entering the system through throughfall (Knoepp et al. 2008).

Previous work on the Coweeta gradient plots has documented greater rates of summer N mineralization at the NH plot, containing mostly tree species commonly found in the cool moist forests of New England (Knoepp et al. 2008, Knoepp and Vose 2007). This high rate of mineralization is interesting, as N mineralization is generally enhanced by warmer temperatures (Melillo et al. 2002), and the NH plot is the coolest of the Coweeta series (Knoepp & Swank 1998, Knoepp et al. 2008, Knoepp and Vose 2007). However, summertime (July, August) N mineralization rates at the Harvard Forest LTER are often not stimulated by soil warming, as microbial activity is limited by soil moisture during this part of the year (Melillo et al., in press). Coweeta‟s NH gradient plot is also the wettest of the plots, and thus may be able to sustain greater rates of N mineralization in the spring and summer. It was also concluded by Knoepp and Swank (1998) that species composition may be driving N mineralization by controlling substrate quality, emphasizing the importance of species composition in addition to temperature and moisture effects.

For soil solution collected from lysimeters Knoepp et al. (2008) found the greatest concentration of NO_3 in the the NH plot while other plots did not differ significantly in regards to NO_3 in soil solution. Similarly, Knoepp et al. (2008) found the NH plot and the MO-L plot had significantly greater NH_4 than the OP plot. This suggests that nutrients in the soil solution mostly indicate spatial and temporal plant nutrient availability, which may be driven by species composition (Knoepp et al. 2008).

These pervious measurements on the Coweeta gradient plots were done from 1991, when the plots were established though 2001. A more current biogeochemical profile of these gradient plots done throughout the year would offer more insight into the possible N and P patterns in these southern Appalachian forests and these dynamics may be changing over time. Thus, N soil transformations, P soil pool fractionation, and soil solution nutrient measurements were once again initiated on the Coweeta gradient plots in October 2009 and were continued through December 2010.

Although these measurements have been done before, in the light of new research and updated technology, the methods for some of these measurements have been changed. For example, previous throughfall samples were collected using six 0.15 x 2.0 meter troughs spaced randomly throughout the intensive gradient plots. These samples were collected weekly, then composited for a monthly throughfall analysis of NH_4, NO_3, and phosphate (PO_4) concentrations (Knoepp et al. 2008). The throughfall troughs required frequent sampling, because the longer a sample is in the field there is a greater risk of sample degradation particularly for NH_4 (Fenn et al. 2009). In contrast the 2010 throughfall measurements were done using mixed bed ion exchange resin columns developed by Fenn and Poth (2004), which have been tested to retain sample concentrations for as long as 12 months in the field (Fenn et al. 2009). The mixed bed ion exchange resin column sampling method not only gives comparable results to wet throughfall measurements while maintaining sample integrity, but it also can greatly reduce the cost of sampling and analysis (Fenn et al. 2002, Fenn et al. 2009, Simkin et al. 2004).

Another method that was changedwas the method for measuring N transformations in the soil. Previously, N transformation measurements were done on the gradient plots using *in situ* closed PVC core incubation 0-10 cm into the mineral soil. After collection the soils were moist sieved and extracted with potassium chloride (KCl) within 24 hours (Knoepp and Swank 1998, Knoepp et al. 2000, Knoepp et al. 2008). While the *in situ* closed PVC core method was retained as it is reported to be the best method for reflecting true site N mineralization (Knoepp and Swank 1995, Van Miegroet and Jandl 2007), the time in which the sample soils were sieved and extracted was shortened from approximately 24 hours to 15-20 minutes for initial samples and 15-45 minutes for field-incubated samples (Knoepp et al. 2008). A study by Ross and Hales (2003) found that sampling could create enough disturbance to increase NH_4 in the soil sample, which suggests that immediate extraction in KCl may give a more realistic estimation of NH_4 concentrations in the soil. Additionally, the soil organic and mineral layers were separated to determine N transformations within the individual layers. Persson and Wirén (1995) found that in soils with a low pH around 4.1–4.5, like the gradient plot soils, nitrification occurred primarily in the organic layer. In contrast Trap et al. (2009) found as forest stands matured nitrification in the organic layer significantly decreased, while N mineralization in the organic layers increased. In addition to soil N transformation methodology changes, P soil analysis was also changed. Previous soil P measurements were done using the initial PVC core taken for N transformations. These samples were analyzed for PO_4-P concretions using a using a double acid extraction (Knoepp et al. 2008, Personal Communication with Knoepp). In order to gain a better understanding of the different soil P pools archived 2008 soil samples taken at three different depths on the gradient plots were extracted using a modified Psenner P fractionation. This modified Psenner P fractionation determined amounts of labile P, reducible iron (Fe) P, aluminum (Al) and some Fe-P, exposed apatite-P, and refractory and residual P pools (Psenner et al. 1988, SanClements 2009, SanClements et al. 2009). The fractionation procedure allows for comparisons between the various pool sizes to better understand the plant available P pools and unavailable P pools in the gradient plot soils.

The methodology which remained the most consistent between the previous measurement and the 2010 measurement was that of nutrient soil solution measurements. Like the previous methods the 2010 soil solutions were collected using lysimeters placed at two different depths in the soil: 15 cm into the soil and 30 to 85 cm into the soil into the lower area of the B horizon (Knoepp et al. 2008, Knoepp et al. 2000). The only changes that were made were done in regards to when and how the samples were collected and handled. Previously lysimeter samples were collected weekly, but were composited for monthly analysis (Knoepp et al. 2008, Knoepp et al. 2000). In contrast in 2010 lysimeters samples were collected every-other week and paired for monthly analysis. This was done on the basis of a better understanding of sample handing in the lab to better preserve sample integrity.

Finally, to gain a better understand of what effects these nutrients (N and P) will have in southern Appalachian forests a predictive model was developed using STELLA®. The model was parameterized with the most recent data collected on the gradient plots and was modified with temperature, precipitation and deposition rates predicted with future global change.

These methods were used to explore the following questions:

1) Have patterns of N dynamics in the gradient plots changed as a result of warmer temperatures and increased N deposition representing N input to the system? (Chapter 2 and Chapter 4)

2) Has N deposition caused a saturation effect and thus changed nutrient limitation dynamics in the system? (Chapter 2 and Chapter 4)

3) Will N deposition continue to be a concern for future southern Appalachian forests such as those represented by the gradient plots? (Chapter 3 and Chapter 4)

4) Have patterns of PO_4 dynamics in the gradient plots changed as a result of increased PO_4 deposition and thus P input to the system? (Chapter 2 and Chapter 4)

5) Has plant-available P become limited possibly as a result of increased N availability? (Chapter 2 and Chapter 4)

6) What effects will global climate change have on P dynamics in future southern Appalachian forests such as those represented by the gradient plots? (Chapter 3 and Chapter 4)

ACKNOWLEDGEMENTS

The author would like to acknowledge Jennifer D. Knoepp for in-depth descriptions of measurement methods used on the Coweeta LTER gradient plots.

LITERATURE CITED

Aber, John D., Knute J. Nadelhoffer, Nitrogen saturation in northern forest ecosystems. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39(6): 378-386.

Fenn, Mark E., and Mark A. Poth. 2004. Monitoring Nitrogen Deposition in Throughfall Using Ion Exchange Resin Columns: A Field Test in the San Bernardino Mountains. Journal of Environmental Quality 33:2007–2014.

Fenn, Mark E., Mark A. Poth, and Micheal J. Arbaugh. 2002. A hroughfall Collection Method Using Mixed Bed Ion Exchange Resin Columns. The Science World Journal 2: 122-130.

Fenn, Mark E. J.O. Sickman, A. Bytnerowicz, D.W. Clow, N.P. Molotch, J.E. Pleim, G.S.

Tonnesen, K.C. Weathers, P.E. Padgett and D.H. Campbell. 2009. Chapter 8: Methods for Measuring Atmospheric Nitrogen Deposition Inputs in Arid and Montane Ecosystems of Western North America Developments in Environmental Science, Volume 9: 179-228. Elsevier Ltd.

Galloway, James N., Hiram Levy, II, Prasad S. KasibhatlaSource. 1994. Year 2020: Consequences of Population Growth and Development on Deposition of Oxidized Nitrogen. Ambio 23(2): 120-123.

Galloway, James N., Alan R. Townsend, Jan Willem Erisman, Mateete Bekunda, Zucong Cai, John R. Freney, Luiz A. Martinelli, Sybil P. Seitzinger, and Mark A. Sutton. 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320: 889-892.

Goulding, K.W.T., N.J. Bailey, N.J. Bradbury, P. Hargreaves, M. Howe, D.V. Murphy, P.R. Poulton, and T.W. Willison. 1998. Nitrogen Deposition and its Contribution to Nitrogen Cycling and Associated Soil Processes. New Phytologist 139(1): 49-58.

Houlton, Benjamin Z., Ying-Ping Wang, Peter M. Vitousek, and Christopher B. Field. 2008. A unifying framework for dinitrogen fixation in the terrestrial biosphere. Nature 454(7202): 327-U334.

Intergovernmental Panel on Climate Change (IPCC). 2007. Climate Change 2007: Mitigation of Climate Change. Summary for Policymakers e Working Group III contribution to the Environmental Panel on Climate Change Fourth Assessment Report: 35.

Iverson, Louis R., and Anantha Prasad. 1998. Predicting abundance of 80 species following climate change in the Eastern United States. Ecological Monographs 68(4): 465-485.

Knoepp, Jennifer D., and Wayne T. Swank. 1995. Comparison of Available Soil Nitrogen Assays in Control and Burned Forested Sites. Soil Science Society of America 59(6): 1750-1754.

Knoepp, Jennifer D., and Wayne T. Swank. 1998. Rates of Nitrogen Mineralization across an Elevation and Vegetation Gradient in the Southern Appalachians. Plant and Soil 204: 235-241.

Knoepp, Jennifer D. and James M. Vose. 2007. Regulation of nitrogen mineralization and nitrification in Southern Appalachian ecosystems: Separating the relative importance of biotic vs. abiotic controls. Pedobiologia 51: 89-97.

Knoepp, Jennifer D., David C. Coleman, D.A. Crossley Jr., and James S. Clark. 2000. Biological indices of soil quality: an ecosystem case study of their use. Forest Ecology and Management 138: 357-368.

Knoepp, Jennifer D., James M. Vose, and Wayne T. Swank. 2008. Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests. International Journal of Environmental Studies 65: 389-408.

Lafleur, Benoit, David Pare´, Alison D. Munson, and Yves Bergeron. 2010. Response of northeastern North American forests to climate change: Will soil conditions constrain tree species migration? Environmental Reviews 18: 279–289.

LeBauer, D.S. and K.K. Treseder. 2008. Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. Ecology 89: 371-379.

Li, Wenhong, Laifang Li, Rong Fu2 Yi Deng, and Hui Wang. 2010. Changes to the North Atlantic Subtropical High and Its Role in the Intensification of Summer Rainfall Variability in the Southeastern United States. Journal of Climate: http://journals.ametsoc.org/doi/abs/10.1175/2010JCLI3829.1

Luyssaert, Sebastiaan, E. -Detlef Schulze, Annett Börner, Alexander Knohl, Dominik Hessenmöller, Beverly E. Law, Philippe Ciais, and John Grace. 2008. Old-Growth Forests as Global Carbon Sinks. Nature 455: 213-216.

Mahowald, Natalie, Timothy D. Jickells, Alex R. Baker, Paulo Artaxo, Claudia R. Benitez-Nelson, Gilles Bergametti, Tami C. Bond, Ying Chen, David D. Cohen, Barak Herut, Nilgun Kubilay, Remi Losno, Chao Luo, Willy Maenhaut, Kenneth A. McGee, Gregory S. Okin, Ronald L. Siefert, and Seigen Tsukuda. 2008. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. Global Biogeochemical Cycles 22.

Melillo J.M., P. A. Steudler, J. D. Aber, K. Newkirk, H. Lux, F. P. Bowles, C. Catricala, A. Magill, T. Ahrens, and S. Morrisseau. 2002. Soil warming and carbon-cycle feedbacks to the climate system. Science 298: 2173–2176.

Melillo, J. M., S. Butler, J. Johnson, J. E. Mohan, P. A. Steudler, H. Lux, E. Burrows, F. Bowles, R. Smith, T. Hill, C. Vario, A. J. Burton, Y. Zhou, J. Tang. 2011. Soil Warming, carbon-nitrogen, integrations and forest carbon budgets. Proceedings of the National Academy of Sciences.

Parton, W. J., J. W. B. Stewart, and C. V. Cole. 1988. Dynamics of C, N, P and S in Grassland Soils. Biogeochemistry 5: 109-31.

Perring, Michael P., Lars O. Hedin, Simon A. Levin, Megan McGroddy, and Claire de Mazancourt. 2007. Increased plant growth from nitrogen addition should conserve phosphorous in terrestrial ecosystems. PNAS 15(6): 1971-1976.

Persson, T. and A. Wirén. 1995. Nitrogen mineralization and potential nitrification at different depths in acid forest soils. Plant and Soil 168-169: 55-65.

Psenner, R., B. Bostrom, M. Dinka, K. Petterson, R. Pucsko, and M. Sager. 1988 Fractionation of phosphorus in suspended matter and sediment. Arch Hydrobiol Beih Ergebn Limnol 30: 98-103.

Ross, Donald S. and Heidi C. Hales. 2003. Sampling-Induced Increases in Net Nitrification in the Brush Brook (Vermont) Watershed. Soil Science Society of America 67(1): 318-326.

SanClements, Michael D. 2009. The Chemistry of Acidic Soils in Humid, Temperate Forested Watersheds with Emphasis on Phosphorus, Aluminum, and Iron. University of Maine, Orono, ME.

SanClements, Michael D., Ivan Fernadndez, and Stephen A. Norton. 2009. Forest Ecology and Management 258: 2318-2325.

Schlesinger, William H. 1997.Biogeochemistry :An Analysis of Global Change. NY Academic Press. Simkin, Samuel M., David N. Lewis, Kathleen C. Weathers, Gary M. Lovett, and Kirsten and Schwarz. 2004.Determination of sulfate, nitrate, and chloride in throughfall using ion-exchange resins. Water, Air, and Soil Pollution 153: 343–354.

Trap, Jean, Frabrice Bureau, Marthe Vinceslas-Akpa, Richard Chevalier, and Michael Aubert. 2009. Changes in soil N mineralization and nitrification pathways along a mixed forest chronosequence. Forest Ecology and Management 258(7): 1284-1292.

United States Global Change Research Program (USGCRP). 2009. State of the knowledge report of Global Climate Change impacts in the U.S.

Van Miegroet, Helga. 1995. Inorganic nitrogen determined by laboratory and field extractions of two forest soils. Soil Science Society American Journal 59:549-553.

Van Miegroet, Helga, and Robert Jandl. 2007. Are nitrogen-fertilized forest soils sinks or sources of carbon? Environmental Monitoring and Assessment 128: 121-131.

Vitousek, P.M. and R.W. Howarth. 1991. Nitrogen limitation on land and in the sea – how can it occur? Biogeochemistry 13: 87–115.

CHAPTER 2

SOIL NITROGEN DYNAMICS IN FIVE SOUTHERN APPALACHIAN FOREST LOCATED IN THE COWEETA LONG-TERM ECOLOGICAL REASEACH GRADIENT PLOTS

McLean, K.J., J.E. Mohan, and K.D. Knoepp. To be submitted to *Biogeochemistry*.

ABSTRACT

Nitrogen (N) dynamics have long been considered critical components of boreal and temperate forest functioning, but are currently being impacted by increased N deposition and increasing global and regional temperatures. Five plots were established at the Coweeta Hydrologic Laboratory in Otto, NC along a natural elevation, temperature, moisture, and vegetation gradient. These plots were established for long-term observational measurements including throughfall, N soil transformations, and soil solution leachate to better understand the effects of global climate change on temperate forest biogeochemical cycles. Based on previous measurements at this site it was hypothesized that the highest elevation site would receive the most N input into the system via throughfall and as one of the most climatically extreme sites, would also have the greatest biogeochemical responses to increased N deposition, temperature, and moisture dynamics. These hypotheses were supported by throughfall N amounts, N soil transformations, and quantities of N in soil solution leachates in 2010.

INDEX WORDS: Nitrogen, N, southern Appalachian forests, throughfall, mineralization, nitrification, soil solution

INTRODUCTION

It is projected that under global climate change scenarios that the southeastern United States will become warmer and drier, with decreased summer precipitation (USCCS 2009), increased summer temperatures (USGCRP 2009), increased summer (growing season) precipitation variability, with increased periods of both drought and intense rainfall (IPCC 2007, Li et al. 2010). In addition to temperature and precipitation impacts, nutrient dynamics are expected to change as anthropogenic nitrogen (N) deposition increases. Galloway et al. (1994) predicted that from 1980 to 2020, N deposition in North America will increase more than 50% (Galloway et al. 2008). Nitrate (NO_3) has a short mean residence time in the atmosphere (Schlesinger 1997) and generally deposits near anthropogenic sources;

thus, as the southeastern United States become more urbanized, as predicted, atmospheric nitrate (NO_3) deposition is expected to further increase (IPCC 2007, Li et al. 2010, Schlesinger 1997). A study by Aber et al. (1989) found that with increased N deposition forests may decline in productivity as a result of N saturation and acidification, which can cause forests to become a source for N rather than a sink (Galloway et al. 1994, Galloway et al. 2008, Goulding et al. 1998, Van Miegroet and Jandl 2007, Vitousek et al. 1997).

The temperate forest systems of the southern Appalachian Mountains have conventionally been considered to be N-limited (Knoepp et al. 2008, Knoepp and Vose 2008). Yet high-elevation red spruce-Fraser fir forests in the Southern Appalachian Mountains have some of the greatest rates of N deposition measured in North America (Nodvin et al. 1995). Thus, investigations of N nutrient dynamics have become increasingly important as the upper elevations in the southern Appalachians continue to receive high amounts of anthropogenic N deposition (Knoepp et al. 2008).

It is expected that over the long-term there will be large migrations of tree species as a result of climate change (Iverson et al. 1998, Iverson & Prasad 1998, 2002). This may pose a challenge in predicting biogeochemical cycling of future forests as species composition plays a key role in how an ecosystem functions, especially in regards to soil N processes (Hooper and Vitousek 1997, Lovett et al. 2009, Meier and Bowman 2008, Tilman et al. 1997, Vitousek et al. 1997). Conversely, while species redistribution is expected as a consequence of climate change, the ability to recruit and migrate may be constrained by soils (Lafleur et al. 2010). This is further supported by work at the Harvard Forest LTER, which is finding that many of the climate-warming impacts on tree species are mediated through climatic warming impacts on soil nutrient processes (Melillo et al. in press). This presents a question as to how traditionally cool and moist systems such as southern Appalachian forests will function as a result of global climate change in regards to temperature, N nutrient dynamics, and species composition.

In order to better understand the effects of climate change in southern Appalachian forests this study focuses on five established gradient plots, which are part of the Coweeta Long-term Ecological Research

(LTER) project, funded by the National Science Foundation (Clark et al. 1998, Knoepp and Swank 1998). The plots were placed along a natural gradient in elevation, temperature, moisture, and vegetation at Coweeta (Table 2.1). The five sites represent five southern Appalachian forest types, which were categorized by dominant tree species, moisture regime, and elevation as follows: mixed oak-pine (OP), cove hardwoods (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH) (Clark et al. 1998, Knoepp et al. 2000, Knoepp and Vose 2007, Knoepp et al. 2008). The gradient plots were established in 1991 as 20 m x 40 m plots for intensive measurement purposes such as throughfall chemistry from July 1992 through November 1997, nitrogen transformations from May 1991 through October 1996, soil solution chemistry from May 1994 through December 2001, and aboveground vegetation productivity (Clark et al. 1998, Knoepp et al. 2008). Previous work on these plots suggested early evidence of N saturation from N deposition and suggested that increased temperatures may accelerate N saturation at the highest elevations (Knoepp et al. 2000 , Knoepp and Vose 2007).

Previous N Throughfall Measurements

From July 1992 through November 1997, throughfall measurements were recorded using six 0.15 x 2.0 meter troughs spaced randomly throughout the intensive gradient plots. The throughfall troughs were collected weekly, then composited for a monthly analysis of ammonium (NH_4) and NO_3 at the Coweeta Hydrologic Laboratory in Otto, NC. The NH_4 and NO_3 concentrations were reported as mg/L of the sample, which was converted to g/ha using the specific volume of each throughfall sample and the area of the throughfall collector trough (0.3 m^2) (Knoepp et al. 2008).

Table 2.1 Gradient Sites

Site	Site ID	Elevation (m)	Dominant Vegetation	Air Temperature (1 m)	Soil Temperature (20 cm)	Rainfall (cm)	Moisture Regime	pH	Total C (%)	Total N (%)	Soil C to N Ratio
Mixed Oak-Pine (OP)	118	788	*Quercus prinus, Quercus rubra, Carya spp., Kalmia latifolia*	15.1	14.8	210.2	xeric	3.9	3.17	0.08	38.67
Cove Hardwood (CH)	218	801	*Liriodendron tulipifera, Quercus rubra, Tsuga canadensis, Carya spp.*	14.5	14	212.4	mesic	4.2	6.71	0.37	18.01
Low Elevation Mixed Oak (MO-L)	318	860	*Quercus coccinea, Quercus prinus, Rhododendron maxima*	15	13.5	222.9	mesic	4.0	3.52	0.16	22.55
High Elevation Mixed Oak (MO-H)	427	1094	*Quercus rubra, Carya spp., Rhododendron maxima*	13.6	12.8	264.9	mesic	4.0	4.11	0.14	28.68
Northern Hardwood (NH)	527	1389	*Betula allegheniensis, Liriodendron tulipifera, Quercus rubra, Acer saccharum*	11.8	10.8	267.6	mesic	4.0	9.92	0.67	14.71

The values for site elevation, dominate species, air temperature, soil temperature, rainfall, and moisture regime from Knoepp and Vose (2007) and Knoepp et al. (2008). Average pH values were calculated from Coweeta Long-Term Ecological Research Program records data. Average soil %C, %N, and C to N ratios were calculated from 1994 to 1996 measurements from Coweeta Long-Term Ecological Research Program records.

Knoepp et al. (2008) found that NO_3 concentrations in throughfall were greatest in the NH and the MO-L plots, and NO_3 concentrations in throughfall in these plots were significantly greater than NO_3 concentrations in the OP and CH sites (the lowest elevation sites). In regard to NH_4, Knoepp et al (2008) found that NH_4 concentrations in throughfall were greatest in the NH and the MO-H plots, both of which were significantly greater than the mixed-oak pine and cove hardwood sites. Seasonal variability was also observed in NO_3 throughfall concentrations with significantly greater concentrations in August and September, however a similar pattern was not observed for NH_4 concentrations in throughfall (Knoepp et al. 2008).

Previous Soil N Transformation Measurements

Thirty-four soil N transformation measurements were done on the gradient plots from May 1991 through October 1996 using *in situ* closed PVC cores, 0-10 cm into the soil surface (modified method from Adams and Attiwill 1986, Knoepp and Swank 1998, Knoepp et al. 2008). The N transformation measurements were initiated May 1991 on a bimonthly basis, which was continued through 1992 (Knoepp and Swank 1998, Knoepp et al. 2000, Knoepp et al. 2000). In 1993 and 1994, the N transformation measurements were continued seasonally, four times throughout the year (Knoepp and Swank 1998, Knoepp et al. 2000). In 1995 and 1996 the N transformation measurements were done on a monthly basis from April through October and then once in the dormant season from January through February (Knoepp and Swank 1998, Knoepp et al. 2000, Knoepp et al. 2008). To measure the soil N transformations two 15-cm long PVC cores with an interior diameter of 4.3 cm, were driven 10 cm into the mineral soil. One was removed immediately for the „time zero" determination of soil N, the second was capped and was incubated in the field for 28 days. Following collection, cores were kept cool until stored in a 4˚C laboratory refrigerator until analyzed. Within 24 hours the mineral soil from the cores was moist-sieved to <6 mm and divided into two samples: a 20 g sample and a 5 g sample. The 20 g sample was dried in an oven at 105˚C for >12 hours to determine the oven-dry weight. The 5 g sample was shaken in 20 mL of 2 *M* KCl for 1 hour to extract soil NH_4 and NO_3-N. The soil and KCl was then centrifuged at 6000 rpm for 15 minutes. The supernatant was then analyzed for NH_4- and NO_3-N on an auto analyzer at the Coweeta Hydrologic Laboratory in Otto, NC and the findings were reported as mg/kg (Knoepp and Swank 1998, Knoepp et al. 2008).). Net N mineralization rates were calculated as the NH_4 + NO_3-N concentrations at day 28 minus the NH_4 + NO_3-N concentrations at time zero and were reported as mg/kg/28 days (Knoepp and Swank 1998, Knoepp et al. 2008). Plot means ($n = 4$) from each sample date were used to determine seasonal N transformations (Knoepp and Swank 1998).

Previous work found that both nitrification and mineralization rates differed significantly across all sites and months, and were significantly greater in the summer months, with significant interactions between site and months. The highest elevation site, the NH site, had the greatest N mineralization rates, but it was followed by the second low-elevation site, the CH site (Knoepp and Swank 1998, Knoepp and Vose 2007, Knoepp et al. 2008).

Previous N Soil Solution Measurements

From May 1994 through December 2001, tension lysimeters were used to measure soluble constituents in soil water. Each intensive gradient plot had 10 lysimeters, five of which were placed 15 cm into the soil and five of which were placed 30 to 85 cm into the soil into the lower area of the B-horizon. The lysimeters were sampled weekly, and composited for monthly analysis of NH_4, NO_3-N, and quarterly for total organic N (TKN), and other ions at the Coweeta Hydrologic Laboratory in Otto, NC and were reported as mg/L (Knoepp et al. 2008, Knoepp et al. 2000).

Knoepp et al. (2000, 1008) found that mean soil NO_3-N was significantly greater in the NH plot, while there was no significant difference in mean soil NO_3-N concentrations for the rest of the plots. In contrast, the only significant difference in regards to mean soil NH_4 concentrations was that the mean NH_4 concentrations of the NH, and low elevation oak plots were significantly greater than the OP plot (Knoepp et al. 2008). There was no significant difference by gradient plot or month or among months for soil NO_3-N and NH_4 concentrations in shallow lysimeters, but TKN was significantly greater for September (Knoepp et al. 2008).

To gain an even better understand of N dynamics in these plots under global climate change these measurements were reinstated in October 2009. Based on previous work the objectives of this study were to determine if the patterns of N dynamics in the gradient plots have changed as a result of N deposition and climate change in regards to 1) the amount of increased N deposition leading to saturation, 2) temperature and 3) moisture effects on N transformations. It was hypothesized that the highest elevation site would receive the most N input into the system via throughfall and as one of the most extreme sites, also have the strongest biogeochemical response to increased N deposition, temperature, and moisture dynamics.

MATERIALS AND METHODS

Site Description

The study was done at the Coweeta Hydrologic Laboratory of the USDA Forest service, which is a 2180 ha facility located in the southern Appalachian Mountains in western North Carolina. The average annual precipitation is about 1900 mm with most monthly precipitation averaging greater than 100 mm. The growing season begins in early May and extends to early October. The greatest mean monthly temperatures occur June through August at about 20˚C, with the lowest mean monthly temperature occurring December though January at about 5˚C (Knoepp and Swank 1998, Knoepp et al. 2005, Knoepp and Vose 2007, Knoepp et al. 2008).

The study took place in two north-facing reference watersheds, watershed 18 and watershed 27, in the Coweeta Hydrologic Laboratory basin. Both of these watersheds have been undisturbed and uncut since 1929 (Knoepp et al. 2005, Knoepp and Vose 2007, Knoepp et al. 2008).

N Throughfall Measurements

Throughfall measurements were taken seasonally in 2010 using ion exchange resin columns developed by Fenn and Poth (2004). The resin columns were built with 1.3 x 35.6 centimeter round PVC pipe with a drain cap on the bottom attached to a 22.9 cm diameter funnel. The columns were filled with Rohm and Haas Amberlite IRN 150 mixed bed ion-exchange resin. Five resin throughfall collectors were spaced randomly throughout each of the intensive gradient plots and were collected seasonally. The first season was the growing season, which included April (from bud break) through September. The second season, during the dormant season, included throughfall from October to December. The columns were collected after each season and extracted individually with 100 mL of 2N KCl and analyzed in an Astoria 2 Autoanalyzer for NO_3 and NH_4 at the Coweeta Hydrologic Laboratory in Otto, NC (Fenn and Poth 2004, Fenn et al. 2009). NO_3 and NH_4 concentrations in KCl extract were reported in mg/L, which was converted to g/ha based on the throughfall collector funnel area (411.87 cm^2) and the extractant volume (100 mL).

Soil N Transformations

From October 2009 through October 2010, monthly N transformation measurements were done on the gradient plots using *in situ* closed PVC soil cores using a modified method from Knoepp et al. (2008). Five 1 m^2 sample subplots were randomly stratified, and located within each of the gradient plots. Along with the five primary subplots, an adjacent 1 m^2 subplot was also located to capture nutrient variability at small spatial scales (totaling 10, 1 m^2 sample plots per gradient plot). To measure the soil N transformations, two 15 cm long, PVC cores with an interior diameter of 4.0 cm, were driven 10 cm into the mineral soil. One was removed immediately for the time zero determination of the soil N, the second was capped and was incubated in the field for 28 days. Within 15 minutes of removal the time zero core was separated into organic and mineral layers and then moist sieved to <6mm. Approximately 5 g of sieved soil from each layer was placed in a separate, pre-weighed bottled containing 100 mL of 2 *M* KCl to extract soil NH_4 and NO_3-N (Van Miegroet 1995). Upon collection of the final cores, within 15 minutes to 1 hour the field- incubated core was separated by organic and mineral layers and then moist sieved to <6mm, and approximately 5 g of sieved soil from each soil layer was placed in a separate pre-weighted bottled of 100 mL of 2 *M* KCl, to extract soil NH_4 and NO_3-N. The remaining soil samples were kept in air-tight bags and were later used to determine oven-dry weight (Knoepp and Swank 1998, Knoepp et al. 2008). The bottles containing the KCl soil mixture were weighed to determine the exact amount of soil in the extraction, shaken, and within 48 hours filtered using Whatman® 42 filter papers. The filtered sample was frozen until analysis for NH_4 and NO_3-N. The NH_4 and NO_3-N analyses were done on auto analyzer at the University of Georgia, Athens, GA. All NH_4 and NO_3-N were reported as mg/L, and converted to mg/kg using the oven dry soil weight for each sample. Net N mineralization rates were calculated using the mg/kg values, as the NH_4 and NO_3 concentrations at day 28 minus the NH_4 and NO_3 concentrations at time zero, which were reported as mg/kg/28 days (Knoepp and Swank 1998, Knoepp et al. 2008).

N Soil Solution in Lysimeters

From April 2010 through December 2010, soil solution was collected every other week using tension lysimeters to measure soluble constituents in the water in the soil. Five pairs of lysimeters were placed randomly in the intensive gradient plots. The lysimeter pairs consisted on one lysimeter which was placed 15 cm into the soil ("shallow lysimeter") and one located nearby which was placed 30 to 85 cm into the soil, into the lower area of the B horizon ("deep lysimeter") (Knoepp et al. 2008, Knoepp et al. 2000). It should be noted that the lysimeters for the 2010 measurements replaced lysimeters from the historical measurements and were placed in the exact same holes. The lysimeters were evacuated to between 30 and 35 centibars to collect the plant available water in the soil pores (Schwab 2000). The lysimeters were pumped out every other week. The first sample was analyzed for NH_4-N, NO_3-N, and other ions, and the second sample (two weeks later) was analyzed for total nitrogen (TN) and dissolved organic carbon (DOC) at the Coweeta Hydrologic Laboratory in Otto, NC. These sample values are reported on a monthly basis and reported as mg/L since the exact area or volume of soil from which the samples were leached cannot be determined.

Statistical Analysis

Throughfall statistical analysis was done using SAS® 9.1.2. Due to equal sample sizes per plot and season (n=5) analysis of variance (ANOVA) at $\alpha=0.05$ was performed on the data to compare main-effect significance of nutrient concentrations across all plots, and significance of each plot and season for each nutrient (NH_4 and NO_3). T-tests were also performed for each plot to compare nutrient concentrations between seasons (growing and fall). In addition to the ANOVA analysis a Tukey range test was also done at $\alpha=0.05$ to compare plots for each season.

For soil N transformations, statistical analysis was done in SAS® 9.1.2 using the general linear model (GLM) function at $\alpha=0.05$. The GLM was used to compare soil NH_4 and NO_3 concentrations, nitrification rates, mineralization rates, and percent soil water for all of the plots by month and layer. NH_4 and NO_3 concentrations and percent soil water in the initial soil core (t=0) for each plot, were compared by month and by layer (organic and mineral). In addition to the comparison by layer, NH_4 and NO_3 concentrations in the initial soil core (t=0) were also compared by month. Nitrification and mineralization rates for each plot were compared by month and by layer (organic and mineral). In addition to the comparison by layer, nitrification and mineralization rates were also compared by month. The average values of NH_4 concentrations, NO_3 concentrations, nitrification rates, mineralization rates, and percent soil moisture were graphed with standard error values for visual comparisons (Figures 2.5 through 2.14).

For soil solution NH_4, NO_3, and TN concentrations collected by lysimeters, SAS® 9.1.2 was used to do t-test comparisons of shallow and deep lysimeters for each plot. GLM at $\alpha=0.05$ was used to compare concentrations per plot by lysimeter depth (shallow and deep), by month, and by season (spring 2010 (April through May), summer 2010 (June through August), fall 2010 (September through

November), and winter 2010 (December)). Mean NH_4, NO_3, and TN concentrations were also graphed by depth, plot, and month for visual comparisons (Figures 2.15 through 2.20).

RESULTS

For throughfall NH_4 concentrations, there a significant plot and season interaction (P=0.0517). The t-test analysis comparing mean monthly NH_4 concentrations for the growing season (April through September) and the fall season (October through December) showed significant difference between the seasons for both the low (P=0.0016) and high (P=0.0122) elevation mixed oak plots, with greater mean throughfall concentrations of NH_4 in the growing season for both of these (Figure 2.1). In addition, the two low elevation plots tended to have greater mean monthly concentrations of NH_4 in throughfall during the fall, in contrast to the high elevation plots. In the Tukey range test for the growing season the MO-L plot exhibited greater NH_4 concentrations than all other plots (P=0.0012). In the fall season, there was no significant difference for throughfall NH_4 concentrations between of the plots (Figure 2.2).

For throughfall NO_3 concentrations there was an important interaction between plots-by-season (P<0.0001). The t-test analysis comparing the mean monthly growing season and the fall season exhibited significantly greater mean monthly NO_3 concentrations in throughfall during the fall season for all the plots (Figure 2.3). For just the growing season, the Tukey range test showed no significant difference (P=0.5428) between throughfall NO_3 concentrations among all plots. In the Tukey range test for the fall season the NH plot displayed a significantly greater (P=0.0070) mean throughfall NO_3 concentration than the xeric OP plot and the cove hardwood plot (Figure 2.4).

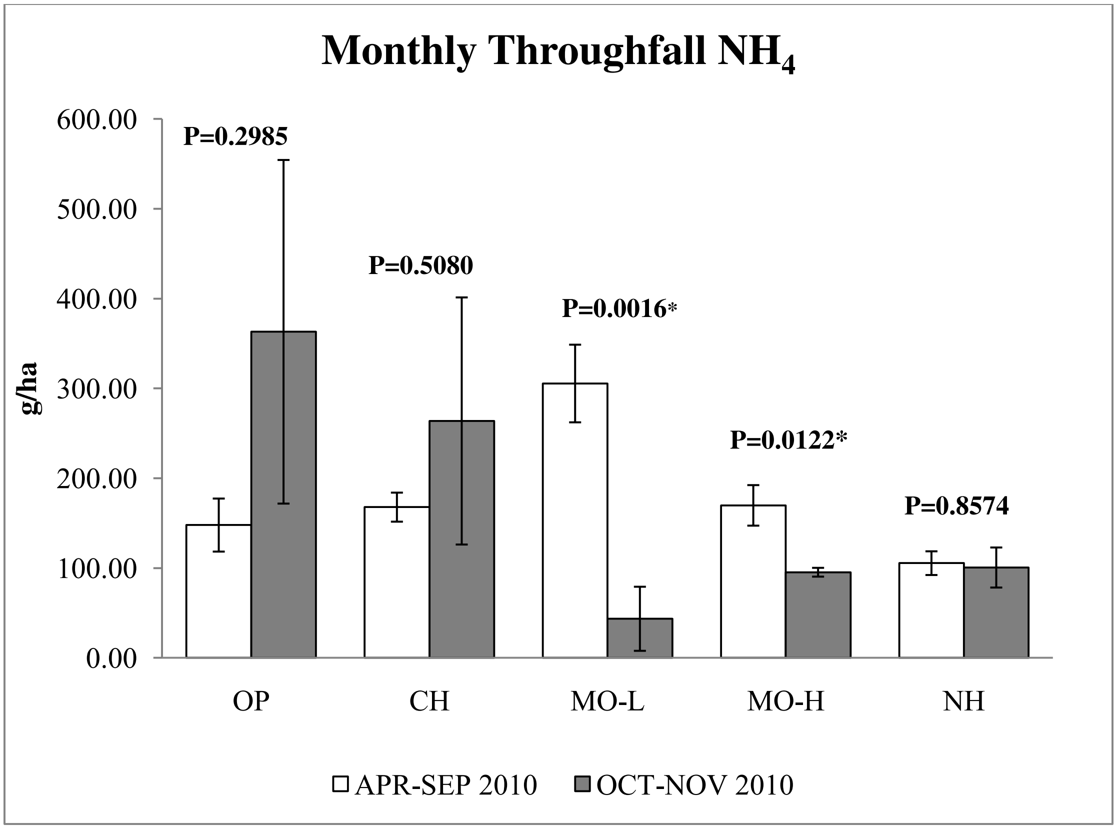

Figure 2.1 Average monthly throughfall NH_4 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH). P-values above each plot are the result of T-test analysis comparing NH_4 concentrations for the 2010 growing season (April through September) and the 2010 fall season (October through December). Significant p-values are noted with a "*".

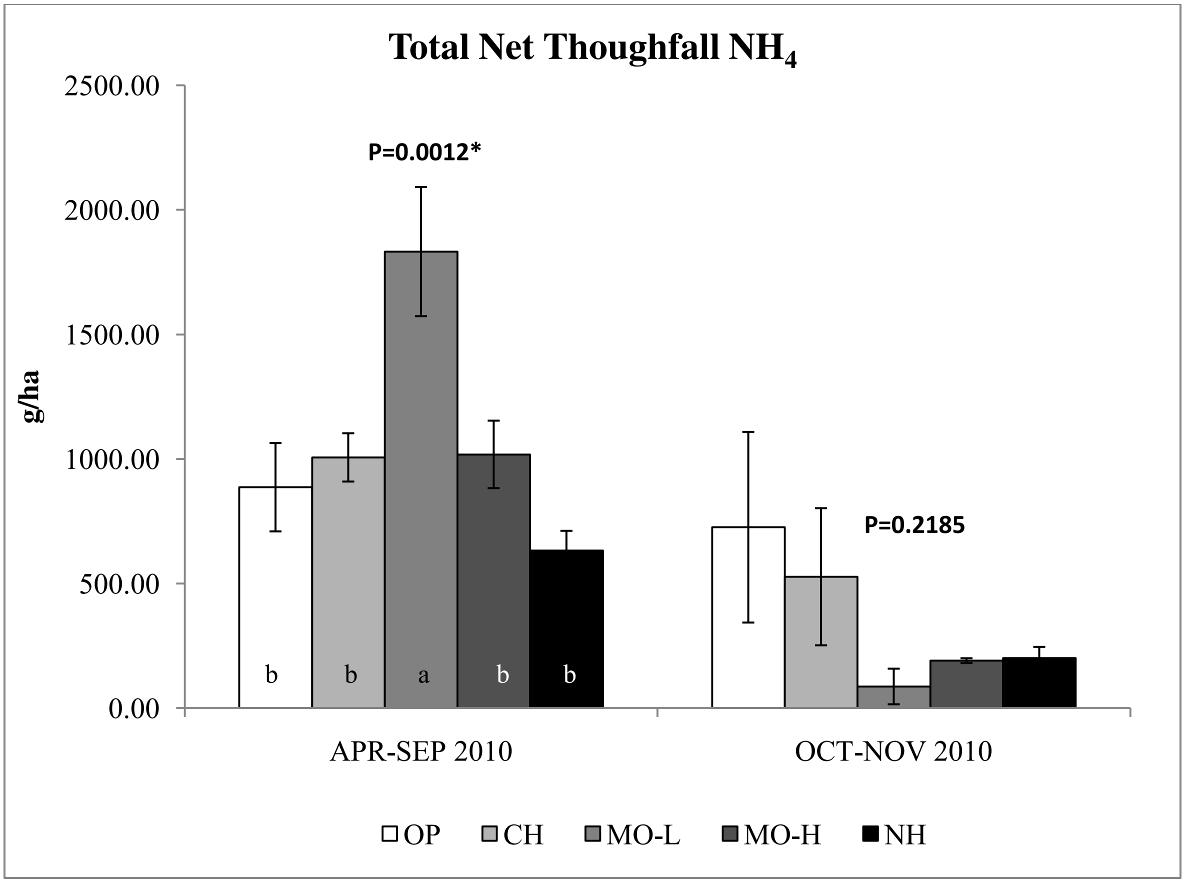

Figure 2.2 Average throughfall NH_4 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH), divided up by season. P-values above each plot are the result of Tukey range test analysis comparing NH_4 concentrations for the plots in each season, the 2010 growing season (April through September) and the 2010 fall season (October through December). Significant p-values are noted with a "*". Tukey range test analysis differences are also noted with "a" and "b."

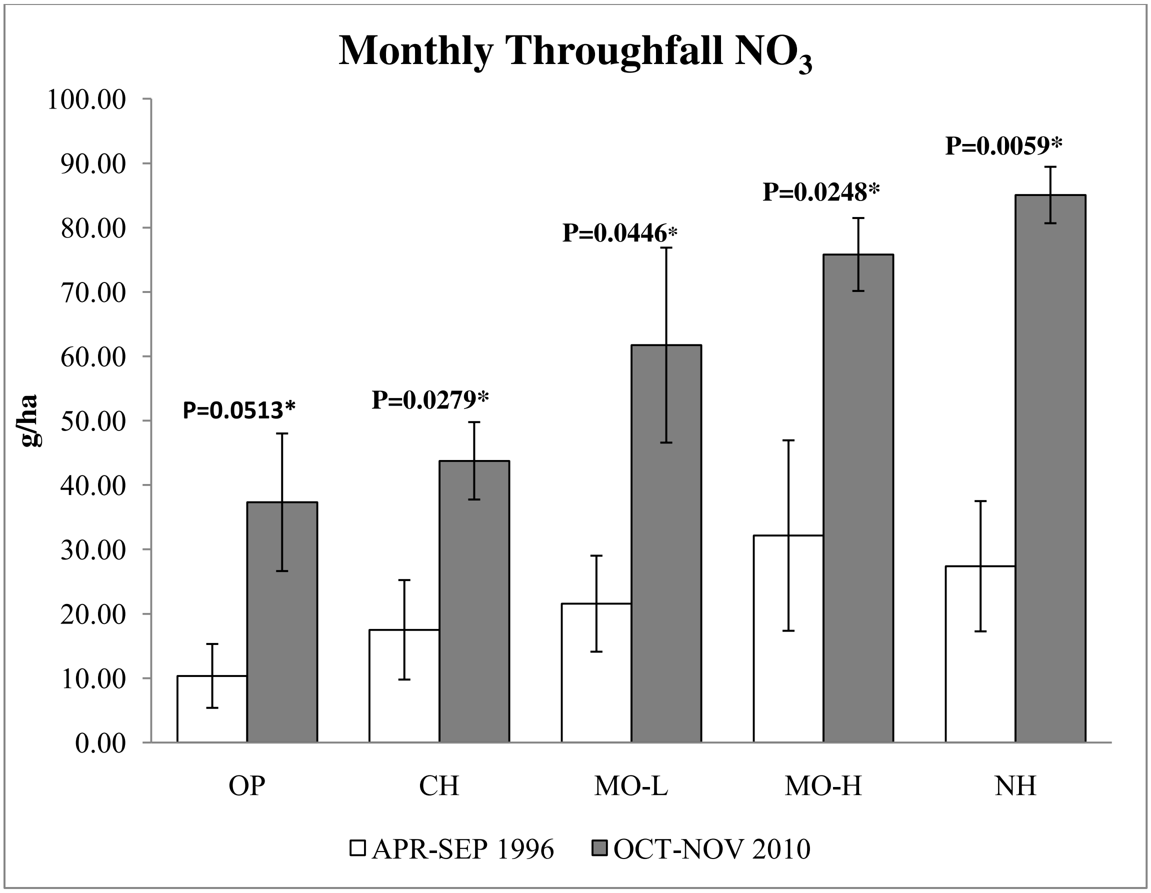

Figure 2.3 Average monthly throughfall NO_3 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH). P-values above each plot are the result of T-test analysis comparing NO_3 concentrations for the 2010 growing season (April through September) and the 2010 fall season (October through December). Any significant p-values are noted with a "*".

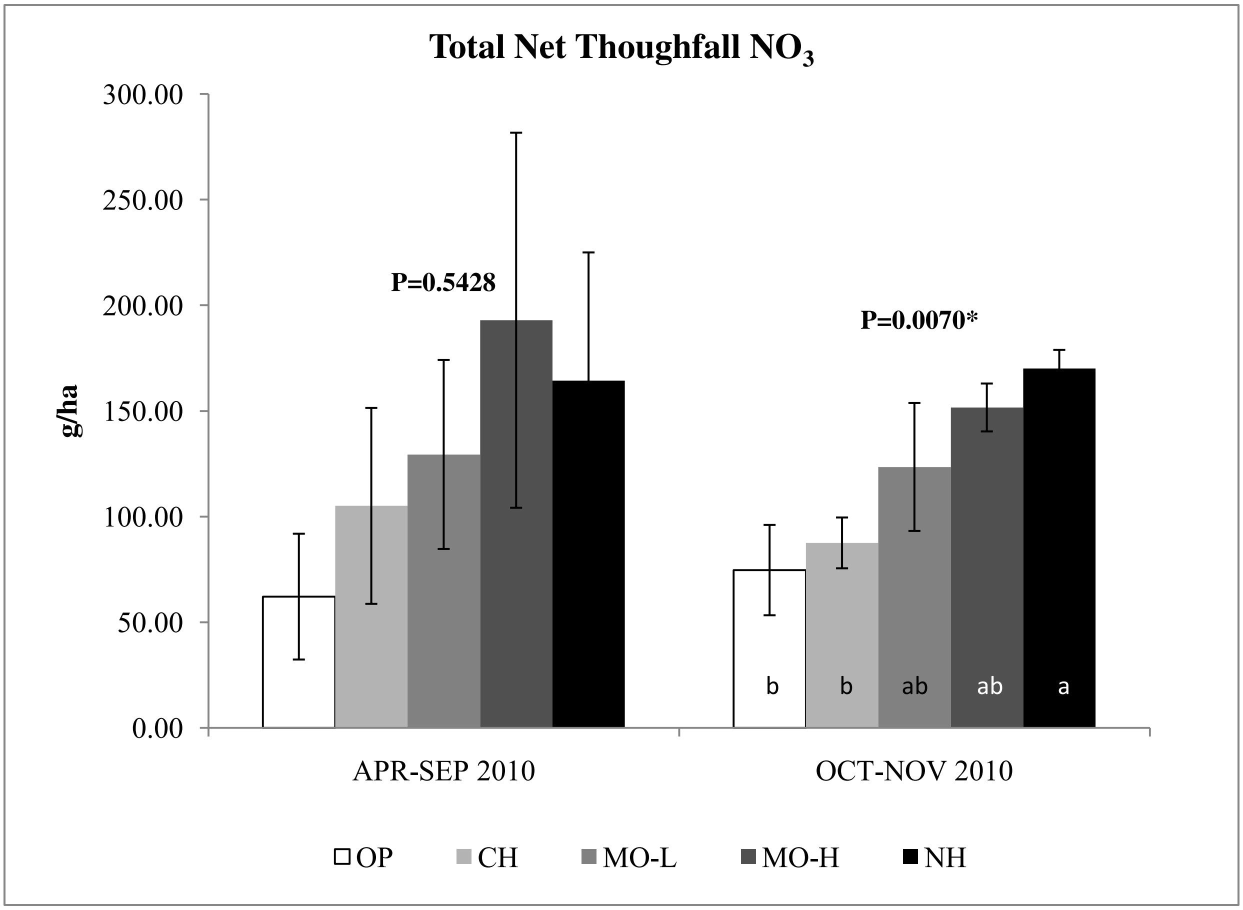

Figure 2.4 Average throughfall NO_3 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH), divided up by season. P-values above each plot are the result of Tukey range test analysis comparing NO_3 concentrations for the plots in each season, the 2010 growing season (April through September) and the 2010 fall season (October through December). Significant p-values are noted with a "*". Tukey range test analysis differences are also noted with "a," "b," or "ab."

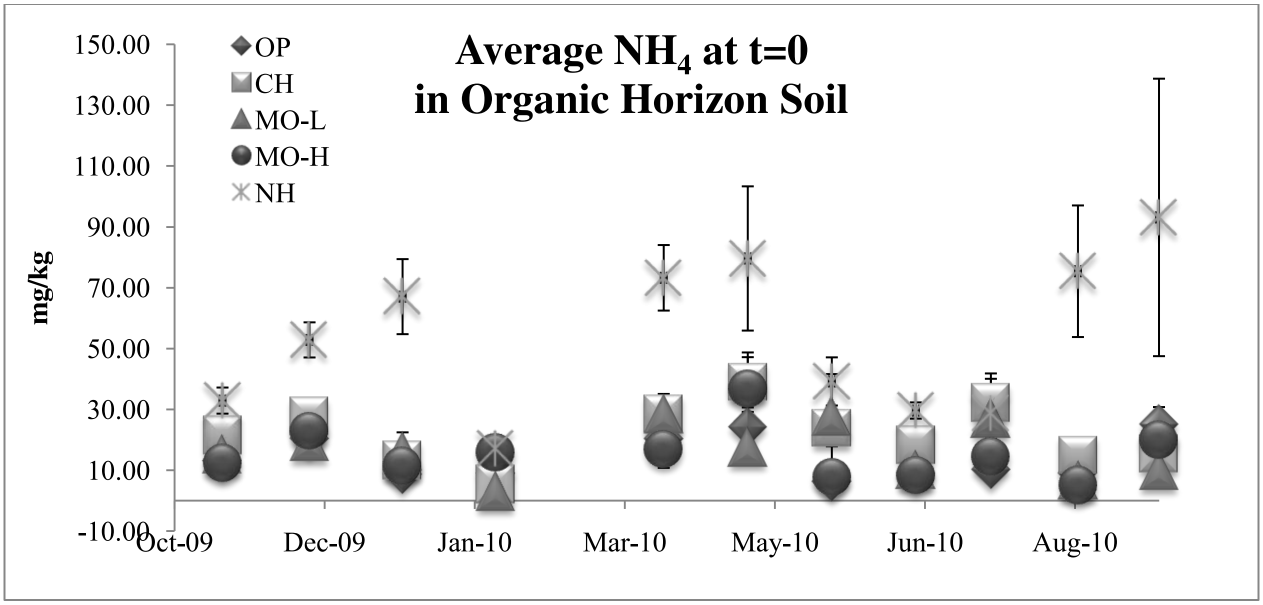

Figure 2.5 Average NH$_4$ concentrations in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH). The figure shows a greater average NH$_4$ concentration in the organic layer of the NH plot ($P<0.0001$).

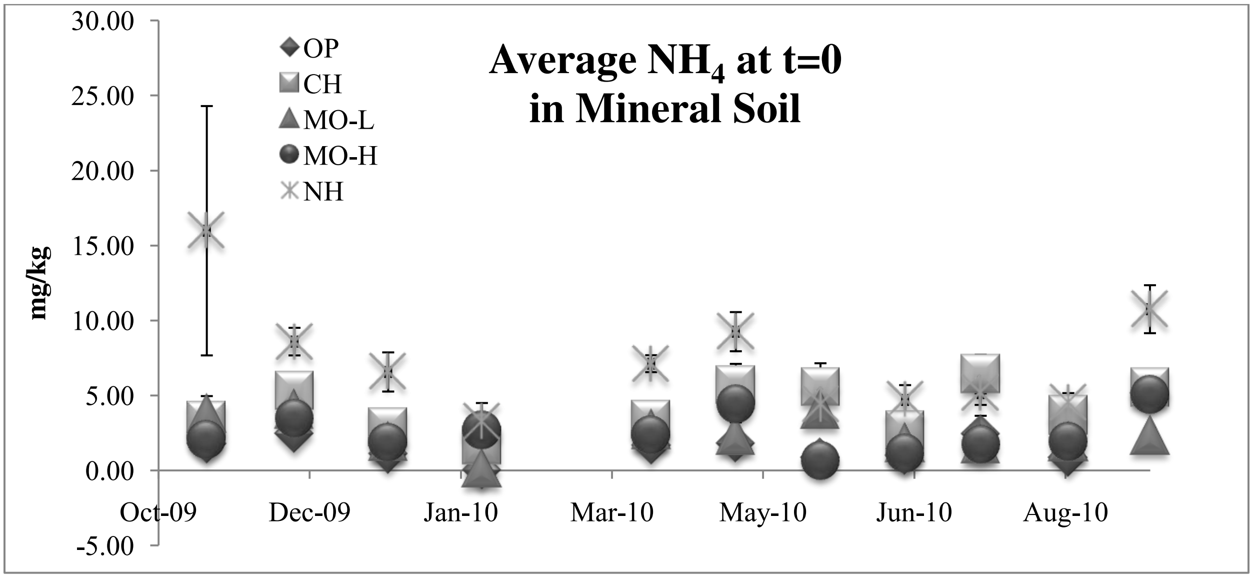

Figure 2.6 Average NH$_4$ concentrations in the mineral layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

For soil N transformations, NH_4 concentrations in the initial soil core (t=0) differed significantly by plot ($P<0.0001$), month ($P<0.0001$), and by layer ($P<0.0001$), with all interactions also being significant. When examining the organic layer mean NH_4 concentrations, the NH plot had the greatest amount of NH_4 (Figure 2.5). It should also be noted that the NH_4 concentrations in the initial soil core (t=0) differed significantly by layer ($P<0.0001$), with the greatest mean concentrations of NH_4 in the organic layer (Figure 2.5).

When soil NO_3 concentrations in the initial soil core (t=0) were examined in the organic versus the mineral layer, they differed significantly by plot ($P<0.0001$), month ($P=0.0310$), and by layer ($P=0.0133$), with the layer and month interaction were not significant interaction ($P=0.6198$) suggesting an important overall seasonal effect. NO_3 concentrations in the initial soil core (t=0) tended to be greatest in the NH plot during the 2010 growing season (April through September) (Figures 2.7 and 2.8). Like the NH_4 concentrations, the NO_3 concentrations in the initial soil core (t=0) differed significantly by layer, with the greatest mean concentrations of NO_3 in the organic layer (Figures 2.7 and 2.8).

When soil nitrification rates were examined by layer, they differed significantly by plot ($P<0.0001$), month ($P<0.0001$), and by layer ($P=0.0055$), with all interactions being found significant. Mean soil nitrification rates in the NH plot during the 2010 growing season (April through September), was significantly greater than most of the other plots (Figures 2.9 and 2.10). Nitrification rates differed significantly by layer, with the greatest mean nitrification rates in the organic layer, following the same pattern as the NO_3 concentrations (Figures 2.9 and 2.10).

When soil mineralization rates were examined by layer, they differed significantly by plot ($P<0.0001$), month ($P<0.0001$), and by layer ($P<0.0001$), with all interactions being found significant. Similar to mean soil nitrification rates, mean mineralization rates in the NH plot was greater during the 2010 growing season (April through September) than the rest of the plots (Figures 2.11 and 2.12). Similar to NH_4, NO_3 concentrations and the nitrification rates, mineralization rates were also significantly greater in the organic layer (Figures 2.11 and 2.12).

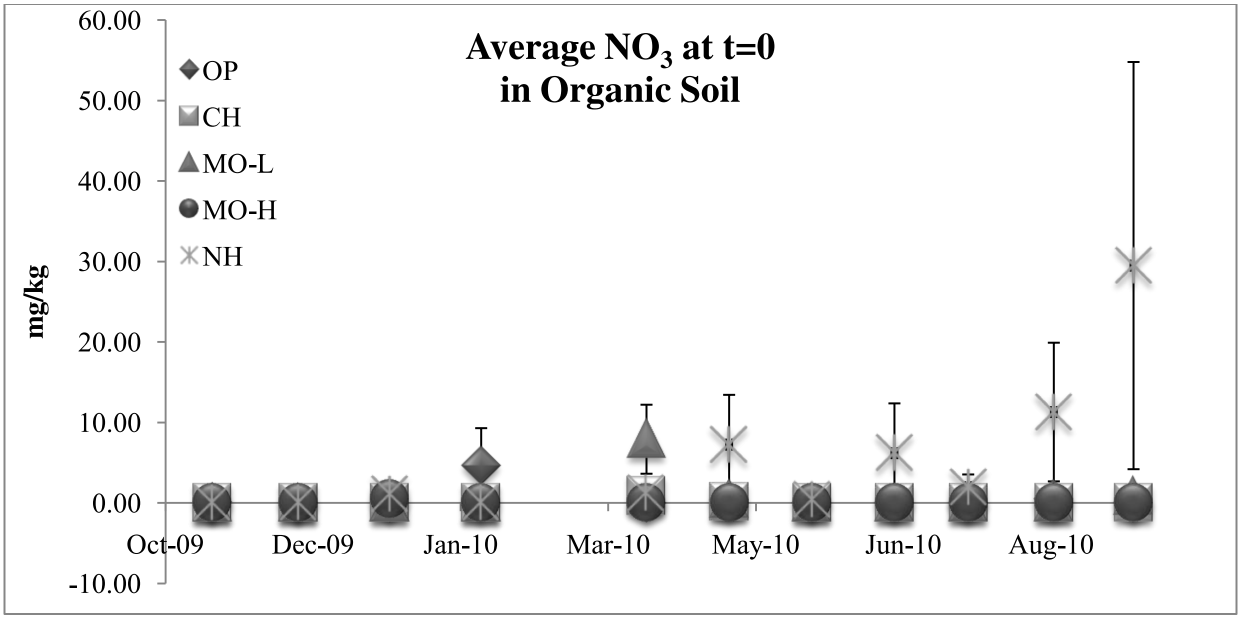

Figure 2.7 Average NO$_3$ concentrations in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

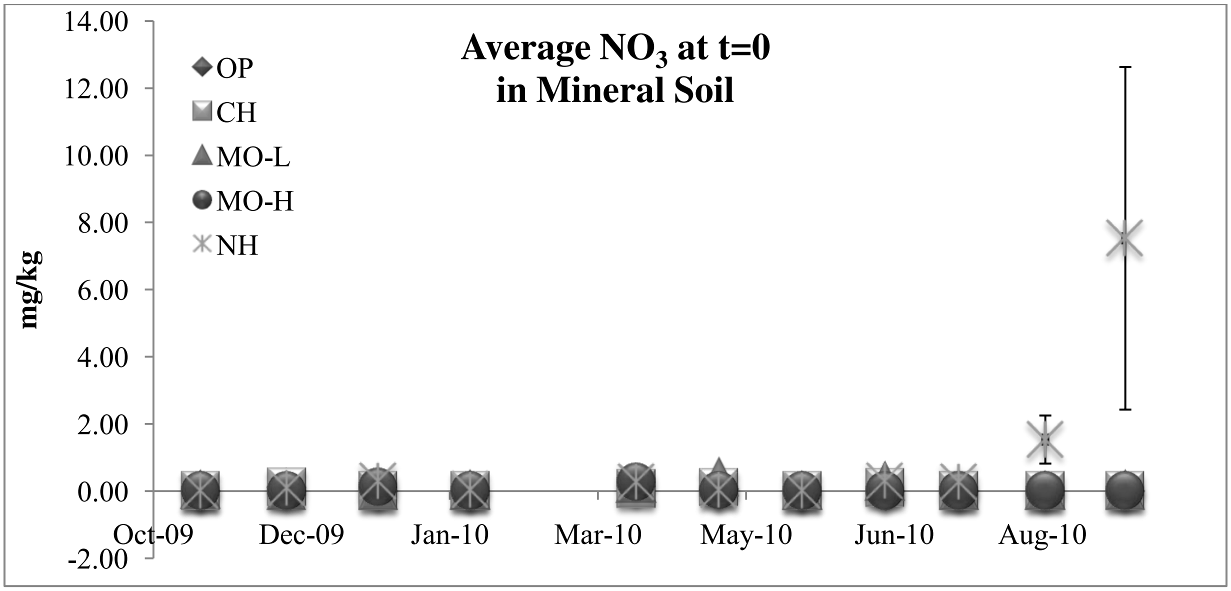

Figure 2.8 Average NO$_3$ concentrations in the mineral layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

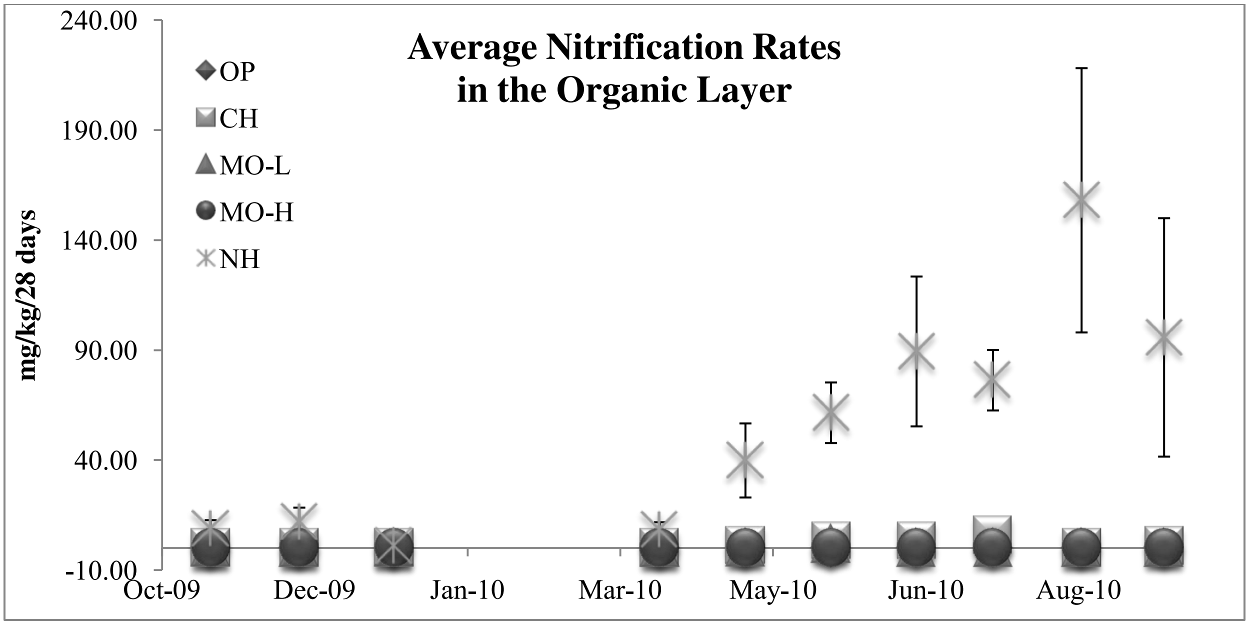

Figure 2.9 Average nitrification rates in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

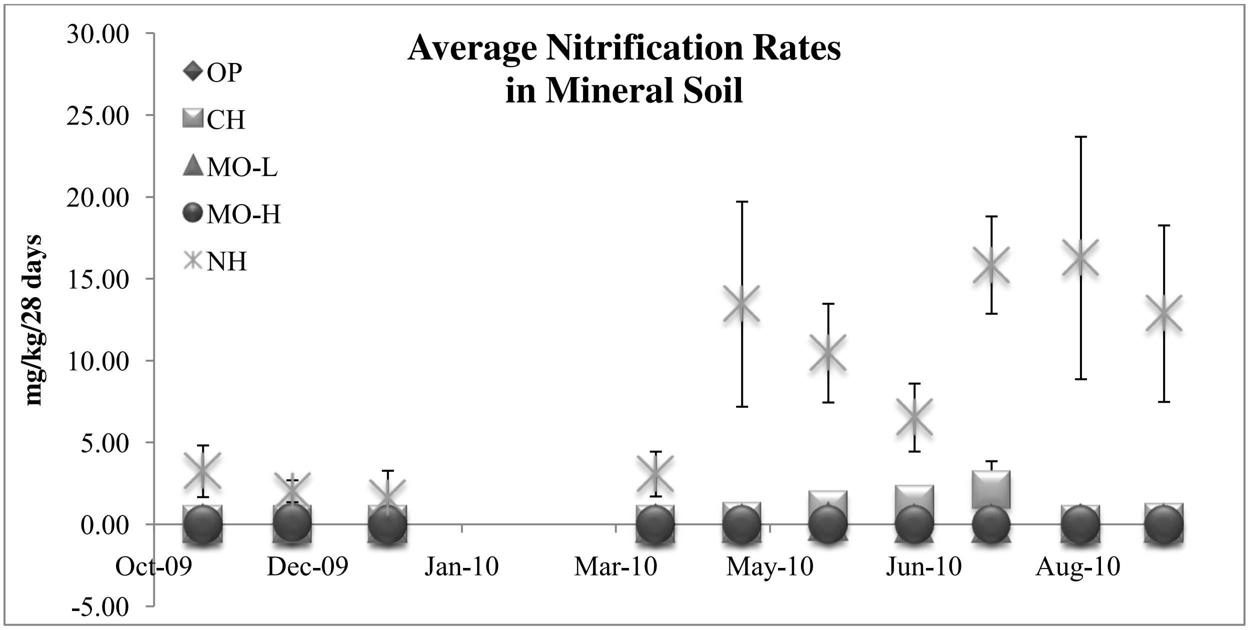

Figure 2.10 Average nitrification rates in the mineral layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

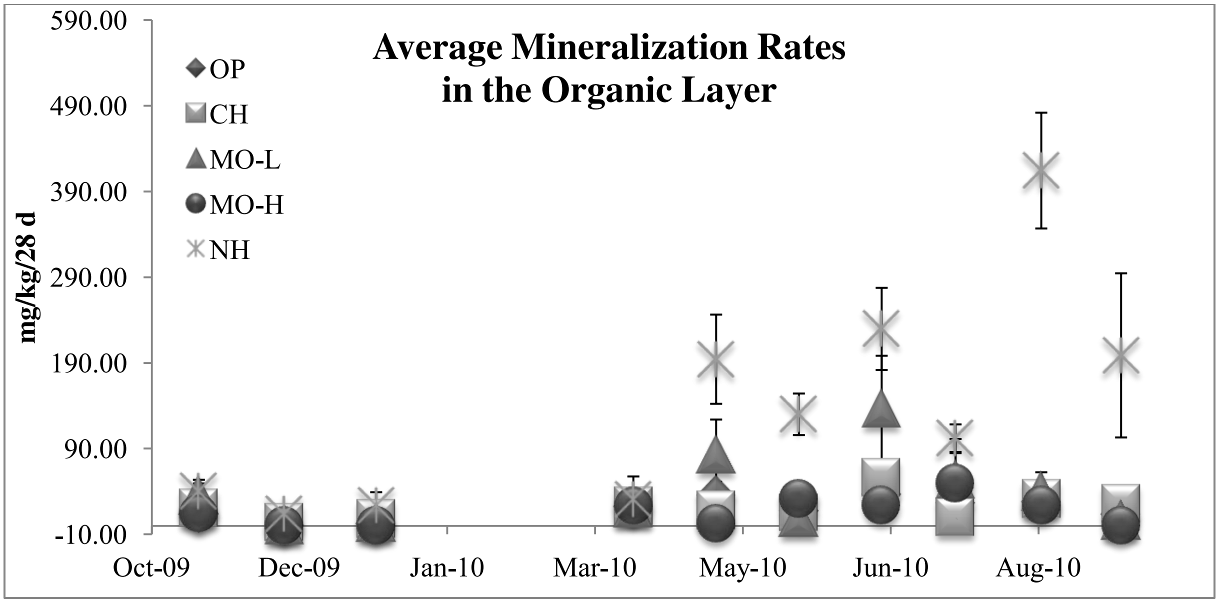

Figure 2.11 Average mineralization rates in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

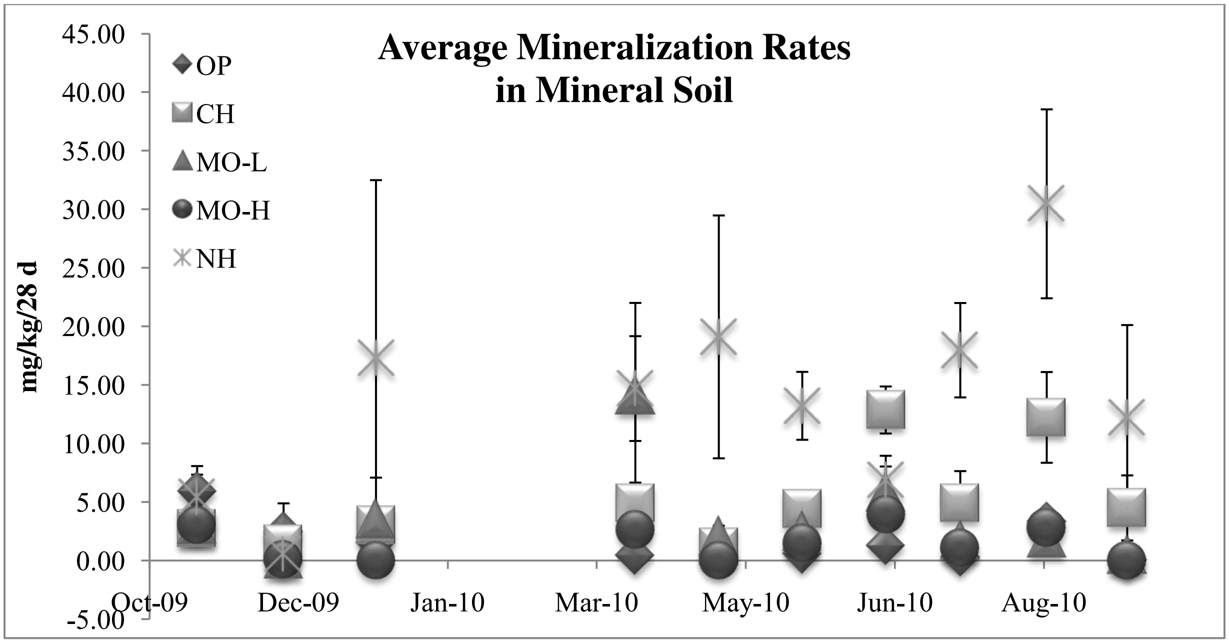

Figure 2.12 Average mineralization rates in the mineral layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

Soil moisture also differed significantly by plot ($P<0.0001$), layer ($P<0.0001$), and by month ($P<0.0001$), with the plot-by-month interaction being the only non-significant interaction ($P=0.0895$). The percent soil moisture in the plots followed the moisture gradient previously known, with the highest elevation plot (NH) having the greatest percent moisture and the lowest elevation plot (OP) having the lowest percent moisture (Figures 2.13 and 2.14).

NH_4 leachate in soil solution collected in lysimeters did not differ significantly by depth, plot, or month. However, when examining t-test comparisons of NH_4 leachate in soil solution collected in lysimeters at two different depths (shallow and deep), both the cove hardwood plot ($P=0.0322$) and the MO-L plot ($P=0.0480$) had significantly more NH_4 in the shallow lysimeter. No other main effects or interactions significantly explained variation in soil solution NH_4 concentrations (Figures 2.15 and 2.16).

NO_3 in soil solution was a greater ($P=0.0163$) amount of NO_3 leachate in the shallow lysimeters in the NH plot (s Figures 2.17 and 2.18). There was also a significant plot-by-season interaction ($P=0.0031$) for NO3 leachate concentrations collected in spring 2010 (April-May), summer (June-Aug), fall (Sept-Nov) and winter (December). Figures 2.17 and 2.18 illustrate the greater mean NO_3 leachate in the fall (September- November) and winter months (December and January), likely reflecting the uptake of NO_3 by vegetation in the growing season.

When examining t-test comparisons of TN leachate in soil solution collected in lysimeters at two different depths (shallow and deep), all but the highest elevation plot had significantly more TN leachate collected in the shallow lysimeter than in the deep (Table 2.2). These t-test comparisons were further supported by the GLM analysis, which showed a significant depth-by-month interaction for TN in the lowest elevation plots: the OP plot ($P=0.0199$), the cove hardwood plot ($P<0.0001$), and the MO-L plot ($P=0.0007$). This interaction was also found to be significant ($P=0.0255$) when the plots were compared by depth and season (spring 2010 (April- May), summer 2010 (June- August), fall 2010 (September- November), and winter 2010 (December) (Figures 2.19 and 2.20).

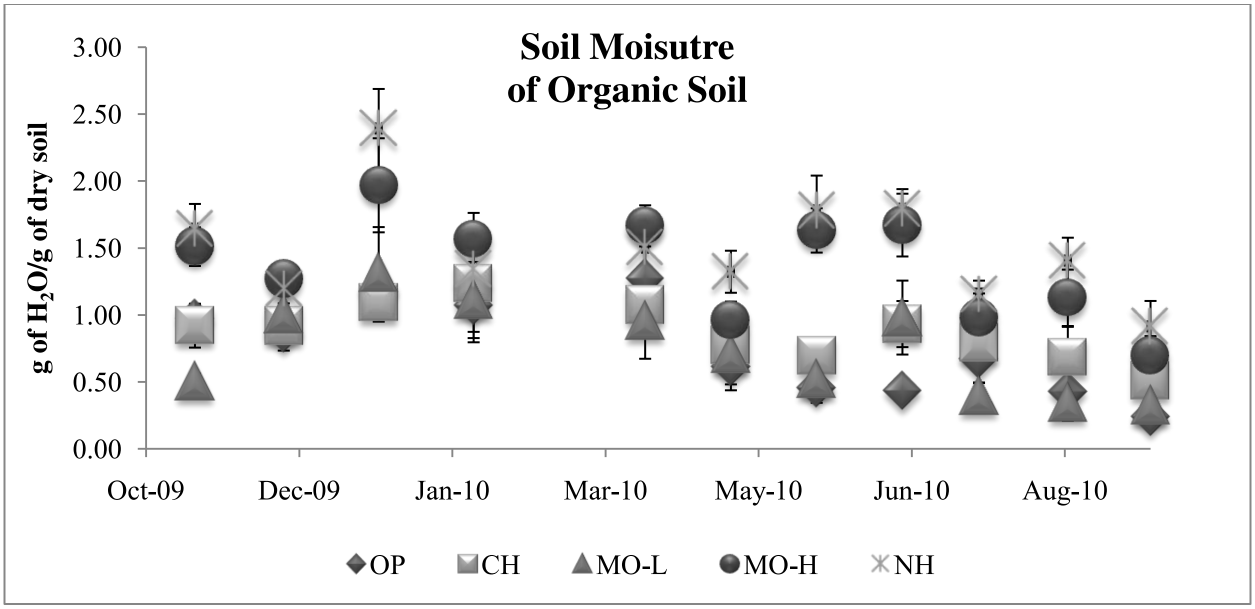

Figure 2.13 Average % soil moisture in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

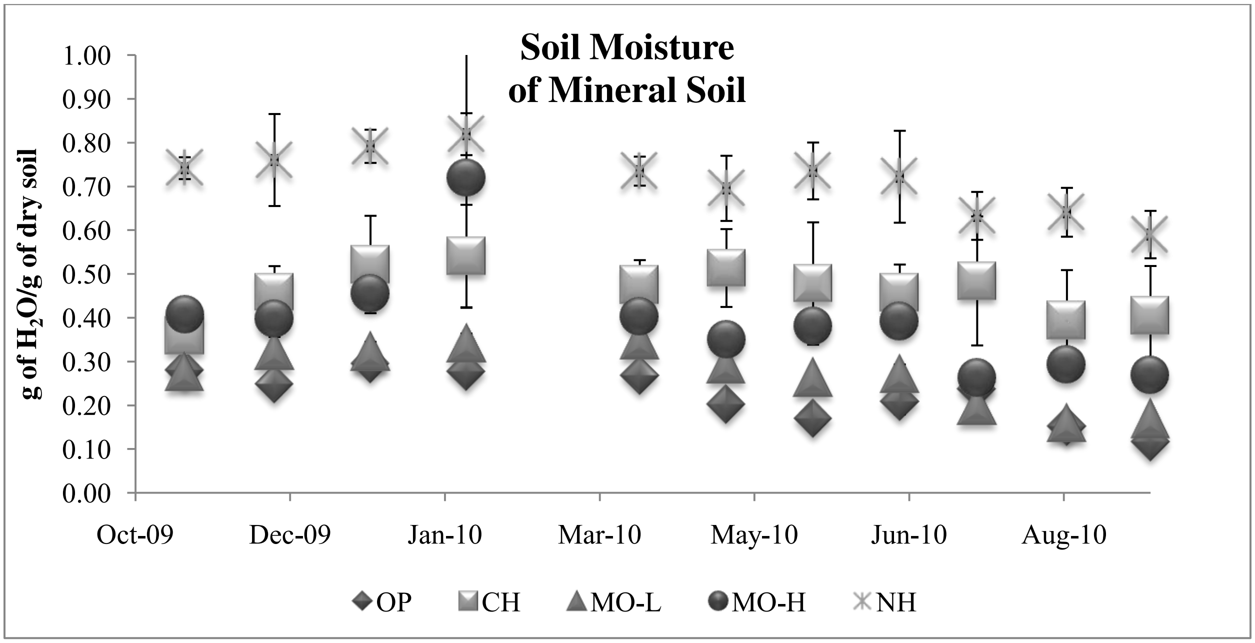

Figure 2.14 Average % soil moisture in the organic layer of the initial soil core (t=0) for each month by plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

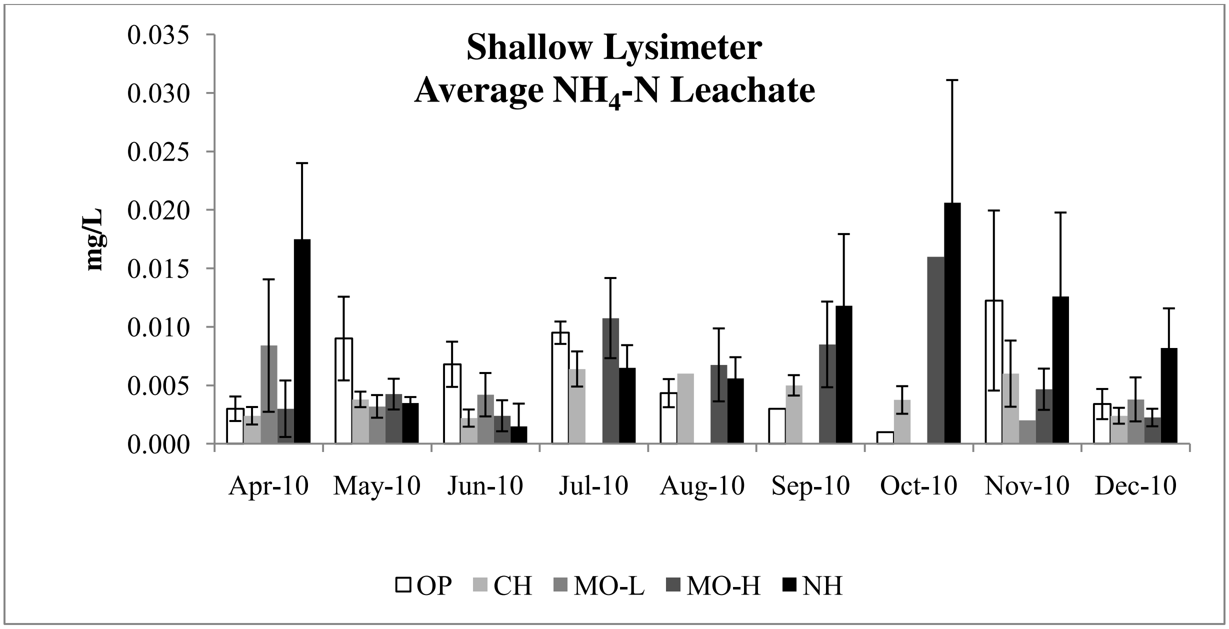

Figure 2.15 Average NH_4-N leachate in shallow lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

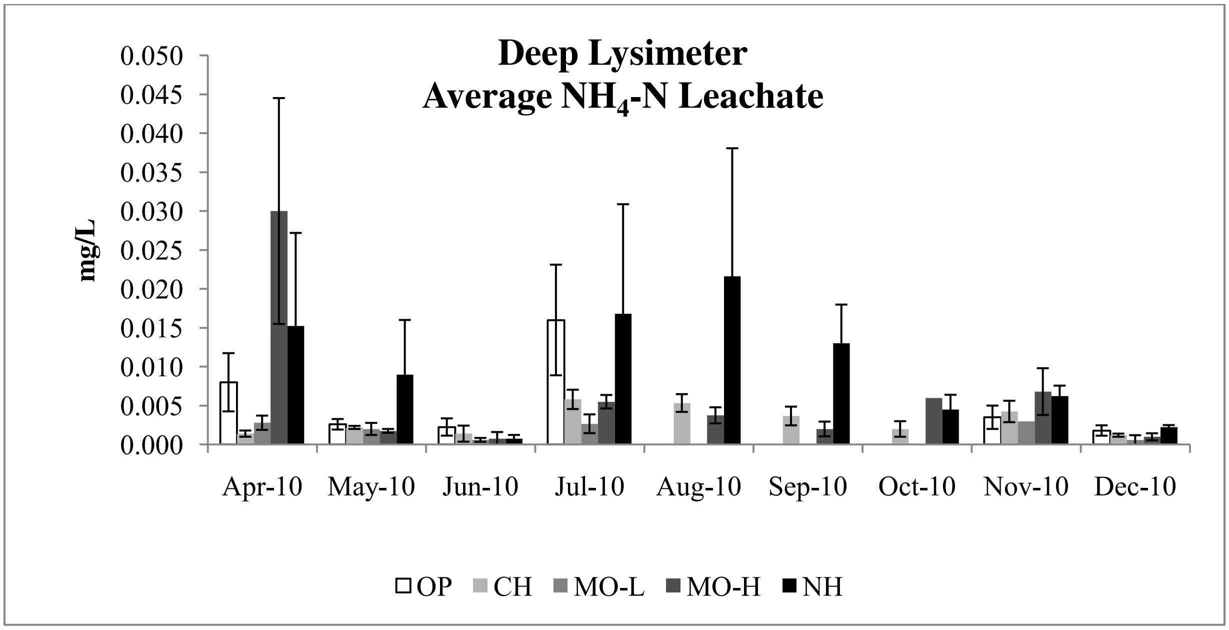

Figure 2.16 Average NH_4-N leachate in deep lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

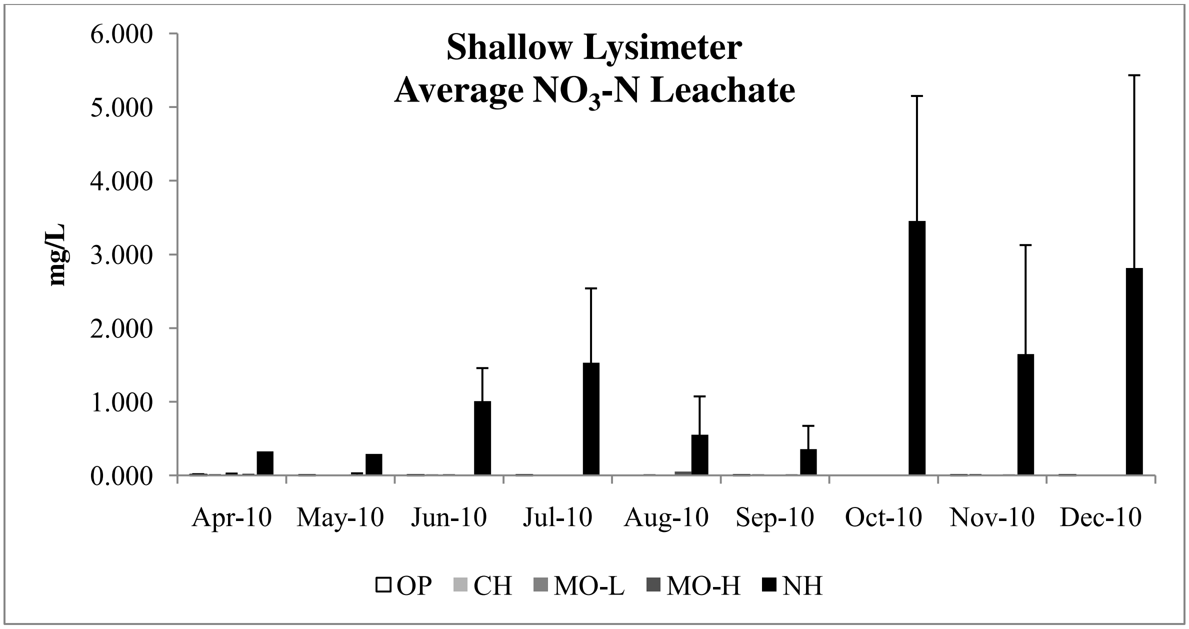

Figure 2.17 Average NO_3-N leachate in shallow lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

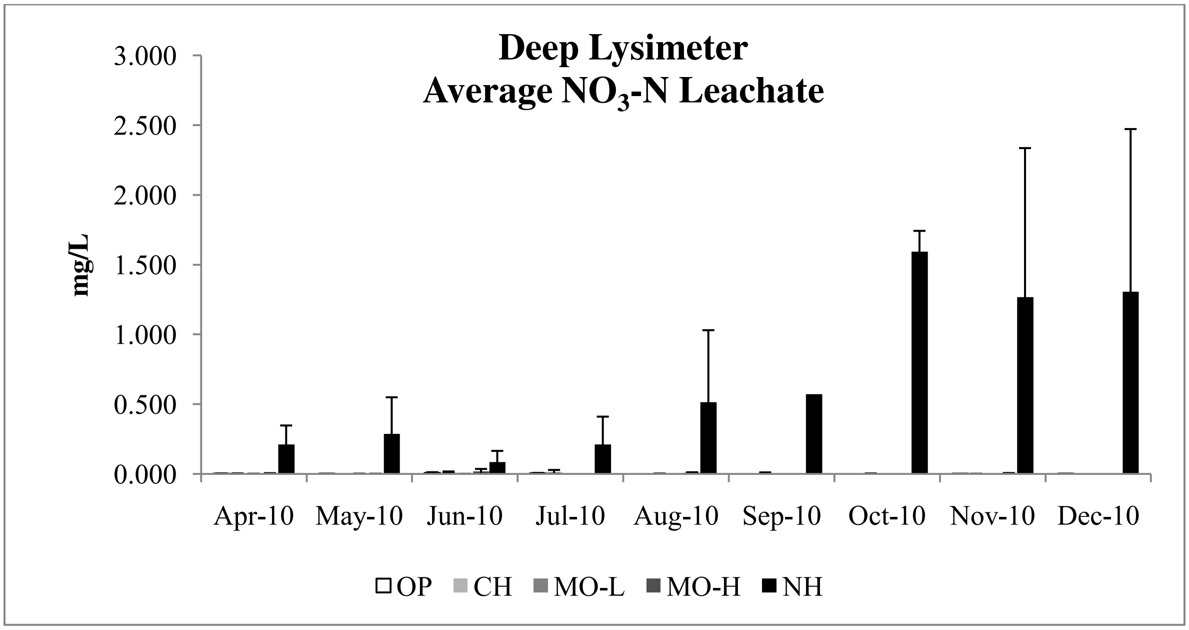

Figure 2.18 Average NO_3-N leachate in deep lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

DISCUSSION

In previous research on throughfall in these plots, Knoepp et al., found NH_4 concentrations to be greater in the MO-H plot and the NH plot (2008). This was not observed by the 2010 throughfall data. Analysis comparing mean monthly NH_4 concentrations for the growing season (April through September) and the fall season (October through December), showed that there was significantly greater mean throughfall concentrations of NH_4 in the growing season for both the low and MO-H plots (Figure 2.1). In contrast, though it was not significant, the two lowest elevation plots tended to have greater mean monthly concentrations of NH_4 in throughfall during the fall. Knoepp et al. (2008) found throughfall NO_3 concentrations to be greatest in the NH and the MO-L plots. The 2010 throughfall measurements of NO_3 found a similar pattern for the NH plot, but not for the mixed oak plots, supporting the initial hypothesis that the highest elevation plot would receive the greatest N input. Mean monthly NO_3 concentrations in throughfall were significantly greater during the fall season for all plots. This may in part be explained by canopy presence and NO_3 uptake (Potter et al. 1993).

In addition to increasing N deposition, there is significant N deposition variability along elevational gradients in the southern Appalachian Mountains. Lovett and Lindberg (1993) found that N deposition in low elevations in the Great Smokey Mountains is about 10 kg of N/ha per year, while N deposition in high elevations could be as high as 28 kg of N/ha per year. This phenomenon has been attributed to greater dry deposition and greater wet deposition from fog and clouds (Cai et al. 2010, Lovett and Lindberg 1993). Both the previous and 2010 throughfall measurements of NH_4 could be explained by this, as in both cases it is the highest elevation plots with significantly greater NH_4 concentrations in throughfall. The 2010 NO_3 throughfall measurements may also be explained by this phenomenon, where the highest elevation plot has significantly greater NO_3 concentrations in throughfall. The previous data supports this to an extent, but the high NO_3 concentrations in throughfall for the mid-elevation plot may need to be explained by another factor such as species composition or high spatial variability (Cai et al. 2010, Finzi et al. 1998a, Finzi et al. 1998b, Lovett and Lindberg 1993).

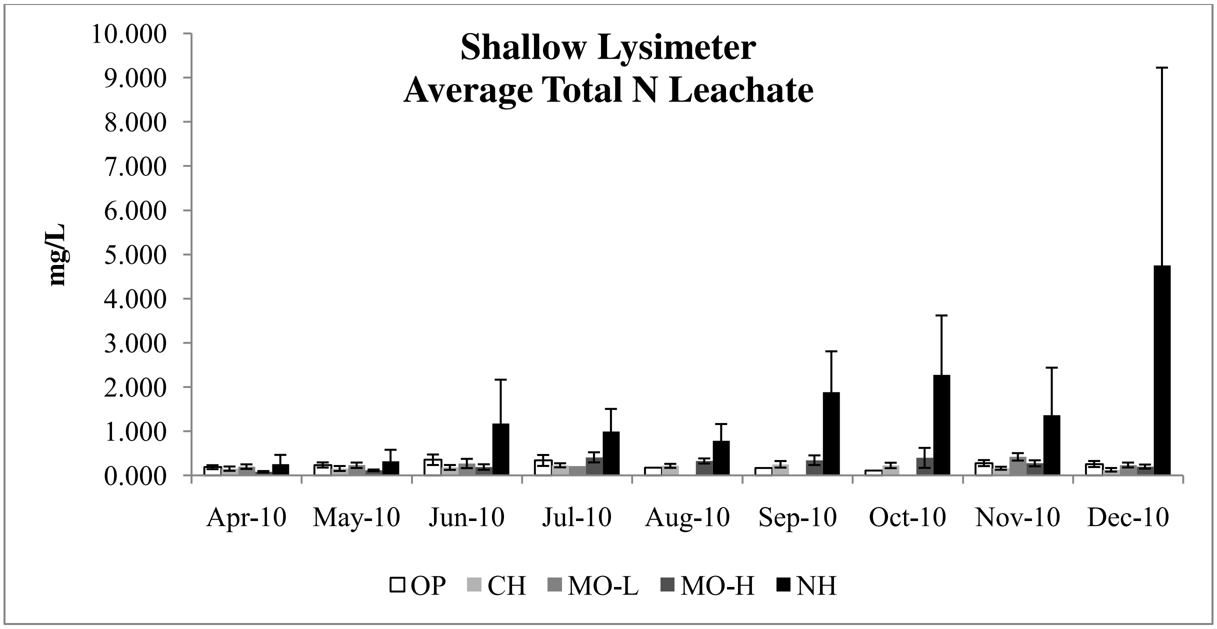

Figure 2.19 Average total N (TN) leachate in shallow lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

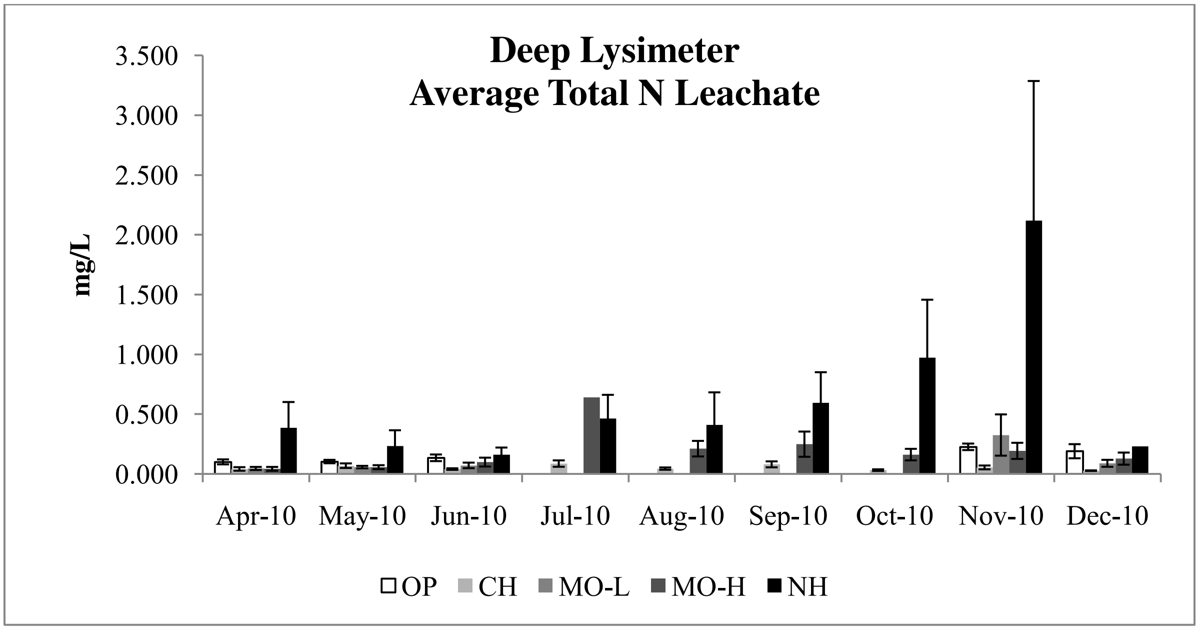

Figure 2.20 Average total N (TN) leachate in deep lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

Table 2.2 T-test P-values for Leachate Depth Comparisons

Plot	**NH4**	**NO3**	**TN**
mixed oak-pine	0.8328	0.7061	0.0034*
cove hardwood	0.0322*	0.1654	<0.0001*
low elevation mixed oak	0.0480*	0.1601	0.0002*
high elevation mixed oak	0.3323	0.7391	0.0477*
northern hardwood	0.8780	0.0808*	0.0730*

The p-values for the soil solution leachate depth comparisons were calculated using SAS® 9.1.2 to do t-test comparisons of NH_4, NO_3, and total N (TN) concentrations at two different lysimeter depths (shallow and deep), which were used to collect soil solution leachate. These t-tests were done for each individual plot.

There is much research suggesting that it is difficult to use throughfall to estimate bulk deposition (Barker et al. 2002, Raat et al. 2002, Shubzda et al. 1995). Throughfall, however, is a useful index for determining input of nutrients to a system below the canopy (Garten et al. 1999) thus it is important to look at N deposition in relation to N soil transformations. Cai et al. (2010) found that NH_4 in was significantly greater in throughfall when compared to NH_4 in the soil A-horizon. However, Cai et al. (2010) found the opposite relationship between NO_3 in throughfall and NO_3 in the soil A-horizon, with greater NO_3 concentrations in the A-horizon than in throughfall.

Previous examinations of overall trends in N transformations found that the greatest mineralization rates occurred during the summer months and in the highest elevation plot, the NH plot, and in the mid-elevation plot, the cove hardwood plot (Knoepp and Swank 1998, Knoepp and Vose 2007, Knoepp et al. 2008). In the 2010 N transformation measurements this trend was only observed for the highest elevation plotwhich supports the hypothesis that the highest elevation plot would have the greatest effect on N transformations, based on increased N deposition and temperature and moisture effects. Garten (2000) found greater N mineralization and nitrification rates in coves than in ridges, which might explain the high mineralization rates found in the cove hardwood plot in pervious measurements. It is also possible that species composition may be partly driving the soil N transformations (Finzi et al. 1998a, Finzi et al. 1998b). This was supported by the 2010 measurements which were done on the organic and mineral layers separately. The organic layer exhibited significantly greater N transformations across all plots, suggesting that “new” carbon such as leaf litter plays an important role in soil N dynamics.

Single time and/or localized measurements of soil NO_3 and NH_4 concentrations give a general idea of N availability to plants and ecosystems, yet soil NO_3 and NH_4 concentrations tend to vary both spatially and temporally (Cain et al. 1999, Kay et al. 2006, & Robertson et al. 1988). Cain et al. (1999) specifically looked at soil NO_3 and NH_4 concentrations and found significant spatial and temporal variability. Kay et al. (2006) found that both weather and time of the year can significantly affect plant available N. Furthermore, other forms of N might also be available to plants via N fixation by lightning or by free-living and symbiotic microbes (Schlesinger 1997). If measurements of soil NO_3 and NH_4 concentrations are done over space and time, taking into account variability, soil NO_3 and NH_4 concentrations could then be used as a base index for plant available N. To better understand what is really happening with the plant available forms of N, it is important to examine N in soil solution.

Previous measurements by Knoepp et al. found high concentrations of NO_3 in soil solution in the highest elevation plot, the NH plot, which suggested that there was N saturation occurring in this plot (Knoepp et al 2000, Knoepp et al. 2008). The same pattern was seen with the 2010 measurements in soil solution leachate in the NH plot, supporting the hypothesis that N dynamics would be significantly different in the most extreme plot, based on overall conditions. Previous soil solution NH_4 concentrations were found to be high in the mid-elevation plot, the low mixed oak plot, and the high elevation plot; however, this trend was not observed in 2010. It is possible that the variation in significance for soil solution NH_4 concentrations between the previous measurements and the 2010 measurements is due to changes in N dynamics due to global change, but it is also possible that the change in measurement methods may be the cause. A study done in high-elevation spruce- fir forests of the Great Smoky Mountains National Park found evidence to suggest that N availability in soils and NO_3 leaching will increase in response to warming and acid deposition (decreased soil pH), which is supported by both the previous and the 2010 soil solution measurements (Garten 2000, Johnson et al. 1999). Although different from what is observed on the gradient plots, Ross and Hales (2003) found that NO_3 and NH_4 leaching followed the same patterns as one another in Camels Hump State Forest in Huntington and Duxbury, VT.

Overall, most of the trends seen in previous measurements were observed in the 2010 measurements. The slight differences may be attributed to global change, but it is also possible that changes in measurement methodologies are the cause of slight differences between previous and 2010 measurements. Only by continuing observations under the effects of global climate change can there be a better understanding. Furthermore, with advances in measurement techniques and technology it is likely that we will gain a more realistic view of what is occurring in N processes in forests.

ACKNOWLEDGEMENTS

The author would like to acknowledge Jennifer D. Knoepp for in-depth descriptions of N measurement methods used on the Coweeta LTER gradient plots.

LITERATURE CITED

Aber, John D., Knute J. Nadelhoffer, Nitrogen saturation in northern forest ecosystems. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39(6): 378-386.

Adams, M.A. and P.M. Attiwill. 1986. Nutrient cycling and nitrogen mineralization in eucalypt forests of south-eastern Australia, 2: indices of nitrogen mineralization. Plant and Soil 92: 341-362.

Barker, M., Helga Van Miegroet, N. S. Nicholas, and I. F. Creed. 2002. Variation in overstory nitrogen uptake in a small, high-elevation southern Appalachian spruce–fir watershed. Canadian Journal of Forest Research 32: 1741-1752.

Cai, Meijun, John S. Schwartz, R. Bruce Robinson, Stephen E. Moore, and Matt A. Kulp. 2010. Long-Term Effects of Acidic Deposition on Water Quality in a High-Elevation Great Smoky Mountains National Park Watershed: Use of an Ion Input–Output Budget. Water, Air, and Soil Pollution 209(1-4): 143-156.

Cain, Michael L., Scott Subler, Jonathan P. Evans, & Marie-Josée Fortin. 1999. Sampling spatial and temporal variation in soil nitrogen availability. Oecologia 118: 397-404.

Clark, James S., Eric Macklin, and Leslie Wood. 1998. Stages and spatial scales of recruitment limitation in southern Appalachian forests. Ecological Monographs 68(2): 213-235.

Fenn, Mark E. J.O. Sickman, A. Bytnerowicz, D.W. Clow, N.P. Molotch, J.E. Pleim, G.S. Tonnesen, K.C. Weathers, P.E. Padgett and D.H. Campbell. 2009. Chapter 8: Methods for Measuring

Atmospheric Nitrogen Deposition Inputs in Arid and Montane Ecosystems of Western North America Developments in Environmental Science, Volume 9: 179-228. Elsevier Ltd.

Fenn, Mark E., and Mark A. Poth. 2004. Monitoring Nitrogen Deposition in Throughfall Using Ion Exchange Resin Columns: A Field Test in the San Bernardino Mountains. Journal of Environmental Quality 33:2007–2014.

Finzi, Adrien C., Charles D. Canham, and Nico Van Breeman. 1998b. Canopy Tree-Soil Interactions within Temperate Forests: Species Effects on pH and Cations. Ecological Applications 8(2): 447-454.

Finzi, Adrien C., Nico Van Breeman, and Charles D. Canham. 1998a. Canopy Tree-Soil Interactions within Temperate Forests: Species Effects on Soil Carbon and Nitrogen. Ecological Applications 8(2): 440-446.

Galloway, James N., Alan R. Townsend, Jan Willem Erisman, Mateete Bekunda, Zucong Cai, John R. Freney, Luiz A. Martinelli, Sybil P. Seitzinger, and Mark A. Sutton. 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320: 889-892.

Galloway, James N., Hiram Levy, II, Prasad S. KasibhatlaSource. 1994. Year 2020: Consequences of Population Growth and Development on Deposition of Oxidized Nitrogen. Ambio 23(2): 120-123.

Garten, C. T., Jr. 2000. Nitrogen Saturation and Soil N Availability in a High-Elevation Spruce and Fir Forest. Water, Air, and Soil Pollution 120: 295-313.

Garten, C.T., W.M. Post, P.J. Hanson, and L.W. Cooper. 1999. Forest soil carbon inventories and dynamics along an elevation gradient in the southern Appalachian Mountains. Biogeochemistry 45(2): 115-145.

Goulding, K.W.T., N.J. Bailey, N.J. Bradbury, P. Hargreaves, M. Howe, D.V. Murphy, P.R. Poulton, and T.W. Willison. 1998. Nitrogen Deposition and its Contribution to Nitrogen Cycling and Associated Soil Processes. New Phytologist 139(1): 49-58.

Hooper, David U., and Peter M. Vitousek. 1997. The Effects of Plant Composition and Diversity on Ecosystem Processes.Science 277: 1302-1305.

Intergovernmental Panel on Climate Change (IPCC). 2007. Climate Change 2007: Mitigation of Climate Change. Summary for Policymakers e Working Group III contribution to the Environmental Panel on Climate Change Fourth Assessment Report: 35.

Iverson, Louis R., Anantha Prasad, Mark W. Schwartz. 1998. Modeling potential future individual tree-species distributions in the eastern United States under a climate change scenario: a case study with Pinus virginiana. Ecological Modeling 115: 77-93.

Iverson, Louis R., and Anantha Prasad. 1998. Predicting abundance of 80 species following climate change in the Eastern United States. Ecological Monographs 68(4): 465-485.

Johnson, D. W., R. B. Susfalk, P. F. Brewer, and Wayne T. Swank. 1999. Simulated Effects of Reduced Sulfur, Nitrogen, and Base Cation Deposition on Soils and Solutions in Southern Appalachian Forests. Journal of Environmental Quality 28: 1336-1346.

Kay, B.D., A.A. Mahboubi, E.G. Beauchamp, & R.S. Dharmakeerthi. 2006. Integrating Soil and Weather Data to Describe Variability in Plant Available Nitrogen. Soil Science Society of America Journal 70: 1210-1221.

Knoepp, Jennifer D. and James M. Vose. 2007. Regulation of nitrogen mineralization and nitrification in Southern Appalachian ecosystems: Separating the relative importance of biotic vs. abiotic controls. Pedobiologia 51: 89-97.

Knoepp, Jennifer D., and Wayne T. Swank. 1998. Rates of Nitrogen Mineralization across an Elevation and Vegetation Gradient in the Southern Appalachians. Plant and Soil 204: 235-241.

Knoepp, Jennifer D., Barbara C. Reynolds, D.A. Crossley Jr., and Wayne T. Swank. 2005. Long-term changes in forest floor processes in southern Appalachian forests. Forest Ecology and Management 220: 300-312.

Knoepp, Jennifer D., David C. Coleman, D.A. Crossley Jr., and James S. Clark. 2000. Biological indices of soil quality: an ecosystem case study of their use. Forest Ecology and Management 138: 357-368.

Knoepp, Jennifer D., James M. Vose, and Wayne T. Swank. 2008. Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests. International Journal of Environmental Studies 65: 389-408.

Lafleur, Benoit, David Pare´ , Alison D. Munson, and Yves Bergeron. 2010. Response of northeastern North American forests to climate change: Will soil conditions constrain tree species migration? Environmental Reviews 18: 279–289.

Li, Wenhong, Laifang Li, Rong Fu2 Yi Deng, and Hui Wang. 2010. Changes to the North Atlantic Subtropical High and Its Role in the Intensification of Summer Rainfall Variability in the Southeastern United States. Journal of Climate: http://journals.ametsoc.org/doi/abs/10.1175/2010JCLI3829.1

Lovett, Gary M., Timothy H. Tear, David C. Evers, Stuart E.G. Findlay, B. Jack Cosby, Judy K. Dunscomb, Charles T. Driscoll, and Kathleen C. Weathers. 2009. Effects of Air Pollution on Ecosystems and Biological Diversity in the Eastern United States. The Year in Ecology and Conservation Biology 1162: 99–135.

Lovett, Gray M., and Steven E. Lindberg. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. Canadian Journal of Forest Research 23(8): 1603–1616.

Meier, Courtney L., and William D. Bowman. 2008. Links between plant litter chemistry, species diversity, and below-ground ecosystem function. PNAS 105(50): 19780-19785.

Melillo, J. M., S. Butler, J. Johnson, J. E. Mohan, P. A. Steudler, H. Lux, E. Burrows, F. Bowles, R. Smith, T. Hill, C. Vario, A. J. Burton, Y. Zhou, J. Tang. 2011. Soil Warming, carbon-nitrogen, integrations and forest carbon budgets. Proceedings of the National Academy of Sciences.

Nodvin, S. C., Helga Van Miegroet, Steven E. Lindberg, N. S. Nicholas, and D. w. Johnson. 1995. Acidic deposition, ecosystem processes, and nitrogen saturation in a high elevation Southern Appalachian watershed. Water, Air, and Soil Pollution 85(3): 1647-1652.

Raat, K. J., G. P. J. Draaijers, M. G. Schaap, A. Tietema, and J. M. Verstraten. 2002. Spatial variability of throughfall water and chemistry and forest floor water content in a Douglas fir forest stand. Hydrology and Earth System Sciences 6(3): 363-374.

Robertson, G. Philip, Michael A. Hutson, Francis C. Evans, & James M. Tiedje. 1988. Spatial Variability in a Successional Plant Community: Patterns of Nitrogen Availability. Ecology 69(5): 1517-1524.

Ross, Donald S. and Heidi C. Hales. 2003. Sampling-Induced Increases in Net Nitrification in the Brush Brook (Vermont) Watershed. Soil Science Society of America 67(1): 318-326.

Schlesinger, William H. 1997.Biogeochemistry: An Analysis of Global Change. New York: Academic Press.

Schwab, A. P. 2000. "Chapter 3: The Soil Solution." Handbook of Soil Science. Boca Raton, FL: CRC. B85-B104. Print.

Shubzda, J., Steven E. Lindberg, C. T. Garten, and S. C. Nodvin. 1995. Elevational trends in the fluxes of sulphur and nitrogen in throughfall in the southern Appalachian mountains: Some surprising results. Water, Air, and Soil Pollution 85(4): 2265-2270.

Tilman, David, Johannes Knops, David Wedin, Peter Reich, Mark Ritchie, Evan Siemann. 1997. The Influence of Functional Diversity and Composition on Ecosystem Processes. Science 277: 1300-1302.

United States Global Change Research Program (USGCRP). 2009. State of the knowledge report of Global Climate Change impacts in the U.S.

Van Miegroet, Helga, and Robert Jandl. 2007. Are nitrogen-fertilized forest soils sinks or sources of carbon? Enviromental Monitoring and Assessment 128: 121-131.

Van Miegroet, Helga. 1995. Inorganic nitrogen determined by laboratory and field extractions of two forest soils. Soil Science Society American Journal 59:549-553.

Vitousek, Peter M., John D. Aber, Robert W. Howarth, Gene E. Likens, Pamela A. Matson, David W. Schindler, William H. Schlesinger and David G. Tilman. 1997. Technical Report: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. Ecological Society of America 7(3): 737-750.

CHAPTER 3

SOIL PHOSPHORUS DYNAMICS IN FIVE SOUTHERN APPALACHIAN FORESTS LOCATED IN THE COWEETA LONG-TERM ECOLOGICAL RESEARCH GRADIENT PLOTS

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ABSTRACT

Phosphorus (P) dynamics in forest systems are becoming ever more important with increasing temperatures and acidification of soils from deposition of acidic volatile compounds (SO_4, NO_3, and PO_4). In this study, five plots were established at the Coweeta Hydrologic Laboratory in Otto, NC, along a natural elevation, temperature, moisture, and vegetation gradient. These plots established long-term measurements including throughfall, phosphate (PO_4) soil concentrations, and soil solution leachate, to better understand the effects of global change on forest biogeochemical cycles. Based on previous measurements in the Coweeta gradient plots, it was hypothesized that the highest elevation site would receive the most P input into the system via throughfall and also the greatest response to increased nitrogen (N) and PO_4 deposition, temperature, and moisture dynamics. This hypothesis was supported by soil P pool fractionation measurements and soil solution leachate measurements completed in 2010, but not by throughfall measurements.

INDEX WORDS: Phosphorus (P), southern Appalachian forests, throughfall, P fraction, Psenner, soil solution

INTRODUCTION

Global climate change is expected to affect temperature, precipitation, nutrient availability, and species distributions (Schlesinger 1997, Iverson & Prasad 1998). With increased temperatures due to anthropogenic emissions of heat trapping gases including carbon dioxide (CO_2), the southeastern United States is expected to become warmer with increased summer (growing season) precipitation variability, which would include periods of drought or deluge (IPCC 2007, Li et al. 2010). In the Southeastern U.S., doubled atmospheric CO_2 is predicted to increase annual temperature 3-5 °C and reduce summer precipitation 20-30% (Mearns et al 2003). Temperature and precipitation change can cause changes in nutrient dynamics which are exacerbated by anthropogenic nitrogen (N) deposition increases in the southeastern United States, particularly as the region becomes increasingly urbanized (atmospheric nitrate (NO_3) is relatively short-lived, and generally deposits near anthropogenic sources) (IPCC 2007, Li et al. 2010).

There is some evidence to suggest that phosphorus (P) deposition might also be changing. A study by Mahowald et al. (2008) found that globally only 4.8% of atmospheric (largely particulate) P is the result of anthropogenic influence, but that in areas influenced by industrialization or biomass burning, such as the southeastern United States, as much as 50% of total P deposition can be contributed to anthropogenic influence. Therefore, it remain important to understand how southeastern forests, including traditionally cool and moist southern Appalachian forests, will respond to increased temperatures, changes in precipitation, and increased deposition.

Further, southern Appalachian tree species abundance is expected to change, which in turn may affect both forest sequestration and nutrient availability (Iverson & Prasad 1998). Understanding biogeochemical dynamics and nutrient limitation(s) in southern Appalachian forests under global change is critical for predicting how these forests will look and function in this century and beyond. With the changes expected to occur in this region, it is vital to understand P dynamics in forest systems, particularly in southern Appalachian forests (LeBauer and Treseder 2008, Schlesinger 1997). Across ecosystems, N and P are both important for organismal growth and thus are important for net primary production (NPP) and carbon sequestration (Schlesinger 1997). A solid understanding of N and P limitation(s) in ecosystems is fundamental in understanding overall ecosystem function, particularly for use in future system function. N and P are common limiting factors in temperate and tropical systems. Previous research supports a common N limitation in temperate systems and a P limitation in tropical systems (LeBauer & Treseder 2008, Vitousek & Howarth 1991, Vitousek et al. 2010, & Walker & Syers 1976). With the aging and weathering of temperate soils and predicted increases in N deposition (Schlesinger 1997), it is possible that temperate systems will become P limited or N and P co-limited. The idea of limitation itself has become more complex especially considering future climate predictions and consequent ecosystem changes.. A common understanding of limitation comes from Liebig‟s Law of the Minimum, which states that if one nutrient is lacking, then plant growth will be poor even if other nutrients are in abundance (Danger et al. 2008). However, this can be complicated by such factors as multiple limitations or species-specific responses. For example, a species may be limited by two nutrients causing a co-limitation. This would be common in nutrients with linked cycles such as N and P (Finzi et al. 2011, Schlesinger 1997, Vitousek et al. 2010, & Walker & Syers 1976). Another complication of limitation would be in a system with more than one species. For example, one tree species may be water limited, while another with deeper taproots is not. Another example might be where the plant species are limited by a nutrient, but the surrounding microbial associates are limited by another nutrient. All of these scenarios complicate the generalization of ecosystem nutrient limitation. In addition to limitation, there may be a close linkage between N and P, and N and P ratios are often used to predict carbon sequestration potential (Parton 1988). The relationship between N and P may be a synergistic, where one may enhance the biological action of the other, while both remain important for forest productivity and carbon storage. Work by Houlton et al. (2008) suggests plant-available N may enhance plant acquisition of P by increasing levels of phosphatase enzymes used by plants to acquire P from the soil. Another model proposed by Perring et al. (2007) suggested that if either plant-available N or plant-available P is limited in a system, the other nutrient will become plant-limited as well. This may occur due to the limitation of one nutrient inhibiting a plant‟s ability to acquire the other nutrient from the soil.

The temperate forests of the southern Appalachian Mountains have traditionally been considered to be N-limited systems (Knoepp et al. 2008, Knoepp and Vose 2008). The potential of N limitation of forest productivity and species composition is especially important, given that upper elevations in the southern Appalachians currently receive high levels of anthropogenic N deposition, likely from industrial and agricultural sources (Knoepp et al. 2008). Future deposition rates will depend in part on the continuing exacerbation and development of the southern Appalachian regions. With increased N deposition it is possible that another factor, such as P, will become limiting in southern Appalachian forests. If southern Appalachian forests prove to be limited by N and not P, rates of productivity and carbon storage in these ecosystems may continue to be enhanced through N deposition (LeBauer and Treseder 2008). Conversely, if P limitation is important in these forests and is not alleviated by increases in N availability, anthropogenic N deposition will not enhance the productivity and carbon storage by southern Appalachian forest ecosystems.

In order to achieve a better understanding of climate change in southern Appalachian forests this study focuses on five established gradient plots, which are part of the Coweeta Long-term Ecological Research (LTER) project, funded by the National Science Foundation (Knoepp and Swank 1998). The five sites represent five southern Appalachian forest types, which were categorized by dominant tree species, moisture regime, and elevation as follows: mixed oak-pine (OP), cove hardwoods (CH), low elevation mesic mixed oak (MO-L), high elevation mesic mixed oak (MO-H), and northern hardwood (NH) (Clark et al. 1998, Knoepp et al. 2000, Knoepp and Vose 2007, Knoepp et al. 2008). In addition to being representative of five southern Appalachian forest types these plots were placed along a natural elevation, temperature, and moisture gradient. The gradient plots were established in 1991 as 20 m x 40 m plots for intensive measurement purposes, such as throughfall chemistry from July 1992 through November 1997, soil transformations and pools from May 1991 through October 1996, soil solution chemistry from May 1994 through December 2001, and above ground vegetation productivity (Clark et al. 1998, Knoepp et al. 2008). N has been the primary focus of previous work on these plots, though some P measurements have been done giving some basis for comparison of past measurements to more current measurements.

Previous P Throughfall Measurements

Throughfall measurements were done from July 1992 until November 1997, using six 0.15 x 2.0 meter troughs spaced randomly throughout the intensive gradient plots. These throughfall troughs were collected weekly, but then composited for a monthly throughfall analysis of orthophosphate ($O\text{-}PO_4$). The

O-PO_4 concentrations were reported as mg/L for each sample, which was converted to g/ha using the specific volume of each throughfall sample and the area of the throughfall collector trough (0.3 m^2) (Knoepp et al. 2008).

These previous throughfall measurements recorded little to no O-PO_4 concentrations in any of the plots during the fall season (October through November), with significantly greater throughfall O-PO_4 concentrations during the growing season (April through September) (Knoepp et al. unpublished data). Though the O-PO_4 concentrations were low, the greatest fall O-PO_4 concentrations were observed during the fall of 1992, when the concentrations of O-PO_4 were significantly greater in the MO-L plot and the NH plots, compared to the rest of plots during that season. Though concentrations were still lower than they were in 1992, during the fall of 1993 the NH plot had significantly more O-PO_4 in throughfall when compared to the rest of the plots. However, during the fall of 1994, both the low and MO-H plots had significantly greater O-PO_4 in throughfall when compared to the rest of the plots during that season. Fall 1995 exhibited the lowest recorded O-PO_4 throughfall concentrations during these earlier measurements (Knoepp et al. unpublished data), and the MO-H plot had slightly more O-PO_4 in throughfall than any other plot. During the growing season, the greatest concentrations of O-PO_4 were consistently observed in the high elevation plots. During the 1993 growing season, the three highest elevation plots had significantly more O-PO_4 in throughfall than did the two lowest elevation plots. During the 1994 growing season, this trend continued, but O-PO_4 in throughfall was highest in the two highest elevation plots, the MO-H plot and the NH plot. During the 1995 growing season there was a significant spike in throughfall O-PO_4 concentrations in the MO-H plot and the high-elevation correlating with high O-PO4 relation shifted. Although the MO-H plot had the greatest concentration of O-PO_4 in throughfall, the MO-L plot had the second greatest O-PO_4 concentration. During the 1996 growing season the O-PO_4 in throughfall dropped in the MO-H plot, while the MO-L plot retained the greatest concentration of O-PO_4 in throughfall, followed by the MO-H and the NH plots (Knoepp et al. unpublished data).

Previous Soil P Measurements

Soil cation measurements were done on the gradient plots February 1992, April 1992, August 1992, January 1994, and January 1995, using *in situ*, closed, PVC cores, 10 cm into the mineral soil (modified method from Adams and Attiwill 1986, Knoepp and Swank 1998, Knoepp et al. 2008). Soil cores were taken using 15-cm long PVC cores with an interior diameter of 4.3 cm, which were driven 10 cm into the mineral soil. Following collection cores were kept cool (~4˚C) until analyzed. Within 24 hours of collection, the mineral soils from the cores were moist sieved to <6 mm and divided into two samples, a 20-g sample and a 5-g sample. The 20-g sample was dried in an oven at 105˚C for >12 hours to determine the oven-dry weight. The 5-g sample was extracted using a double acid extraction to extract soil PO_4-P and other cations. The soil was then analyzed for PO_4-P and other cations using an auto analyzer at the Coweeta Hydrologic Laboratory and was reported in µg/g (Knoepp and Swank 1998, Knoepp et al. 2008, Personal Communication with Knoepp).

The soil PO_4-P concentrations tended to be greater in the high elevation plots. Also, PO_4-P concentrations increased significantly from the August 1992 measurement to the January 1994 measurement. These concentrations dropped in the January 1995 measurement, but remained significantly greater than the 1992 measurements for the cove hardwood, low elevation mixed oak, and NH plots (Knoepp et al. unpublished data).

Previous P in Soil Solution Measurements

Previous lysimeter measurements were done from May 1994 through December 2001, to measure soluble P and other constituents in soil solution. Each intensive gradient plot had 10 lysimeters, five of which were placed 15 cm into the soil and five into the lower area of the B horizon. The lysimeters were sampled weekly and composited for monthly analysis of O-PO_4 and other ions and were reported as mg/L (Knoepp et al. 2008, Knoepp et al. 2000).

The soil solution O-PO_4 concentration was observed to be greater in the shallow lysimeters when compared to the deep lysimeters. The soil solution O-PO_4 concentration tended to increase in the deep lysimeters during the winter months (November through March), with the greatest O-PO_4 concentrations commonly observed in the high elevation plots year round (Knoepp et al. unpublished data).

To gain an even better understanding of P dynamics in these plots under global change, throughfall and lysimeter measurements were continued in the spring of 2010, and soil P pool analysis was done of archived gradient plot soils collected in 2008. Based on the previous work on these sites the objectives of this study were to determine if the patterns of P dynamics in the gradient plots have changed as a result of global change in regards to 1) the increase of phosphate (PO_4) deposition that is occurring and increasing the plant available P pool, or 2) if system conditions such as moisture, acidity, and increased N availability are forcing the system into P-limitation. It was hypothesized that the highest elevation site would receive the most PO_4 deposition as measured via throughfall, and as one of the most extreme sites also have the greatest response to increased N and P deposition and moisture dynamics.

MATERIALS AND METHODS

Site Description

The study was done at the 2180 ha Coweeta Hydrologic Laboratory of the USDA Forest Service facility located in the southern Appalachian Mountains in western North Carolina.

This region receives an average annual precipitation of 1900 mm with most monthly precipitation averaging greater than 100 mm. The greatest mean monthly temperature is about 20˚C, occurring June through August. The lowest mean monthly temperature is about 5˚C occurring December through January. The growing season begins early May and extends to early October (Knoepp and Swank 1998, Knoepp et al. 2005, Knoepp and Vose 2007, Knoepp et al. 2008).

The study was located in two north-facing reference watersheds, watershed 18 and watershed 27, in the Coweeta Hydrologic Laboratory basin, which have been undisturbed and uncut since 1929 (Knoepp et al. 2005, Knoepp and Vose 2007, Knoepp et al. 2008). Within these two watersheds, five gradient plots were established in 1991 as part of the Coweeta Long-Term Ecological Research (LTER) project, funded by the National Science Foundation (Knoepp and Swank 1998). The five sites represent four southern Appalachian forest types, which were categorized by dominant tree species, moisture regime, and elevation as follows: mixed oak-pine (OP), cove hardwoods (CH), low elevation mesic mixed oak (MO-L), high elevation mesic mixed oak (MO-H), and northern hardwood (NH). The plots were chosen not only to southern Appalachian forest types, but also to demonstrate a natural elevation, temperature, moisture, and vegetation gradient at Coweeta (Clark et al. 1998, Knoepp et al. 2000, Knoepp and Vose 2007, Knoepp et al. 2008). The gradient plots were established as 20 x 40 m plots used for intensive measurement purposes which included throughfall chemistry, soil cation measurements, soil solution chemistry, and above ground vegetation productivity (Table 3.1) (Clark et al. 1998, Knoepp et al. 2008).

P Throughfall

2010 throughfall measurements were done using ion exchange resin columns developed by Fenn and Poth (2004). The resin columns were built with 1.3 x 35.6 centimeter round PVC pipe with a drain cap on the bottom and were attached at the top to a 22.9 cm diameter funnel. The columns were filled with Rohm and Haas Amberlite IRN 150 mixed bed ion-exchange resin. Five resin throughfall collectors were spaced randomly throughout each of the intensive gradient plots and were collected seasonally. The first throughfall collection season was the growing season, which included April (from bud break) to September. The second season, the fall season, included throughfall from October to December. The columns were collected after each season, and extracted individually with 100 mL of 2N KCl and analyzed on an Astoria 2 Autoanalyzer for PO_4 at the Coweeta Hydrologic Laboratory in Otto, NC (Fenn and Poth 2004, Fenn et al. 2009). The concentrations of PO_4 in KCl extractant were reported in mg/L, which was converted to g/ha, using the area of the throughfall collector funnel (411.87 cm^2) and the extractant volume (100 mL).

Table 3.1 Gradient Sites

Site	Site ID	Elevation (m)	Dominant Vegetation	Air Temperature (1 m)	Soil Temperature (20 cm)	Rainfall (cm)	Moisture Regime	pH
Mixed Oak-Pine (OP)	118	788	*Quercus prinus, Quercus rubra, Carya spp., Kalmia latifolia*	15.1	14.8	210.2	xeric	3.9
Cove Hardwood (CH)	218	801	*Liriodendron tulipifera, Quercus rubra, Tsuga canadensis, Carya spp.*	14.5	14	212.4	mesic	4.2
Low Elevation Mixed Oak (MO-L)	318	860	*Quercus coccinea, Quercus prinus, Rhododendron maxima*	15	13.5	222.9	mesic	4.0
High Elevation Mixed Oak (MO-H)	427	1094	*Quercus rubra, Carya spp., Rhododendron maxima*	13.6	12.8	264.9	mesic	4.0
Northern Hardwood (NH)	527	1389	*Betula allegheniensis, Liriodendron tulipifera, Quercus rubra, Acer saccharum*	11.8	10.8	267.6	mesic	4.0

The site elevation, dominate species, air temperature, soil temperature, rainfall, and moisture regime from Knoepp and Vose (2007) and Knoepp et al. (2008). Average pH values calculated from Coweeta Long-Term Ecological Research Program records data.

Soil P Pools

Soil cores were taken in January 2008 in the gradient plots. The cores were taken at three different locations in the intensive gradient plots at three different depths: 0 - 10 cm, 10 -30 cm, and over-30 cm (as far down as 90 cm in some cases). The soils were collected using a 2.54 cm soil probe, air-dried, and sieved to <2 mm. A double acid extraction was also done to estimate plant available P. The remaining soil samples were archived and stored in glass jars (Personal Commutation with Knoepp). A modified Psenner (1988) five step fractionation was used to extract the different pools of P (Table 3.2) (SanClements 2009, SanClements et al. 2009). One gram of the archived soil was placed in a centrifuged tube along with the first extractant, 25 mL of 1*M* NH_4Cl (pH7), and shaken at 250 rpm, at 25˚C for 1 hour to extract labile P. Then the NH_4Cl and soil mixture was centrifuged at 3000g for 15 minutes. The supernatant was then pipetted out and filtered through a Whatman® 40 filter paper into a 60 mL bottle (labeled "labile P"). This was repeated with another 25mL of 1*M* NH_4Cl (pH7), shaken at 250 rpm at 25°C for one minute, centrifuged at 3000g for 15 minutes, and then filtered through Whatman® 40 filter paper into the same 60 mL bottle (total extractant volume of approximately 50 mL) in order to get any remaining labile P. Second, 25 mL of 0.1M $NaHCO_3$-$Na_2S_2O_4$ was added to the one gram of soil in the original centrifuged tube and shaken (Burrell Wrist Action Shaker, Model 75 set on level 1) at 40˚C for 30 minutes to extract reducible iron P. Then the $NaHCO_3$-$Na_2S_2O_4$ and soil mixture was centrifuged at 3000g for 15 minutes. The supernatant was then pipetted out and filtered through a Whatman® 40 filter paper into a new 60 mL bottle (labeled "reducible iron P"). This was repeated with another 25mL of 0.1M $NaHCO_3$-$Na_2S_2O_4$, shaken (Burrell Wrist Action Shaker, Model 75 set on level 1) at 40˚C for one minute, centrifuged at 3000g for 15 minutes, and then filtered through Whatman® 40 filter paper into the same 60 mL bottle (extractant total volume of approximately 50 mL) in order to get any remaining reducible iron P. Third, 25mL 0.1M NaOH was added to the one gram of soil in the original centrifuged tube and shaken at 250 rpm at 25°C for 16 hours to extract aluminum and some iron P. Then the 0.1 M NaOH and soil mixture was centrifuged at 3000g for 15 minutes. The supernatant was then pipetted out and filtered through a Whatman® 40 filter paper into a new 60 mL bottle (labeled “aluminum and some iron P”). This was repeated with another 25 mL of 0.1M NaOH, shaken at 250 rpm at 25°C for one minute, centrifuged at 3000g for 15 minutes, and then filtered through Whatman® 40 filter paper into the same 60 mL bottle (extractant total volume of approximately 50 mL) in order to get any remaining aluminum and some iron P. For the fourth step, 25 mL of 0.5M HCl was added to the one gram of soil in the original centrifuged tube and shaken at 250 rpm at 25°C for 16 hours to extract exposed apatite-P. Then the HCl and soil mixture was centrifuged at 3000g for 15 minutes. The supernatant was then pipette out and filtered through a Whatman® 40 filter paper into a new 60 mL bottle (labeled “exposed apatite-P”). This was repeated with another 25 mL of 0.5M HCl, shaken at 250 rpm at 25°C for one minute, centrifuged at 3000g for 15 minutes, and then filtered through Whatman® 40 filter paper into the same 60 mL bottle (exactant total volume of approximately 50 mL) in order to get any remaining exposed apatite-P. For the final step, 25 mL of 1M NaOH was added to the one gram of soil in the original centrifuged tube and shaken (Burrell Wrist Action Shaker, Model 75 set on level 1) at 85°C for 24 hours to extract refractory and residual P. Then the 1M NaOH and soil mixture was centrifuged at 3000g for 15 minutes. The supernatant was then pipetted out and filtered through a Whatman® 40 filter paper into a new 60 mL bottle (labeled “refractory and residual P”). This was repeated with another 25 mL of 1M NaOH, shaken (Burrell Wrist Action Shaker, Model 75 set on level 1) at 85°C for one minute, centrifuged at 3000g for 15 minutes, and then filtered through Whatman® 40 filter paper into the same 60 mL bottle (extractant total volume of approximately 50 mL) in order to get any remaining refractory and residual P. The 50 mL extractant from each step was then analyzed for P, Ca, Fe, and Al on the ICP machine at the Coweeta Hydrologic Laboratory in Otto, NC. All P, Ca, Fe, and Al concentrations were reported as mg/L of extractant, which was converted to mg/kg using the dry soil mass (1 g) and the extractant total volume (50 mL) (SanClements 2009, SanClements et al. 2009).

Table 3.2 Modified Psenner Fractionation Steps and Fractions

Step		Fraction extracted	Plant Availability	Turnover
1	1M NH_4Cl pH7 at 25˚C for 1 hour	Labile P	Most Available	Rapid
2	0.1M $NaHCO_3$-$Na_2S_2O_4$ at 40˚C for 30 minutes	Reducible Fe-P	Readily Available	Rapid
3	0.1M NaOH at 25˚C for 16 hours	Al and some Fe-P	Lesser Available*	Slow
4	0.5M HCl at 25˚C for 16 hours	Exposed Apatite-P	Not Available	Slow
5	1M NaOH at 85˚C for 24 hours	Refractory and Residual P	Not Available	

The table illustrates each step in the modified Psenner fractionation, the fraction extracted by each step, the plant availability of each fraction, and the turnover for each fraction (Psenner et al. 1988, SanClements 2009, SanClements et al. 2009). The "*" denotes a plant availability that may be determinate on the soil pH (Havlin et al. 2005, Stevenson 1986).

P Soil Solution in Lysimeter

From April 2010 through December 2010, lysimeter measurements were continued to measure soluble P and other constituents in soil solution. Five pairs of lysimeters were placed in each of the intensive gradient plots. The lysimeter pairs consisted of one lysimeter which was placed 15 cm into the soil and one located nearby which was placed 30 to 85 cm into the soil into the lower area of the B horizon (Knoepp et al. 2008, Knoepp et al. 2000). It should be noted that the lysimeters for the 2010 measurements replaced lysimeters from the historical measurements and were placed in the exact same holes. The lysimeters were placed on a vacuum of 30 to 35 centibars to collect the plant available water in the soil pores (Schwab 2000). The lysimeters were pumped out every other week. These samples were paired. Where the first sample was analyzed for O-PO4, total P (TP), and other ions, and the second sample (two weeks later) was analyzed for TN and dissolved organic carbon (DOC) at the Coweeta Hydrologic Laboratory in Otto, NC. These sample values were assigned on a monthly basis and reported as mg/L since the exact area or volume of soil from which the samples were leached cannot be determined.

Statistical Analysis

Throughfall statistical analysis was done using SAS® 9.1.2. Due to equal sample sizes per plot and season (n=5) analysis of variance (ANOVA) at α=0.05 was done on the data to compare overall significance as well as significance for plot and season effects on PO_4 concentrations. T-tests were also performed for each plot to compare PO_4 concentrations of each season (growing and fall). In addition to the ANOVA analysis a Tukey range test was also done at α=0.05 to compare plots for each season.

Analysis of pools extracted using the modified Psenner fractionation (SanClements 2009, SanClements et al. 2009) was done using SAS® 9.1.2. Due to equal sample sizes per plot and per depth (n=3), ANOVA at α=0.05 was done on the data to compare P and Al concentrations in pools for each plot and at each depth. This analysis was also used explore any significant interactions. In addition to the

ANOVA, which was done for each pool, a range test was also done at $\alpha=0.05$ to compare plots and depths. A linear regression was also done in Microsoft® Excel to examine any relationship between Al and P in the "Al and some Fe-P"pool and in the "refractory and residual" pool (Figures 3.4 and 3.5).

For soil solution PO_4 and TP concentrations collected by lysimeters, SAS® 9.1.2 was used to do t-test comparisons of shallow and deep lysimeters for each plot. GLM at $\alpha=0.05$ was used to compare concentrations per plot by lysimeter depth (shallow and deep), by month, and by season (spring 2010 (April through May), summer 2010 (June through August), fall 2010 (September through November), and winter 2010 (December)). PO_4 and TP concentrations were also graphed by depth, plot, and month for visual comparisons (Figures 3.6 through 3.9).

RESULTS

For throughfall PO_4 concentrations, there were significant main effects ($P<0.0001$) when comparing plots and seasons. PO_4 concentrations in throughfall during the growing season (April - September) were significantly different from the fall season (October- December) for the low elevation plots, the OP ($P=0.0380$), the cove hardwood ($P=0.0028$), and the MO-L ($P=0.0004$) (Figure 3.1). In contrast to the low elevation plots, the highest elevation plot, the NH plot, had significantly greater concentrations of PO_4 during the fall season ($P=0.0680$). When examining the results for just the growing season, the MO-L plot PO_4 concentrations were significantly greater ($P=0.0034$) than the OP plot, the MO-H plot, and the NH plot. When looking at the Tukey range test for just the fall season, the NH plot had significantly greater ($P<0.0001$) mean throughfall PO_4 concentrations than in any of the over plots (Figure 3.2).

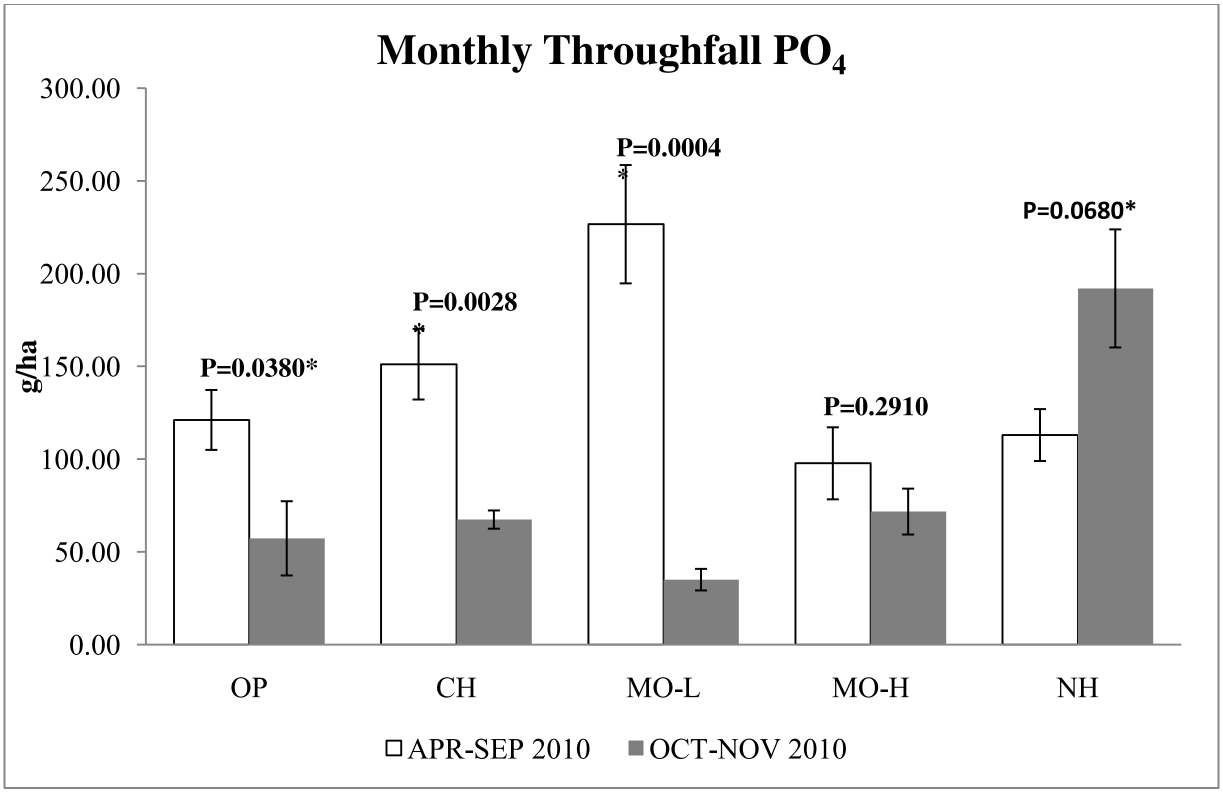

Figure 3.1 Average monthly throughfall PO_4 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH). P-values above each plot are the result of T-test analysis comparing PO_4 concentrations for the 2010 growing season (April through September) and the 2010 fall season (October through December). Any significant p-values are noted with a "*".

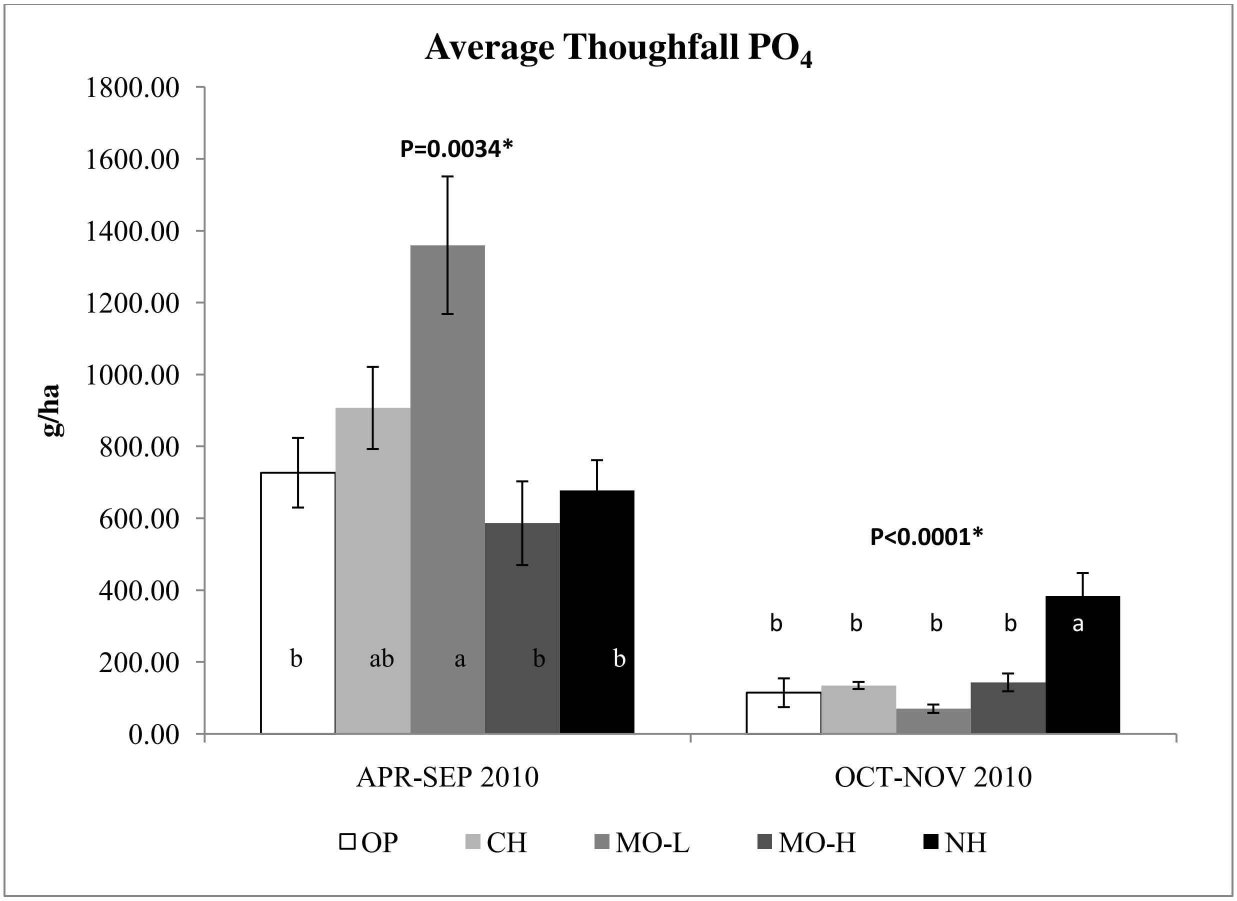

Figure 3.2 Average throughfall PO_4 for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH), divided up by season. P-values above each plot are the result of Tukey range test analysis comparing PO_4 concentrations for the plots in each season, the 2010 growing season (April through September) and the 2010 fall season (October through December). Significant p-values are noted with a "*". Tukey range test analysis differences are also noted with "a," "b," or "ab."

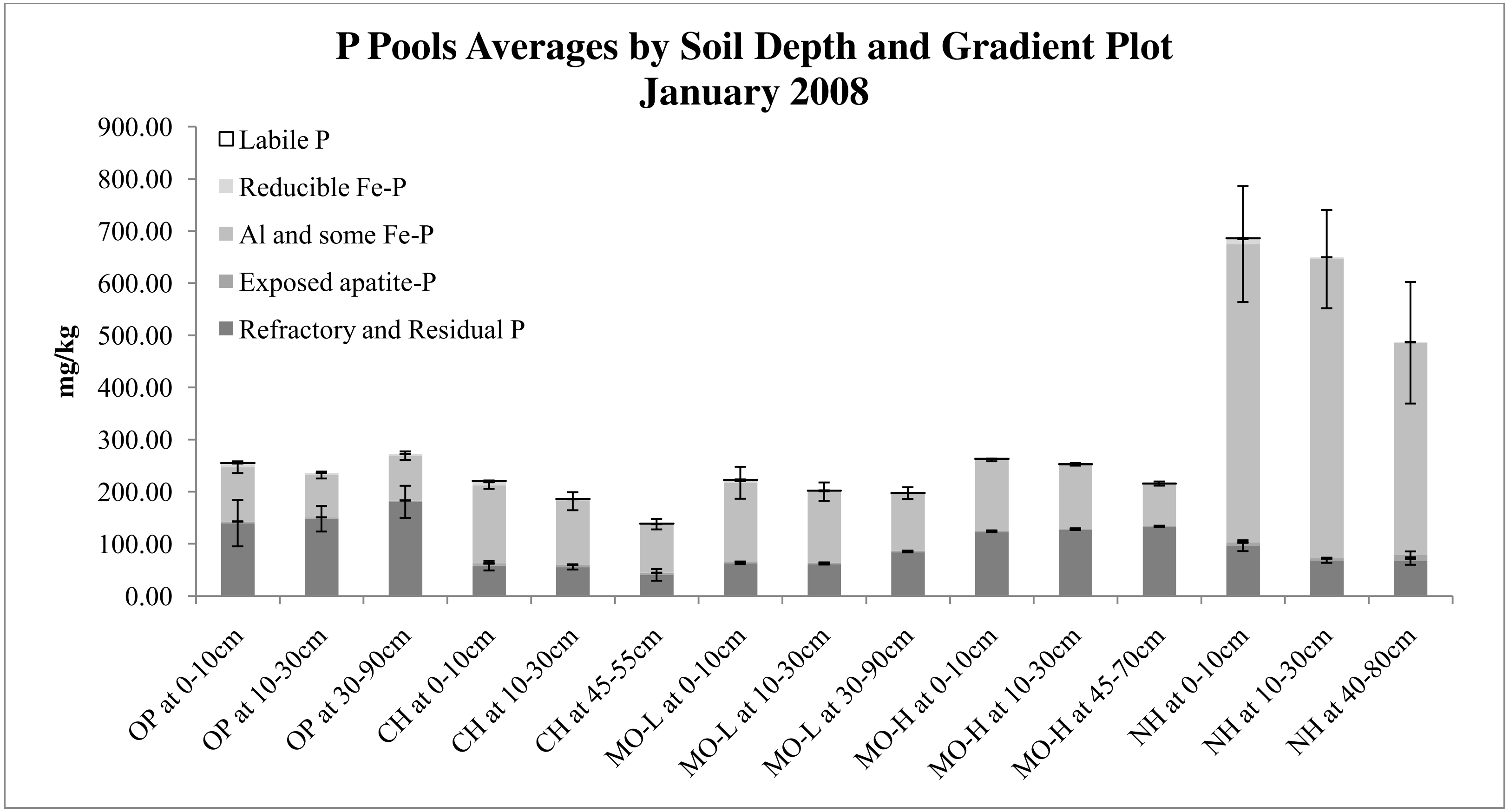

Figure 3.3 Average fractionated P pools for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH), divided up by plot and depth.

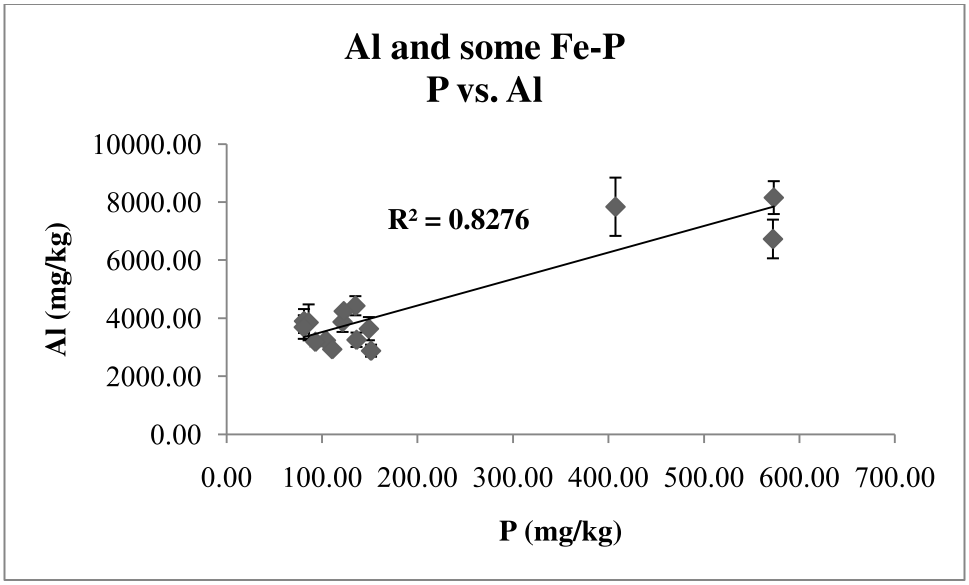

Figure 3.4 Linear regression to examine the correlation between the P concentration and Al concentrations in the Al and some Fe-P fractionated pool.

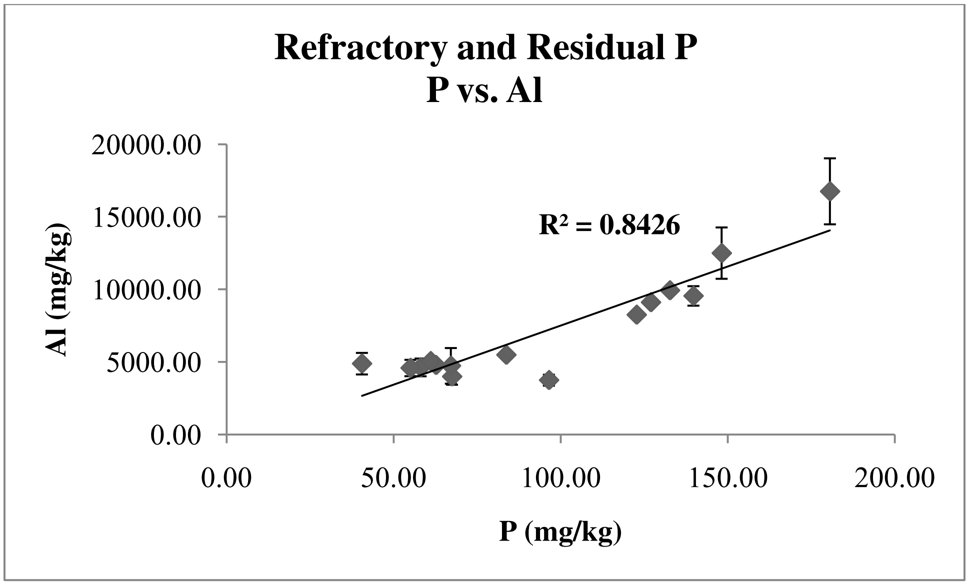

Figure 3.5 Linear regression to examine the correlation between the P concentration and Al concentrations in the refractory and residual P fractionated pool.

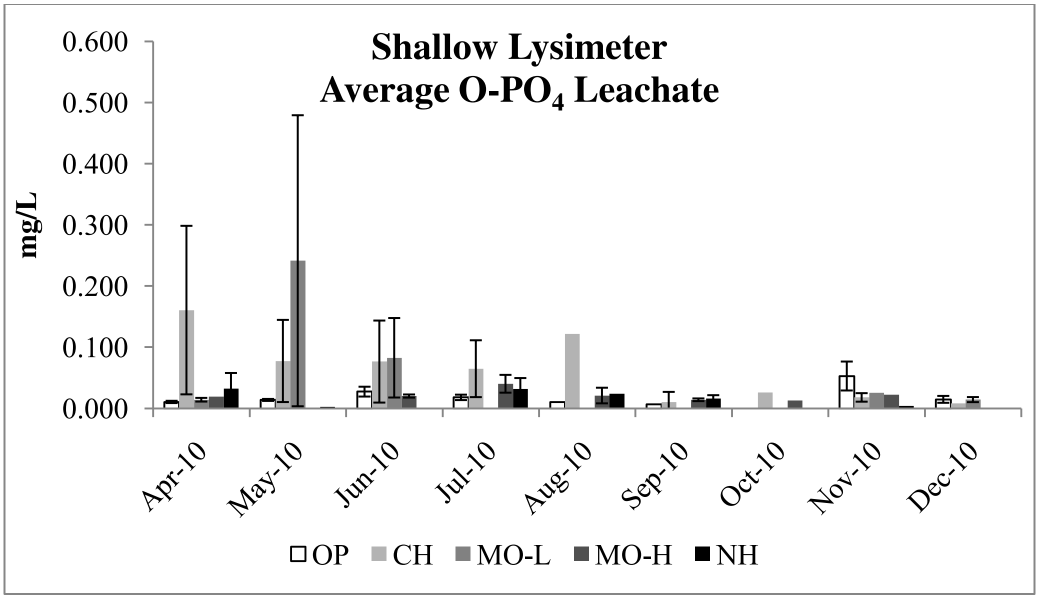

Figure 3.6 Average O-PO$_4$ leachate in shallow lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

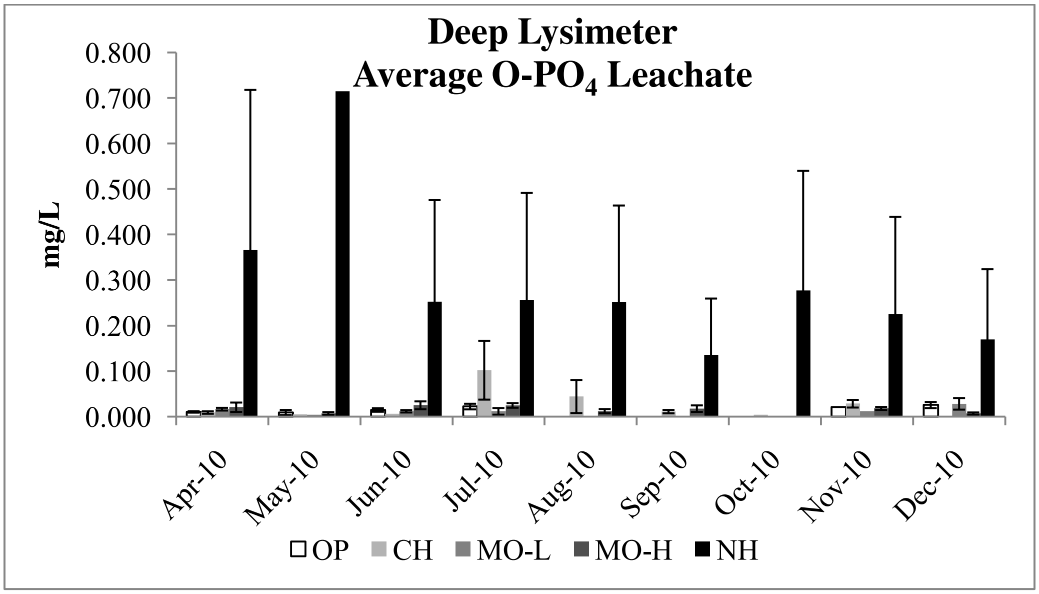

Figure 3.**7** Average O-PO$_4$ leachate in deep lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

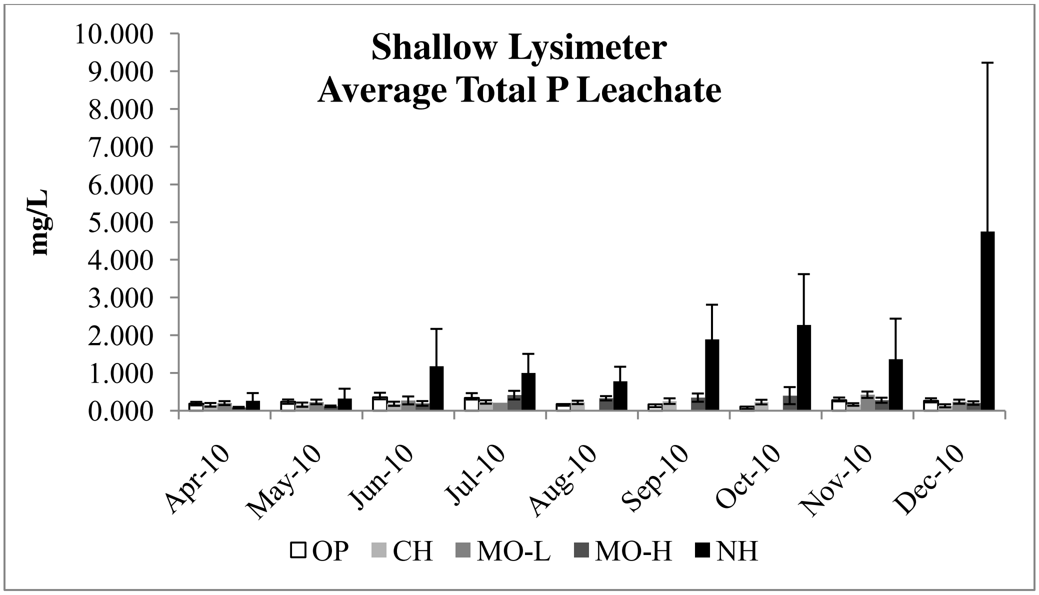

Figure 3.8 Average total P (TP) leachate in shallow lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

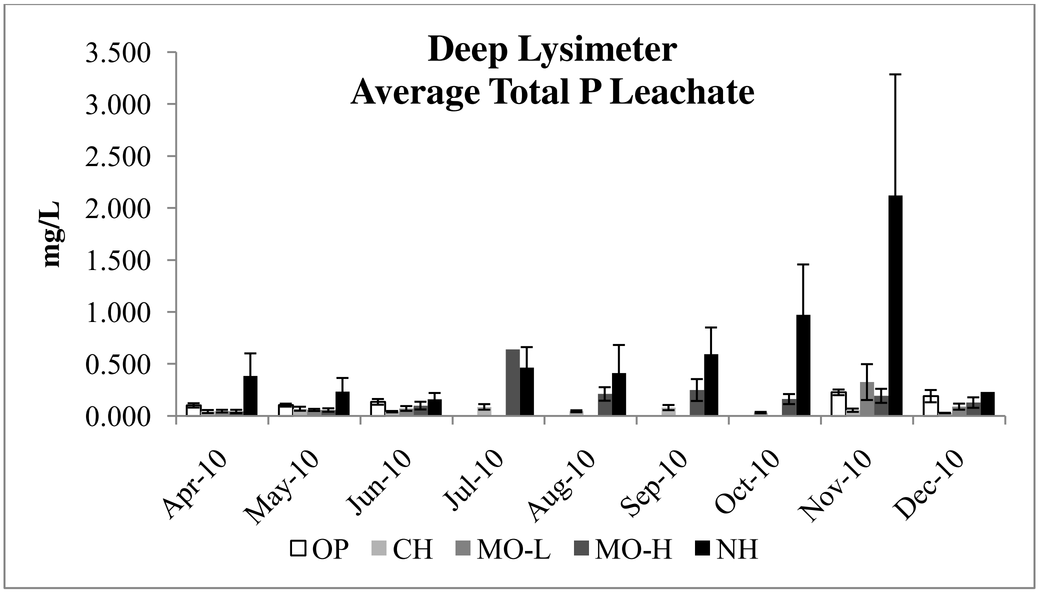

Figure 3.9 Average total P (TP) leachate in deep lysimeters by month plot: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH).

The P fractionation analysis shows overall significant differences between all P fractions at all depths in all plots (P<0.0001; SanClements 2009, SanClements et al. 2009). However, the plot-by-depth interaction was not significant (P=0.3671). For this reason, the focus of the Tukey range tests was on differences between plots, though depth was included in the ANOVA model. When looking at the labile P (most plant available), the cove hardwood plot had a significantly greater (P=0.0032) amount of labile P than the OP plot and the NH plot, while the MO-L plot was the only other plot that had significantly more labile P than the OP plot. When examining the reducible Fe-P, the MO-H plot has significantly less (P<0.0001) reducible Fe-P than the OP, the cove hardwood, and the NH plots, while the MO-L plot only had significantly less reducible Fe-P than the OP and the NH plots. The NH plot was the only plot with a significantly more mean Al and some Fe-P (P<0.0001). Similarly, the NH plot also had a significantly greater mean exposed apatite P (P=0.0065) than the OP, low elevation mixed oak, and MO-H plots. The OP plot and the MO-H plot had significantly more refractory and residual P (the most unavailable P pool) than the cove hardwood, low elevation mixed oak, and the NH plots (Figure 3.3).

Due to the strong significance (P<0.0001) of the NH plot when examining the “Al and some Fe-P” pool, further statistical analysis was done comparing the Al concentrations in P pools extracted using the modified Psenner fractionation (SanClements 2009, SanClements et al. 2009). Similar to the P concentration ANOVA there was an overall significant difference between all pools at the different depths in the different plots (P<0.0001), but the plot-by-depth interaction was not significant (P=0.1283). Thus, the focus again was on differences between plots for the Tukey range tests, though depth was included in the ANOVA model. The NH plot had significantly more average Al in the labile pool (P=0.0185) than the OP plot and the MO-H plot. The two lowest elevation plots, the OP plot and the cove hardwood plot, both had significantly more average Al in the reducible Fe-P pool than the MO-L plot and the NH plots. Much like the P concentrations for the “Al and some Fe-P” pool, the Al concentrations in the “Al and some Fe-P” pool were significantly greater (P<0.0001) in the NH plot when compared to all other plots. In addition to this significance, the MO-H plot had a significantly greater mean Al concentration in the “Al and some Fe-P” pool than the MO-L plot. Due to the strong significance exhibited by the Al concentrations in the “Al and some Fe-P” pool, a linear regression was done to examine the relationship between the P and Al concentrations in this pool, which exemplified a positive correlation ($R^2 = 0.8276$, Figure 3.4). Upon examination of the Al concentrations for plots in the exposed apatite pool, it was shown that the lowest elevation plot, the OP, had significantly less Al in the exposed apatite pool ($P=0.0002$) than any other plot. In complete contrast to the exposed apatite pool, the mean Al concentration in the refractory and residual pool for the lowest elevation plot, the OP, was significantly greater ($P<0.0001$) than the rest of the plots, followed by the MO-H plot, which had significantly more Al in the refractory and residual pool than the cove hardwood, low elevation mixed oak, and the NH plots. Due to the strong significance exhibited by the Al concentrations in the refractory and residual pool, a linear regression was done to investigate the relationship between the P and Al concentrations in this pool, which illustrated a positive correlation ($R^2 = 0.8426$, Figure 3.5).

When examining PO_4 leachate in soil solution collected in lysimeters and analyzed using GLM by plot, depth, and month, there was a significant ($P=0.0116$) depth-month interaction. Similarly, when examining PO_4 leachate in soil solution, collected in lysimeters and analyzed using GLM by plot, depth, and season (spring 2010 (April through May), summer 2010 (June through August), fall 2010 (September through November), there was a significant ($P=0.0215$) depth-month interaction. This interaction was significant in only one plot when the GLM analysis was done by individual plots, the NH plot. Furthermore, when examining the results of the t-test comparison of PO_4 leachate in soil solution collected in shallow versus deep lysimeters, the NH plot was the only plot with a significant difference ($P=0.0312$) between PO_4 leachate in shallow versus deep lysimeters. The NH plot had significantly more PO_4 leachate in the deep lysimeter than in the shallow lysimeter (Figures 3.6 and 3.7).

There was no significant outcome when examining TP leachate in soil solution collected in lysimeters analyzed using GLM by plot, depth, and month. However, when examining TP leachate in soil solution, collected in lysimeters and analyzed using GLM by plot, depth, and season (spring 2010 (April through May), summer 2010 (June through August), fall 2010 (September through November), there was a significant ($P=0.0289$) depth-month interaction. GLM analysis done for individual plots, found a significant interaction between depth and month for the CH plot ($P=0.0037$) and the NH plot ($P=0.0017$). Furthermore, when examining the results of the t-test comparison of TP leachate in soil solution collected in shallow versus deep lysimeters, both the CH plot ($P=0.0070$) and the NH plot ($P=0.0080$) has significantly more TP leachate in the deep lysimeter (Figures 3.8 and 3.9).

DISCUSSION

When comparing trends in throughfall input of PO_4, both the 1992 through 1997 measurements (Knoepp et al. unpublished data) and the 2010 measurements observed that significantly greater PO_4 concentrations occurred during the growing season (April through September) in the low elevation plots. The previous measurements constantly measured significantly more PO_4 in throughfall from greater elevation sites, but this trend was not observed in the 2010 measurements. The 2010 throughfall measurements showed significantly more PO_4 in throughfall from the mid elevation site during the growing season, and in the highest elevation site only during the fall. Though the previous throughfall measurements of PO_4 do have strong overall trends, there is still significant variability from year to year (Knoepp et al. unpublished data).

It is also possible that the changes observed when comparing the previous PO_4 measurements and the 2010 measurements are the result of significant changes to measurement methods. Based on these observations it seems that to get a clear understanding of PO_4 input to the system from throughfall, measurements must be done with consistent methodologies over multiple years in order to account for annual variability. In addition to throughfall measurements, deposition measurements would also be helpful in determining if there is an increase of PO_4 deposition, and if so, can be it linked to anthropogenic sources based on time and location (Mahowald et al. 2008) or is PO_4 leached by the canopy into throughfall (Potter 1992, Potter et al. 1993, Norden 1991). This would help determine if the greater concentrations of PO_4 in throughfall during the growing season are a result of anthropogenic or canopy sources.

Knoepp et al. (unpublished data) found that soil PO_4-P concentrations tended to be greater in the high elevation plots in the 1992, 1994, and 1995 measurements, which was similar to the overall P concentrations in the January 2008 soils. It was also observed that PO_4-P concentrations increased significantly from the August 1992 measurement to the January 1994 measurement. These concentrations dropped in the January 1995 measurement, but remained significantly greater than the 1992 measurements for the cove hardwood, low elevation mixed oak, and NH plots. This observation could not be made for the recent P fractionation measurement, as it was done on one-time sampled soils (Knoepp et al. unpublished data).

Walbridge et al. (1991) found that P sorption capacity was closely linked to Al and Fe concentrations in Coweeta soils, due to observations of PO_4 being tightly bound to Al and Fe hydroxide surfaces. This agrees with the 2008 Reducible Fe-P pool and the “Al and some Fe-P” (Figures 3.4 and 3.5). Walbridge et al. (1991) also observed the greatest P concentrations in the forest floor and decreasing concentrations with depth. This was not observed with the P pools extracted in the 2008 soils at three different depths, but the forest floor was not fractioned for P pools. In contrast to the P concentrations by depth, Walbridge et al. (1991) found that there was no significant variation of Al and Fe concentrations by depth. There is also strong evidence to suggest that along with abundance of Al and Fe, the role of pH is very important in the immobilization of P via absorption onto oxides and clays (Havlin et al. 2005, Stevenson 1986, Figure 3.10). The gradient plot soils have an average pH of 4 (Table 3.1). This explains the large “Al and some Fe-P” pool fractionated from the gradient soils (Figure 3.3).

Though the previous soil P measurements cannot be directly compared to the 2008 fractionated P soil measurements, it is important to recognize that, based on the year-to-year variability observed with the previous soil P measurements, at least a yearly analysis must be done in order to understand soil P pools. It is also important to investigate P pools at different soil depths along the gradient plots, as phosphate availability, particularly in mineral soils, has been shown to increase as altitude decreases (Dighton and Coleman 1992).

Based on the P pool fractionation and low PO_4 concentrations in throughfall, it is likely the gradient plot soils are at least partly P limited. The P pool fractionation displayed very low P concentrations in the most plant available pools, the Labile P and Reducible Fe-P pools. One argument that could be made with the labile P extraction would be as to why the extraction was done with NH_4Cl, buffered to a pH of 7 rather than to that of the soil pH ~4. This step in modified Psenner fractionation was used by SanClements et al. (2009) as a means to control method inconstancies (varying soil pH), as this step was originally done with H_2O (SanClements 2009, Personal Communication with SanClements). However, it is likely that the buffered labile P extraction is underestimating available P by as much as double the recorded concentrations, but even a doubling of the amount of labile P would still lead to low values, averaging 0.5 mg/kg (Personal Communication with SanClements). While P concentrations were high in the "Al and some Fe-P" pool, due to low soil pH and high Al and Fe concentrations, this pool is unavailable, therefore not plant available (Table 3.2, and figures 3.3 and 3.10). This is largely in part due to the metamorphic parent material found in the Coweeta gradient plot soils, which tends to be high in Al and Fe (Qualls et al. 2002, Vitousek et al. 2010, Walbridge et al. 1991).

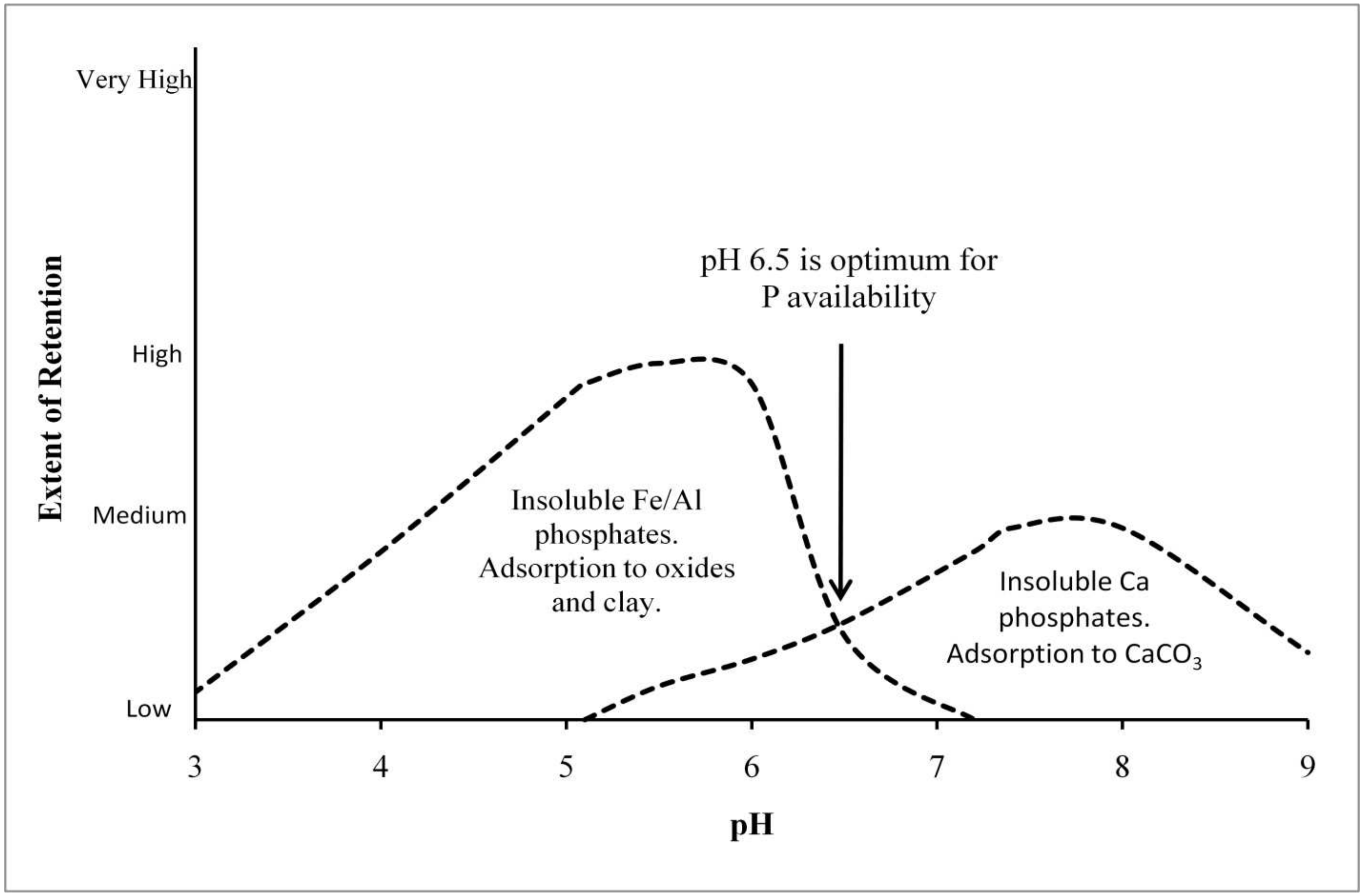

Figure 3.10 Soil pH effects on P adsorption in the presence of Fe, Al, and Ca (adapted from Stevenson 1986).

In previous soil solution measurements, O-PO_4 concentrations were observed to be greatest in the shallow lysimeters, when compared to the deep lysimeters. The soil solution O-PO_4 concentration in leachate tended to be greater in the deep lysimeters during the winter months (November through March), with the greatest O-PO_4 concentrations commonly observed in the high elevation plots year round (Knoepp et al. unpublished data). The 2010 soil solution measurements on TP followed the same trend as the previous soil measurements, with the greatest O-PO_4 concentrations observed during the winter months (November through March) and in the high elevation plots year round. While the O-PO_4 concentrations in the 2010 measurements tended to be greater in the high elevation plots, the seasonal trend was observed to be the inverse of the previous O-PO_4 soil solution measurements, particularly in the shallow lysimeters. Qualls et al. (2002) looked at dissolved organic P (DOP) in soil solution in watershed 2 at the Coweeta Hydrologic Laboratory and found significantly more DOP in soil solutions from the Oa layer, when compared to deeper soil horizons which had negligible DOP concentrations. Qualls et al. (2002), like Walbridge et al. (1991), attributed this phenomenon to DOP adsorption into the highly Fe and Al rich mineral soils.

It was hypothesized that the highest elevation site would receive the most PO_4 deposition into the system measured via throughfall, and as one of the most extreme sites also have the greatest response to increased N and P deposition and moisture dynamics. Though previous PO_4 throughfall measurements observed greater PO_4 concentrations in the highest elevation plot, the 2010 measurements did not observe a significant trend. Despite this, the highest elevation plot did have the largest total soil P pool, though most of the P was unavailable in Fe and Al phosphates, due to low pH and high Fe and Al concentrations in parent soil material. In addition to a greater overall soil pool, the highest elevation plot also had the most TP leachate at both lysimeter depths, and the greatest PO_4 leachate for the deep lysimeters. In all cases, plant available P tended to be low, especially with increasing soil depth. This suggests that PO_4 deposition is not significantly affecting P processes in these southern Appalachian forests, however it is possible that increased N deposition is, by increasing the systems demand for plant available P.

ACKNOWLEDGEMENTS

The author would like to acknowledge Jennifer D. Knoepp for in-depth descriptions of N and P measurement methods used on the Coweeta LTER gradient plots along with access to unpublished data. The author would also like to acknowledge Michael D. SanClements for clarification of the modified Psenner P fractionation methods.

LITERATURE CITED

Adams, M.A. and P.M. Attiwill. 1986. Nutrient cycling and nitrogen mineralization in eucalypt forests of south-eastern Australia, 2: indices of nitrogen mineralization. Plant and Soil 92: 341-362.

Clark, James S., Eric Macklin, and Leslie Wood. 1998. Stages and spatial scales of recruitment limitation in southern Appalachian forests. Ecological Monographs 68(2): 213-235.

Danger, Michael, Tanguy Daufresne, Franc¸oise Lucas, Serge Pissard and Ge´rard Lacroix. 2008. Does Liebig‟s law of the minimum scale up from species to communities? Oikos 117: 1741-1751.

Dighton, John, and David C. Coleman. 1992. Phosphorus relations of roots and mycorrhizas of Rhododendron maximum L. in the southern Appalachians, North Carolina. Mycorrhiza 1: 175-184.

Fenn, Mark E. J.O. Sickman, A. Bytnerowicz, D.W. Clow, N.P. Molotch, J.E. Pleim, G.S. Tonnesen, K.C. Weathers, P.E. Padgett and D.H. Campbell. 2009. Chapter 8: Methods for Measuring Atmospheric Nitrogen Deposition Inputs in Arid and Montane Ecosystems of Western North America Developments in Environmental Science, Volume 9: 179-228. Elsevier Ltd.

Fenn, Mark E., and Mark A. Poth. 2004. Monitoring Nitrogen Deposition in Throughfall Using Ion Exchange Resin Columns: A Field Test in the San Bernardino Mountains. Journal of Environmental Quality 33:2007–2014.

Havlin, John L., James D. Beaton, Samuel L. Tisdale, Wener L. Nelson. 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Upper Saddle River, New Jersey: Peason Education Inc.

Houlton, Benjamin Z., Ying-Ping Wang, Peter M. Vitousek, and Christopher B. Field. 2008. A unifying framework for dinitrogen fixation in the terrestrial biosphere. Nature 454(7202): 327-U334.

Intergovernmental Panel on Climate Change (IPCC). 2007. Climate Change 2007: Mitigation of Climate Change. Summary for Policymakers e Working Group III contribution to the Environmental Panel on Climate Change Fourth Assessment Report: 35.

Iverson, Louis R., and Anantha Prasad. 1998. Predicting abundance of 80 species following climate change in the Eastern United States. Ecological Monographs 68(4): 465-485.

Knoepp, Jennifer D. and James M. Vose. 2007. Regulation of nitrogen mineralization and nitrification in Southern Appalachian ecosystems: Separating the relative importance of biotic vs. abiotic controls. Pedobiologia 51: 89-97.

Knoepp, Jennifer D., and Wayne T. Swank. 1998. Rates of Nitrogen Mineralization across an Elevation and Vegetation Gradient in the Southern Appalachians. Plant and Soil 204: 235-241.

Knoepp, Jennifer D., Barbara C. Reynolds, D.A. Crossley Jr., and Wayne T. Swank. 2005. Long-term changes in forest floor processes in southern Appalachian forests. Forest Ecology and Management 220: 300-312.

Knoepp, Jennifer D., David C. Coleman, D.A. Crossley Jr., and James S. Clark. 2000. Biological indices of soil quality: an ecosystem case study of their use. Forest Ecology and Management 138: 357-368.

Knoepp, Jennifer D., James M. Vose, and Wayne T. Swank. 2008. Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests. International Journal of Environmental Studies 65: 389-408.

LeBauer, D.S. and K.K. Treseder. 2008. Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. Ecology 89: 371-379.

Li, Wenhong, Laifang Li, Rong Fu2 Yi Deng, and Hui Wang. 2010. Changes to the North Atlantic Subtropical High and Its Role in the Intensification of Summer Rainfall Variability in the

Southeastern United States. Journal of Climate: http://journals.ametsoc.org/doi/abs/10.1175/2010JCLI3829.1

Mahowald, Natalie, Timothy D. Jickells, Alex R. Baker, Paulo Artaxo, Claudia R. Benitez-Nelson, Gilles Bergametti, Tami C. Bond, Ying Chen, David D. Cohen, Barak Herut, Nilgun Kubilay, Remi Losno, Chao Luo, Willy Maenhaut, Kenneth A. McGee, Gregory S. Okin, Ronald L. Siefert, and Seigen Tsukuda. 2008. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. Global Biogeochemical Cycles 22.

Norden, U. 1991. Acid Deposition and Throughfall Fluxes of Elements as Related to Tree Species in Deciduous Forest of South Sweden. Water, Air, and Soil Pollution 60(3-4): 209-230.

Parton, W. J., J. W. B. Stewart, and C. V. Cole. 1988. Dynamics of C, N, P and S in Grassland Soils. Biogeochemistry 5: 109-31.

Perring, Michael P., Lars O. Hedin, Simon A. Levin, Megan McGroddy, and Claire de Mazancourt. 2007. Increased plant growth from nitrogen addition should conserve phosphorous in terrestrial ecosystems. PNAS 15(6): 1971-1976.

Potter, Christopher S. 1992. Stemflow Nutrient Inputs to Soil in a Successional Hardwood Forest. Plant and Soil 140(2): 249-254.

Potter, Christopher S., Harvey L. Ragsdale, and Wayne T. Swank. 1991. Atmospheric Deposition and Foliar Leaching in Regenerating southern Appalachian Forest Canopy. Journal of Ecology 79: 97-115.

Psenner, R., B. Bostrom, M. Dinka, K. Petterson, R. Pucsko, and M. Sager. 1988 Fractionation of phosphorus in suspended matter and sediment. Arch Hydrobiol Beih Ergebn Limnol 30: 98-103.

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

SanClements, Michael D. 2009. The Chemistry of Acidic Soils in Humid, Temperate Forested Watersheds with Emphasis on Phosphorus, Aluminum, and Iron. University of Maine, Orono, ME.

SanClements, Michael D., Ivan Fernadndez, and Stephen A. Norton. 2009. Forest Ecology and Management 258: 2318-2325.

Schlesinger, William H. 1997.Biogeochemistry: An Analysis of Global Change. New York: Academic Press.

Schwab, A. P. 2000. "Chapter 3: The Soil Solution. Handbook of Soil Science. Boca Raton, FL: CRC. B85-B104. Print.

Stevenson, F.J. 1986. Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients. New York: John Wiley & Sons.

Vitousek, P.M. and R.W. Howarth. 1991. Nitrogen limitation on land and in the sea – how can it occur? Biogeochemistry 13: 87–115.

Vitousek, P.M., S. Porder, Benjamin Z. Houlton, and Oliver A. Chadwick 2010. Terrestrial phosphorus limitation: mechanisms, implications, and nitrogen-phosphorus interactions. Ecological Applications 20(1): 5-15.

Walker, T. and J. Syers. 1976. The fate of phosphorus during pedogenesis. Geoderma 15: 1–19.

CHAPTER 4

FUTURE PLANT AVAILABLE NITROGEN AND PHOSPHORUS DYNAMICS IN SOILS OF FIVE SOUTHERN APPALACHIAN FORESTS LOCATED IN THE COWEETA LONG-TERM ECOLOGICAL RESEARCH GRADIENT PLOTS

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ABSTRACT

Global climate change is predicted to affect temperatures and precipitation patterns in the southern Appalachian Mountains (Galloway et al. 2004, Galloway et al. 2008, Iverson & Prasad 1998, Mahowald et al. 2008, Schlesinger 1997). Nitrogen (N) and phosphate (PO_4) deposition are increasing due to human activities (Vitousek ref, other refs). Available supplies of N and P play a crucial role for forest productivity and eventual carbon storage. It was hypothesized that under global climate change southern Appalachian forests could become P-limited, due to increased N mineralization resulting from increased N deposition and increased temperatures. It has also been hypothesized that despite increased PO_4 deposition, southern Appalachian forests will remain P-limited due to occlusion of P into Al and Fe phosphates as a result of high concentrations of Al and Fe along with low soil pH (Havlin et al. 2005, Stevenson 1986, Walbridge 2000, Walbridge et al. 1991, Walker and Syers 1976). A predictive model was developed using data collected in five representative southern Appalachian forest types. The model was run comparing current (2010) and predicted climate and nutrient values for 2050. When comparing 2010 model results with 2050 results, we find that southern Appalachian forest systems will continue to be both N and P co-limited as there is no change of N being leached from the system, and P becomes increasingly unavailable rather than being available to plants.

INDEX WORDS: nitrogen (N), phosphorus (P), southern Appalachian, model, deposition

INTRODUCTION

Global climate change is predicted to affect temperatures and precipitation patterns including those in the southern Appalachian Mountains (Galloway et al. 2004, Galloway et al. 2008, Iverson & Prasad 1998, Mahowald et al. 2008, Schlesinger 1997). Nitrogen (N) and phosphate (PO_4) deposition are increasing due to human activities (Vitousek ref, other refs). Previous work at the Harvard Forest LTER has shown that many of the climate warming impacts on tree dynamics are mediated through climatic impacts on soil nutrient processes (Melillo et al. in press). While there is much climate change research targeting the use of forests as carbon sinks, far less is known about potential effects of N and phosphorus (P) limitations on future forest productivity and the potential to diminish or even negate future increases in forest carbon sequestration (LeBauer and Treseder 2008, Schlesinger 1997, Y. Liu ref, Oren et al. 2001).

In order to employ forests as carbon sinks we must determine what gives forests the ability to grow and store carbon in a changing environment, and in turn, how humans can best manage these processes (Luyssaert 2008). Future projections of southeastern climates forecast warmer and drier conditions (Mearns et al. 2003), extended droughts characterized the region from 1998-2002 and 2006-2008 (USGCRP report 2009), which presents a question as to how southeastern forests, including traditionally cool and moist southern Appalachian forests, will respond (IPCC 2007, Li et al. 2010). In addition to climate change, nutrient dynamics are expected to change as anthropogenic nitrogen deposition increases in the southeastern United States, particularly as the region becomes increasingly urbanized as atmospheric NO_3^- is relatively short-lived and generally deposits near anthropogenic sources (Schlesinger 1997). Further, southern Appalachian tree species abundance is expected to change, which in turn may affect both forest sequestration and nutrient availability (Iverson & Prasad 1998, 2002). Understanding biogeochemical dynamics and nutrient limitation(s) in southern Appalachian forests under global climate change is critical for predicting how these forests will look and function in the future.

Elevational gradient plots at the Coweeta Hydrologic Lab in Otto, NC provide a good representation of southern Appalachian forest types, including: mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH). These forest types are the result of the natural gradients in elevation, temperature, precipitation, soils, and species distributions (Clark et al. 1998, Knoepp and Swank 1998; Knoepp et al. 2000, 2008; Table 4.1). Current (2010) nutrient data and predictions for 2050 nutrient and climate were used from the established elevational gradient plots at Coweeta to determine nutrient biogeochemistry of N and P. It was hypothesized that 1) under global climate change, southern Appalachian forests will become P limited due to increased N mineralization resulting from increased N deposition and increased temperatures and 2) that despite increased PO_4 deposition, southern Appalachian forests will remain P limited due to occlusion of P into Al and Fe phosphates as a result of high concentrations of Al and Fe along with low soil pH (Havlin et al. 2005, Stevenson 1986, Walbridge 2000, Walbridge et al. 1991, Walker and Syers 1976). With increasing N deposition, N availability will likely increase pushing these forests towards P-limitation.

METHODS

Study Site

In order to better understand temperature, precipitation, nutrient availability, and species distributions in southern Appalachian forest ecosystems, gradient plots were established in 1991 as a part of the Coweeta Long-Term Ecological Research (LTER) project, funded by the National Science Foundation (Knoepp and Swank 1998, Clark et al. 1998). The gradient plots were established for intensive measurement purposes such as throughfall chemistry, nitrogen transformations, soil solution chemistry, and above ground vegetation productivity (Clark et al. 1998, Knoepp et al. 2008). The gradient currently has five established plots (four forest types) with elevations ranging from 782 meters to 1347 meters (Clark et al. 1998, 2001; Knoepp et al. 2000). The plots are categorized by dominant tree species and fall along a natural elevation, temperature, moisture, and vegetation gradient. This natural gradient allows for comparisons among warmer and drier forest settings, which are predicted for the future southeastern United States (Mearns et al. 2003), transitioning up to cooler, moister habitats dominated by traditionally northern tree species. Nutrient work has been done on these plots examining N mineralization and nitrification, N and P in throughfall, and N and P in soil solution through lysimeters (Knoepp et al. 2000, Knoepp et al. 2008, Knoepp and Swank, 1998 Knoepp and Vose 2007, McLean unpublished data). There has been some pervious work done on total P, but no work has been done specifically on plant-available P or recent profiles of total P (Knoepp et al. 2000). Current research was conducted to build on past N Research and to investigate the availability of P in this southern Appalachian forest system.

Model Development

In order to examine future plant-availability of N and P I developed a model using current rates of biogeochemical transformations and estimates of future temperatures, precipitation and N and P deposition rates to predict future soil nutrient dynamics. While the Coweeta gradient plots represent four southern Appalachian forest types, the focus of this model was to determine what effects increased N and PO_4 deposition would have on southern Appalachian forests. For this reason, to investigate southern Appalachian forest responses, the model was parameterized and run for each individual plot comparing 2010 and 2050 N and P dynamics.

The model was developed to predict N and P dynamics in 1 m^2 of forest soil. The model needed to include N and P input into the system, along with nutrient concentrations and dynamics in various soil layers, which in turn required a measurement output of nutrients from the soil layers (leachate). The model was developed using STELLA® 9.0.3, which is commonly used for modeling and simulations in ecological research (Bonito 2001, Dacko 2010, Keet 2005). As seen in figure 4.1, the conceptual model displays the flow of N and P from throughfall to the soil where the nutrients are turned over and then leached from the system. The model was developed so that precipitation, nutrient input (throughfall and deposition), and temperature affect the rates at which N and P are cycled through the system.

The input of N and P in throughfall was calculated for a square meter. Then a square meter of the A horizon was simulated with turnover rates of N and P, followed by turnover within the soil horizon was modeled using the modifications of the EPIC model developed by Jones et al. (1984). The model was also developed with the ability to switch nutrient amounts, rates, temperature, and moisture to accommodate specific plots or predicted environmental changes (Figure 4.2). Please see appendix for full model and parameters. In addition to the square meters, nutrient concentrations were applied as grams and grams per liter with a monthly time step. Averages of total N and P and average cycling rates from the plots were used to parameterize the model. N soil dynamics were further estimated by the N transformation rates from the CNSOIL Model (Molina et al. 1983). Soil P dynamics were further estimated with an N to P ratio. P

N and P Throughfall

Predicted N deposition into throughfall was increased by 600%, which was the estimated increase of N deposition for the southern Appalachians for 2050 (estimated from Galloway et al. 2004). This 600% increase was used to parameterize the model for N deposition in 2050. Based on the 2.5 ratio between current (2008) and preindustrial (before 1750) PO_4 deposition, there was a 250% increase in atmospheric PO_4 deposition from 1750 to 2010 (Ashton 1948, Mahowald et al. 2008). Assuming that this increase of PO_4 deposition is following the pattern of carbon dioxide (CO_2), as a result of increased fossil and bio-fuel emissions, it can be estimated that from 1750 to 2050 the atmospheric PO_4 deposition could increase by about 320% (IPCC 2007, Galloway et al. 1994, Galloway et al. 2008, Mahowald et al. 2008). These estimates were used to parameterize the model for PO_4 deposition in 2050, which was estimated to be a 43.0% increase from 2010 to 2050. Average monthly ammonium (NH_4), nitrate (NO_3), and PO_4 throughfall concentrations from measurements collected in 2010 were used to parameterize throughfall input into the first soil layer (McLean unpublished data). All throughfall concentrations were converted to g/m^2/month.

Soil N Transformations, P Soil Pools

Average soil NH_4, NO_3, nitrification rates, and mineralization rates measured from October 2009 to September 2010 (McLean unpublished data), parameterized the model‟s organic and mineral soil layer components. The plant available (or rapid) P soil pools were parameterized by summing the labile and reducible Fe-P pools for each depth from the extractions done on the January 2008 gradient soils. The unavailable (or slow) P soil pools were parameterized by summing the "Al and some Fe-P", the exposed apatite-P, and the refractory and residual P pools for extractions done for each depth of archived gradient soils from January 2008 (McLean unpublished data). All soil concentrations were converted to grams per m^3 and all rates were converted to g/m^3/month. Temperature and moisture have significant effects on soil processes, particularly in regards to nitrification and mineralization (Melillo et al. 2002). For this reason, the model was parameterized with temperature, moisture, and precipitation driving these soil processes (see appendix).

N and P Soil Solution in Lysimeters

Concentrations of NH_4, NO_3, and PO_4, from soil solution collected by lysimeters at two different depths, were used to parameterize soil solution leachate into the different soil depths (McLean unpublished data). These values were maintained at g/L and averaged for all gradient plots.

Simulation Output Testing

The model was run comparing nutrient cycle outputs into the watershed under average current (2010) nutrient and climate parameterization, and under future, predicted nutrient and climate parameterization (2050). The model was run for 12 months at both ambient and predicted parameterization. The 2010 and 2050 nutrient pools along with leachate concentrations were compared using a two-tailed t-test ($\alpha=0.10$). Mean difference values were also calculated by subtracting the 2010 outputs from the 2050 outputs to determine pool and rate changes.

Table 4.1 Gradient Sites

Site	Site ID	Elevation (m)	Dominant Vegetation	Air Temperature (1 m)	Soil Temperature (20 cm)	Rainfall (cm)	Moisture Regime	Total N (%)
Mixed Oak-Pine (OP)	118	788	*Quercus prinus, Quercus rubra, Carya spp., Kalmia latifolia*	15.1	14.8	210.2	xeric	0.08
Cove Hardwood (CH)	218	801	*Liriodendron tulipifera, Quercus rubra, Tsuga canadensis, Carya spp.*	14.5	14	212.4	mesic	0.37
Low Elevation Mixed Oak (MO-L)	318	860	*Quercus coccinea, Quercus prinus, Rhododendron maxima*	15	13.5	222.9	mesic	0.16
High Elevation Mixed Oak (MO-H)	427	1094	*Quercus rubra, Carya spp., Rhododendron maxima*	13.6	12.8	264.9	mesic	0.14
Northern Hardwood (NH)	527	1389	*Betula allegheniensis, Liriodendron tulipifera, Quercus rubra, Acer saccharum*	11.8	10.8	267.6	mesic	0.67

The values for site elevation, dominate species, air temperature, soil temperature, rainfall, and moisture regime from Knoepp and Vose (2007) and Knoepp et al. (2008). Average pH values were calculated from Coweeta Long-term Ecological Research Program records data. Average soil %N was calculated from 1994 to 1996 measurements from Coweeta Long-Term Ecological Research Program records.

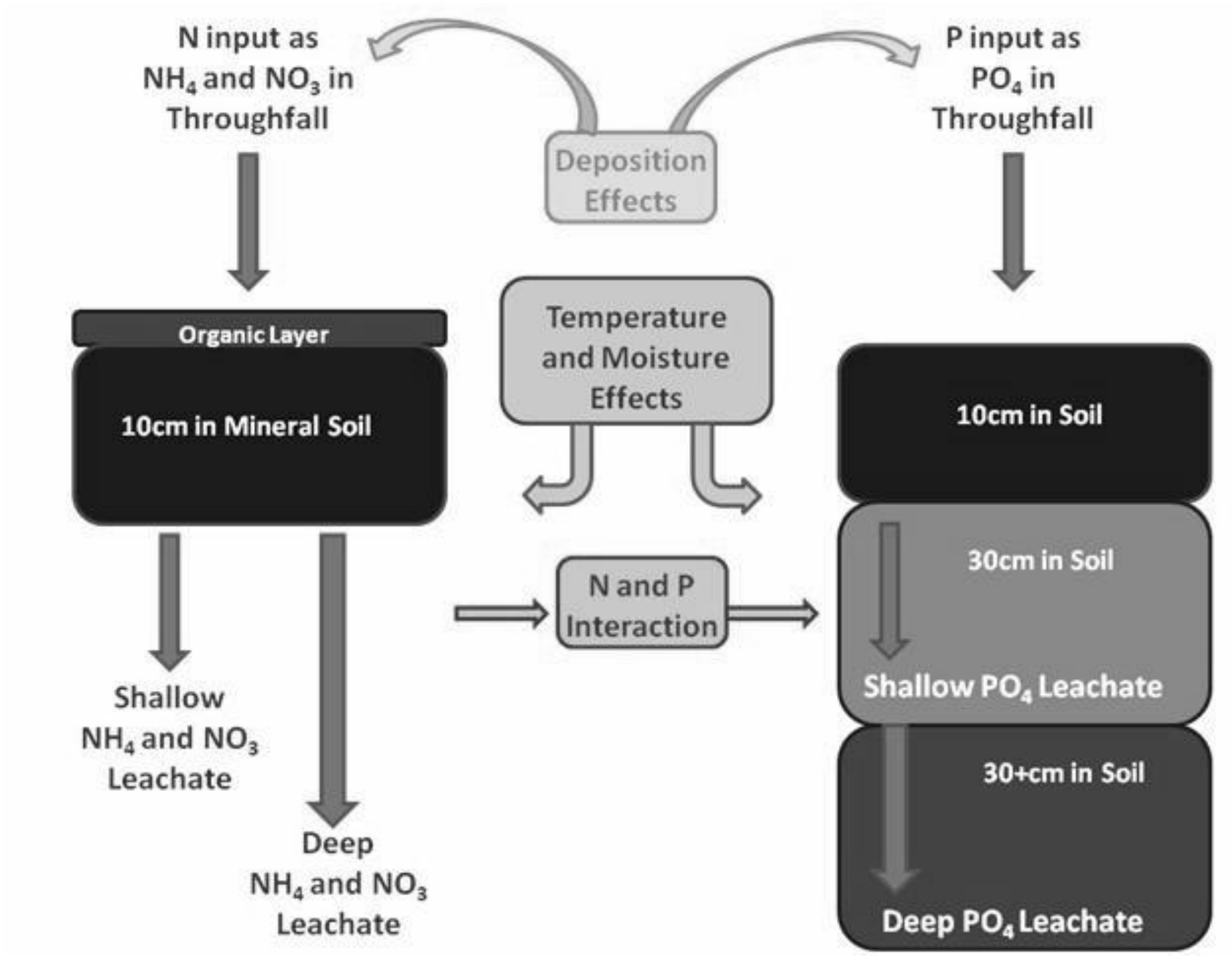

Figure 4.1 Demonstration of the model development with input effects and output effects.

movement of N and P to the B horizon (Figures 4.2 and 4.3). Next, a square meter of B horizon was simulated with turnover rates of N and P, followed by movement of N and P leaching out of the system.

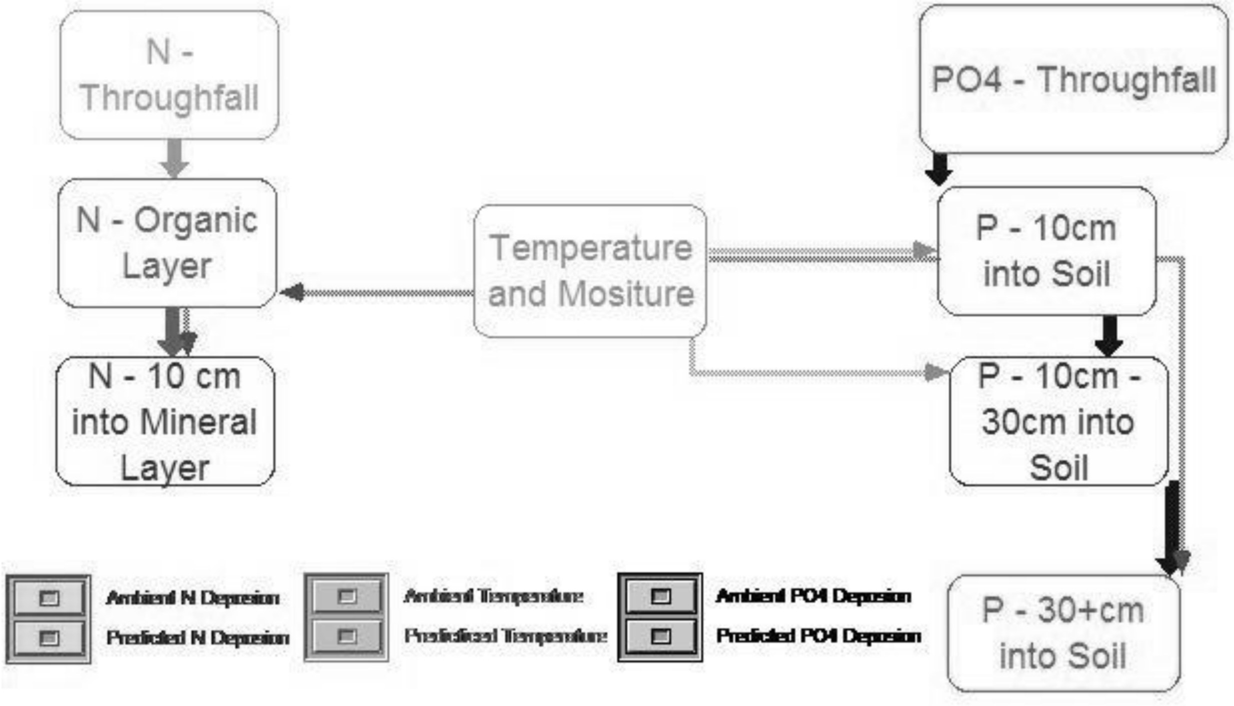

Figure 4.2 Interface in STELLA® 9.0.3, which displays flows and interactions between each soil layer. The toggle switches are also visible, which can be used to switch the model between the ambient (2010) parameterization and the predicted (2050) parameterization.

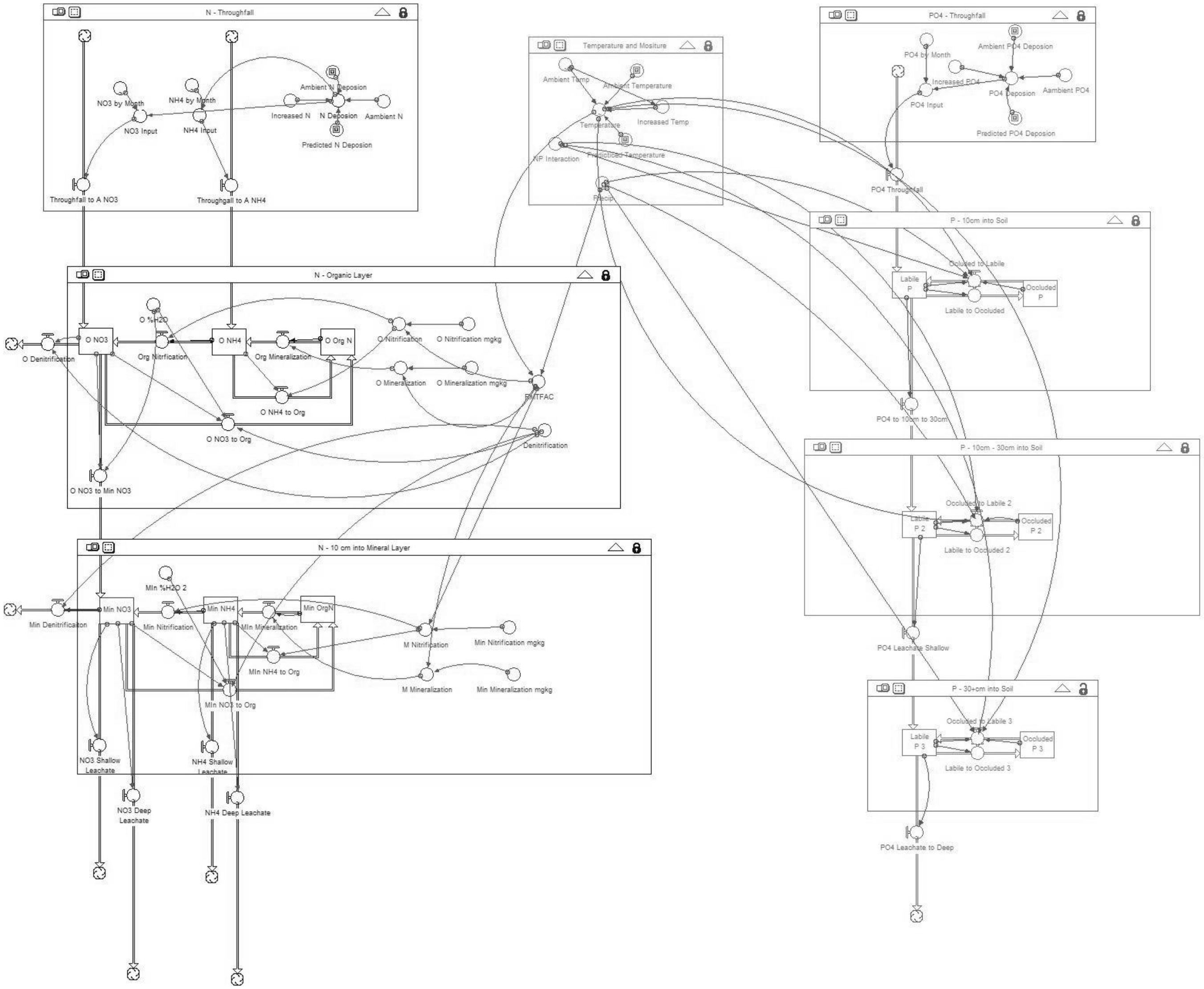

Figure 4.3 N and P Model in STELLA® 9.0.

RESULTS

When comparing the 2010 model output for throughfall with the 2050 model output, all throughfall concentrations of NH_4, NO_3, and PO_4 increased as expected under global climate change. All throughfall nutrient concentrations were significant ($P<0.0006$ or less) for all plots (Tables 4.2 and 4.3). When comparing the 2010 and 2050 model outputs for the organic layer, all plot models a significant increase in NH_4 and NO_3 under the 2050 predictions. This trend was continued for NO_3 in the mineral layer (to 10cm) for all the plots except the NH plot. However, the only plot with any significant change in NH_4 concentrations in mineral layer was the MO-H plot, which increased from the 2010 parameterization to the 2050 parameterization ($P<0.0001$). All plots had a significant decrease in plant available P for mineral soil from 10-30cm and from 30 to the bottom of the B horizon (Table 4.2 and 4.3). This decrease of plant available P was in conjunction with an increase of unavailable P in all soil layers (Table 4.2 and 4.3). In the 0 to 10cm of mineral soil all models showed a significant increase in unavailable P from 2010 to the predicted 2050. Similarly, in the 10cm to 30cm mineral soil layer all plots had a significant increase in unavailable P. In the mineral layer which went from 30cm to the bottom of the B horizon the OP plot ($P=0.0009$), the low elevation mixed hardwood plot ($P=0.0006$), the high elevation mixed hardwood plot ($P=0.0002$), and the NH plot ($P<0.0001$) all had had a significant increase in unavailable P. In the OP plot model ($P=0072$), the MO-H plot model ($P=0.0504$), and the NH model ($P<0.0001$) there was a significant increase in plant available NO_3 concentrations. The NH plot model was the only plot with a significant increase in NO_3 concentrations in leachate ($P<0.0001$).

Table 4.2 P-Values for 2010 to 2050 T-Test Comparison

Pool or Flux	OP Comparison p-value	CH Comparison p-value	MO-L Comparison p-value	MO-H Comparison p-value	NH Comparison p-value
Throughfall NH_4	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*
Throughfall NO_3	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*
Throughfall PO_4	0.0006*	<0.0001*	0.0003*	<0.0001*	<0.0001*
Soil NH_4 in O Horizon	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*
Soil NO_3 in O Horizon	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*
Soil NH_4 0-10cm in Mineral Soil	n/a	n/a	n/a	<0.0001*	0.2061
Soil NO_3 0-10cm in Mineral Soil	<0.0001*	<0.0001*	<0.0001*	<0.0001*	0.2260
Plant Available Soil P 0-10cm	0.2973	0.4761	0.1838	0.3834	0.3052
Plant Available Soil P 10-30cm	0.0115*	0.0243*	0.0141*	0.0031*	0.0004*
Plant Available Soil P 30+cm	0.0006*	0.0110*	0.0005*	<0.0001*	0.0235*
Unavailable Soil P 0-10cm	<0.0001*	<0.0001*	0.0003*	<0.0001*	<0.0001*
Unavailable Soil P 10-30cm	0.0652*	<0.0001*	0.0729*	0.0115*	0.0005*
Unavailable Soil P 30+cm	0.0009*	0.8018	0.0006*	0.0002*	<0.0001*
Plant AvailableNH_4 in Soil Solution	n/a	n/a	n/a	n/a	n/a
NH_4 Leachate in Deep Lysimeter	n/a	n/a	n/a	0.6596	n/a
Plant Available NO_3 in Soil Solution	0.0072*	n/a	0.5623	0.0504*	<0.0001*
NO_3 Leachate in Deep Lysimeter	n/a	n/a	n/a	n/a	<0.0001*
Plant Available PO_4 Soil Solution 10cm	1.0000	1.0000	1.0000	1.0000	1.0000
Plant Available PO_4 Soil Solution	1.0000	0.8477	1.0000	1.0000	1.0000
PO_4 Leachate in Deep Lysimeter	1.0000	1.0000	1.0000	1.0000	0.8699

The table contains for each p-value for t-tests comparing 2010 outputs to 2050 outputs for an overall averaged model and models for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH). Any significant p-values are noted with a "*" while "n/a" denotes any p-vales that could not be calculated due to low value limitations reported by STELLA® 9.0.3.

Table 4.3 Mean Difference (2050-2010)

Pool or Flux	OP Mean Difference	CH Mean Difference	MO-L Mean Difference	MO-H Mean Difference	NH Mean Difference
Throughfall NH_4 (g/m^2)	0.7535	0.3679	1.4721	0.3102	0.5192
Throughfall NO_3 (g/m^2)	0.0538	0.0421	0.1123	0.0856	0.1477
Throughfall PO_4 (g/m^2)	0.0483	0.0258	0.0977	0.0179	0.0425
Soil NH_4 in O Horizon (g/m^3)	0.3004	0.1339	0.5908	0.1135	0.2006
Soil NO_3 in O Horizon (g/m^3)	0.2594	0.1212	0.5157	0.0890	0.1435
Soil NH_4 0-10cm in Mineral Soil (g/m^3)	0.0000	0.0000	0.0000	0.1069	0.0008
Soil NO_3 0-10cm in Mineral Soil (g/m^3)	0.1522	0.0661	0.2980	0.0773	0.0041
Plant Available Soil P 0-10cm (g/m^3)	0.0327	0.0086	0.0824	-0.0104	-0.0508
Plant Available Soil P 10-30cm (g/m^3)	-0.0463	-0.0037	-0.0394	-0.0535	-0.1171
Plant Available Soil P 30+cm (g/m^3)	-0.0388	-0.0555	-0.0269	-0.0369	-0.0120
Unavailable Soil P 0-10cm (g/m^3)	0.3282	0.1437	0.5894	0.1112	0.3880
Unavailable Soil P 10-30cm (g/m^3)	0.0457	0.0504	0.0392	0.0547	0.1180
Unavailable Soil P 30+cm (g/m^3)	0.0380	0.0090	0.0267	0.0363	0.1282
Plant AvailableNH_4 in Soil Solution (g/L)	0.0000	0.0000	0.0000	0.0000	0.0000
NH_4 Leachate in Deep Lysimeter (g/L)	0.0000	0.0000	0.0000	-0.0006	0.0000
Plant Available NO_3 in Soil Solution (g/L)	0.0017	0.0000	0.0002	0.0010	0.1842
NO_3 Leachate in Deep Lysimeter (g/L)	0.0000	0.0000	0.0000	0.0000	0.0300
Plant Available PO_4 Soil Solution 10cm (g/L)	0.0000	0.0000	0.0000	0.0000	0.0000
Plant Available PO_4 Soil Solution (g/L)	0.0000	-0.0012	0.0000	0.0000	0.0000
PO_4 Leachate in Deep Lysimeter (g/L)	0.0000	0.0000	0.0000	0.0000	-0.0031

The table contains mean differences comparing 2010 outputs to 2050 outputs for an overall averaged model and models for each plot, the mixed oak-pine (OP), the cove hardwood (CH), the low elevation mixed oak (MO-L), the high elevation mixed oak (MO-H), and the northern hardwood (NH).

DISCUSSION

It was hypothesized that increased temperature and increased N deposition would increase N mineralization rates and contribute to a more P-limited system. This was supported by the model‟s P outputs, suggesting with an increase in PO_4 deposition rates and a future warmer, drier climate a decline in plant-available P pools and an increase in unavailable, unavailable soil P (Table 4.3). Based on the model outputs there was a significant increase in mineralization (NH_4 and NO_3), especially in the organic layer. This could drive increased P-limitation based on N and P stoichiometric ratios. While the model did show an increase of NO_3 in throughfall, the only full shift to saturation was seen in the NH plot supporting the hypothesis for the most extreme site (highest elevation and more deposition). It was also hypothesized that with increased temperatures and despite increased PO_4 deposition, southern Appalachian forests will still be P limited due to occlusion of P into Al and Fe phosphates, as a result of high concentrations of Al and Fe along with low soil pH. This hypothesis was supported, primarily by the decrease in plant available P in all soil pools and the significant increase of unavailable P in all pools. Furthermore, though there was an increase of PO_4 in throughfall into the system, the input was not enough to prevent system limitation of plant available P. Currently, precipitation predictions are uncertain under global climate change. Perhaps with more certain precipitation predictions the model could be parameterized to better predict moisture effects on N and P processes.

More research is needed to better understand the N and P linkage mechanism. In light of a better understanding of N and P linkages, the model could be adjusted making P more susceptible to N deposition. Ultimately this model can be used as a step toward predicting nutrient cycling in the southern Appalachians. With a better understanding of nutrient cycling, particularly of N and P, there will be a better understanding of overall forest function both in the past and in the future.

LITERATURE CITED

Ashton, T. S. 1948. Some Statistics of the Industrial Revolution in Britain. The Manchester School 16(2): 214–234.

Bonito, Gregory M. 2001. Factors Regulating Nitrogen Mineralization Rates of an Oak Pine and Hardwood Forest Along an Elevation Gradient. The University of Georgia, Athens, GA.

Clark, James S., Eric Macklin, and Leslie Wood. 1998. Stages and spatial scales of recruitment limitation in southern Appalachian forests. Ecological Monographs 68(2): 213-235.

Dacko, Mariusz. 2010. Systems Dynamics in Modeling Sustainable Management of Environment and Its Resources. Polish Journal of Environmental Studies 19(4): 699-706.

Galloway, James N., Alan R. Townsend, Jan Willem Erisman, Mateete Bekunda, Zucong Cai, John R. Freney, Luiz A. Martinelli, Sybil P. Seitzinger, and Mark A. Sutton. 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science 320: 889-892.

Galloway, James N., F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vorosmarty. 2004. Nitrogen Cycles: Past, Present, and Future. Biogeochemistry 70(2): 153-226.

Havlin, John L., James D. Beaton, Samuel L. Tisdale, Wener L. Nelson. 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Upper Saddle River, New Jersey: Peason Education Inc.

Intergovernmental Panel on Climate Change (IPCC). 2007. Climate Change 2007: Mitigation of Climate Change. Summary for Policymakers e Working Group III contribution to the Environmental Panel on Climate Change Fourth Assessment Report: 35.

Iverson, Louis R., Anantha Prasad, Mark W. Schwartz. 1998. Modeling potential future individual tree-species distributions in the eastern United States under a climate change scenario: a case study with *Pinus virginiana*. Ecological Modeling 115: 77-93.

Jones, C. A., C. V. Cole, A. N. Sharpley, and J. R. Williams. 1984. A Simplified Soil and Plant Phosphorus Model: I Documentation. Division S-4-Soil Fertility and Plant Nutrition :800-805.

Keet, C. M. 2005. Factors affecting ontology development in ecology. Proceedings from Data Integration in the Life Sciences 3615: 46-62.

Knoepp, Jennifer D. and James M. Vose. 2007. Regulation of nitrogen mineralization and nitrification in Southern Appalachian ecosystems: Separating the relative importance of biotic vs. abiotic controls. Pedobiologia 51: 89-97.

Knoepp, Jennifer D., and Wayne T. Swank. 1998. Rates of Nitrogen Mineralization across an Elevation and Vegetation Gradient in the Southern Appalachians. Plant and Soil 204: 235-241.

Knoepp, Jennifer D., and Wayne T. Swank. 2002. Using soil temperature and moisture to predict forest soil nitrogen mineralization. Biology and Fertility of Soils 36: 177-182.

Knoepp, Jennifer D., David C. Coleman, D.A. Crossley Jr., and James S. Clark. 2000. Biological indices of soil quality: an ecosystem case study of their use. Forest Ecology and Management 138: 357-368.

Knoepp, Jennifer D., James M. Vose, and Wayne T. Swank. 2008. Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests. International Journal of Environmental Studies 65: 389-408.

LeBauer, D.S. and K.K. Treseder. 2008. Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. Ecology 89: 371-379.

Luyssaert, Sebastiaan, E. -Detlef Schulze, Annett Börner, Alexander Knohl, Dominik Hessenmöller, Beverly E. Law, Philippe Ciais, and John Grace. 2008. Old-Growth Forests as Global Carbon Sinks. Nature 455: 213-216.

Mahowald, Natalie, Timothy D. Jickells, Alex R. Baker, Paulo Artaxo, Claudia R. Benitez-Nelson, Gilles Bergametti, Tami C. Bond, Ying Chen, David D. Cohen, Barak Herut, Nilgun Kubilay, Remi Losno, Chao Luo, Willy Maenhaut, Kenneth A. McGee, Gregory S. Okin, Ronald L. Siefert, and

Seigen Tsukuda. 2008. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. Global Biogeochemical Cycles 22.

Mearns, L.O., F. Giorgi, L. McDaniel, and C. Shields. 2003. Climate scenarios for the southeastern US based on GCM and regional model simulations. Climatic Change 60: 7-35.

Melillo J.M., P. A. Steudler, J. D. Aber, K. Newkirk, H. Lux, F. P. Bowles, C. Catricala, A. Magill, T. Ahrens, and S. Morrisseau. 2002. Soil warming and carbon-cycle feedbacks to the climate system. Science 298: 2173–2176.

Melillo, J. M., S. Butler, J. Johnson, J. E. Mohan, P. A. Steudler, H. Lux, E. Burrows, F. Bowles, R. Smith, T. Hill, C. Vario, A. J. Burton, Y. Zhou, J. Tang. 2011. Soil Warming, carbon-nitrogen, integrations and forest carbon budgets. Proceedings of the National Academy of Sciences.

Molina, J. A. E., C. E. Clapp, M. J. Shaffer, F. W. Chichester, and W. E. Larson. 1983. NCSOIL, A Model of Nitrogen and Carbon Transformations in Soil: Description, Calibration, and Behavior. Soil Science Society of America 47(1): 85-91.

Schlesinger, William H. 1997.Biogeochemistry: An Analysis of Global Change. New York: Academic Press.

Stevenson, F.J. 1986. Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients. New York: John Wiley & Sons.

United States Global Change Research Program (USGCRP). 2009. State of the knowledge report of Global Climate Change impacts in the U.S.

Walbridge, Mark R. 2000. Review: Phosphorus Biogeochemistry. Ecology Society of America 81(5): 1474-1475.

Walbridge, Mark R., C.J. Richardson, and Wayne T. Swank. 1991. Vertical distribution of biological and geochemical phosphorus subcycles in two southern Appalachian forest soils. Biogeochemistry 13: 61-85.

Walker, T. and J. Syers. 1976. The fate of phosphorus during pedogenesis. Geoderma 15: 1–19.

APPENDIX – SPECIFIC MODEL PARAMETERS FOR THE OAK-PINE PLOT

N - 10 cm into Mineral Layer

Min_NH4(t) = Min_NH4(t - dt) + (MIn_Mineralization - Min_Nitrification - MIn_NH4_to_Org - NH4_Shallow_Leachate - NH4_Deep_Leachate) * dt

INIT Min_NH4 = 0.00000052

INFLOWS:

MIn_Mineralization = Min_OrgN*M_Mineralization

OUTFLOWS:

Min_Nitrification = Min_NH4*M_Nitrification

MIn_NH4_to_Org = Min_NH4*(1-M_Nitrification)

NH4_Shallow_Leachate = GRAPH(Min_NH4)

(4.00, 0.003), (5.00, 0.009), (6.00, 0.007), (7.00, 0.01), (8.00, 0.004), (9.00, 0.003), (10.0, 0.001), (11.0, 0.012), (12.0, 0.003)

NH4_Deep_Leachate (Not in a sector)

Min_NO3(t) = Min_NO3(t - dt) + (O_NO3_to_Min_NO3 + Min_Nitrification - MIn_NO3_to_Org - Min_Denitrificaiton - NO3_Shallow_Leachate - NO3_Deep_Leachate) * dt

INIT Min_NO3 = 0.00000000

INFLOWS:

O_NO3_to_Min_NO3   (IN SECTOR: N - Organic Layer)

Min_Nitrification = Min_NH4*M_Nitrification

OUTFLOWS:

MIn_NO3_to_Org = Min_NO3*((MIn_%H2O_2)+(1-Denitrification))

Min_Denitrificaiton (Not in a sector)

NO3_Shallow_Leachate = GRAPH(Min_NO3)

(4.00, 0.01), (5.33, 0.002), (6.67, 0.001), (8.00, 0.00), (9.33, 0.001), (10.7, 0.002), (12.0, 0.002)

NO3_Deep_Leachate (Not in a sector)

Min_OrgN(t) = Min_OrgN(t - dt) + (MIn_NO3_to_Org + MIn_NH4_to_Org - MIn_Mineralization) * dt

INIT Min_OrgN = (0.0856795350196769-0.0110367392121019)/1000

INFLOWS:

MIn_NO3_to_Org = Min_NO3*((MIn_%H2O_2)+(1-Denitrification))

MIn_NH4_to_Org = Min_NH4*(1-M_Nitrification)

OUTFLOWS:

MIn_Mineralization = Min_OrgN*M_Mineralization

MIn_%H2O_2 = 0.22280147

Min_Mineralization_mgkg = -0.00000020

Min_Nitrification_mgkg = 0.00000032

M_Mineralization = Min_Mineralization_mgkg*RMTFAC

M_Nitrification = Min_Nitrification_mgkg*RMTFAC

N - Organic Layer

O_NH4(t) = O_NH4(t - dt) + (Throughgall_to_A_NH4 + Org_Mineralization - Org_Nitrfication - O_NH4_to_Org) * dt

INIT O_NH4 = 0.00006479

INFLOWS:

Throughgall_to_A_NH4 (IN SECTOR: N - Throughfall)

Org_Mineralization = O_Org_N*O_Mineralization

OUTFLOWS:

Org_Nitrfication = O_NH4*O_Nitrification

O_NH4_to_Org = O_NH4*(1-O_Nitrification)

O_NO3(t) = O_NO3(t - dt) + (Throughfall_to_A_NO3 + Org_Nitrfication - O_NO3_to_Min_NO3 - O_NO3_to_Org - O_Denitrification) * dt

INIT O_NO3 = 0.00000016

INFLOWS:

Throughfall_to_A_NO3 (IN SECTOR: N - Throughfall)

Org_Nitrfication = O_NH4*O_Nitrification

OUTFLOWS:

O_NO3_to_Min_NO3 = O_NO3*O_%H2O

O_NO3_to_Org = O_NO3*((O_%H2O)+(1-Denitrification))

O_Denitrification (Not in a sector)

O_Org_N(t) = O_Org_N(t - dt) + (O_NO3_to_Org + O_NH4_to_Org - Org_Mineralization) * dt

INIT O_Org_N = (0.173816404880941-0.0109434152669126)/1000

INFLOWS:

O_NO3_to_Org = O_NO3*((O_%H2O)+(1-Denitrification))

O_NH4_to_Org = O_NH4*(1-O_Nitrification)

OUTFLOWS:

Org_Mineralization = O_Org_N*O_Mineralization

Denitrification = 0.849

O_%H2O = 0.74380127

O_Mineralization = O_Mineralization_mgkg*(10^(-6))*RMTFAC

O_Mineralization_mgkg = -0.00002240

O_Nitrification = O_Nitrification_mgkg*(10^(-6))*RMTFAC

O_Nitrification_mgkg = 0.00004223

RMTFAC = (-0.017+0.032*Temperature)*EXP((0.229+(5.819/Temperature))*(Precip))

N - Throughfall

Throughfall_to_A_NO3 = PULSE(NO3_Input)

INFLOW TO: O_NO3 (IN SECTOR: N - Organic Layer)

Throughgall_to_A_NH4 = PULSE(NH4_Input)

INFLOW TO: O_NH4 (IN SECTOR: N - Organic Layer)

Aambient_N = 1

Ambient_N_Deposion = 0

Increased_N = 6

NH4_Input = (NH4_by_Month)*N_Deposion

NO3_Input = (NO3_by_Month)*N_Deposion

N_Deposion = (Aambient_N*Ambient_N_Deposion)+(Increased_N*Predicted_N_Deposion)

Predicted_N_Deposion = 0

NH4_by_Month = GRAPH(TIME)

(4.00, 0.0443), (5.00, 0.0443), (6.00, 0.0443), (7.00, 0.0443), (8.00, 0.044), (9.00, 0.0443), (10.0, 0.0121), (11.0, 0.0121)

NO3_by_Month = GRAPH(TIME)

(4.00, 0.0031), (5.00, 0.0031), (6.00, 0.0031), (7.00, 0.0031), (8.00, 0.0031), (9.00, 0.0031), (10.0, 0.00124), (11.0, 0.00124)

P - 10cm - 30cm into Soil

Labile_P_2(t) = Labile_P_2(t - dt) + (Occluded_to_Labile_2 + PO4_to_10cm_to_30cm - Labile_to_Occluded_2 - PO4_Leachate_Shallow) * dt

INIT Labile_P_2 = 0.0061784778

INFLOWS:

Occluded_to_Labile_2 = IF(Occluded_P_2=Labile_P_2*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P_2-Labile_P_2*((1-NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

PO4_to_10cm_to_30cm (Not in a sector)

OUTFLOWS:

Labile_to_Occluded_2 = Labile_P_2*0.9826391463

PO4_Leachate_Shallow (Not in a sector)

Occluded_P_2(t) = Occluded_P_2(t - dt) + (Labile_to_Occluded_2 - Occluded_to_Labile_2) * dt

INIT Occluded_P_2 = 0.3497071223

INFLOWS:

Labile_to_Occluded_2 = Labile_P_2*0.9826391463

OUTFLOWS:

Occluded_to_Labile_2 = IF(Occluded_P_2=Labile_P_2*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P_2-Labile_P_2*((1-NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

P - 10cm into Soil

Labile_P(t) = Labile_P(t - dt) + (Ocluded_to_Labile + PO4_Throughfall - Labile_to_Occluded - PO4_to_10cm_to_30cm) * dt

INIT Labile_P = 0.0120814151

INFLOWS:

Ocluded_to_Labile = IF(Occluded_P=Labile_P*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P-Labile_P*((1-NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

PO4_Throughfall (Not in a sector)

OUTFLOWS:

Labile_to_Occluded = Labile_P*0.9685672040

PO4_to_10cm_to_30cm (Not in a sector)

Occluded_P(t) = Occluded_P(t - dt) + (Labile_to_Occluded - Ocluded_to_Labile) * dt

INIT Occluded_P = 0.3722755830

INFLOWS:

Labile_to_Occluded = Labile_P*0.9685672040

OUTFLOWS:

Ocluded_to_Labile = IF(Occluded_P=Labile_P*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P-Labile_P*((1-NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

P - 30+cm into Soil

Labile_P_3(t) = Labile_P_3(t - dt) + (Occluded_to_Labile_3 + PO4_Leachate_Shallow - Labile_to_Occluded_3 - PO4_Leachate_to_Deep) * dt

INIT Labile_P_3 = 0.0052106457

INFLOWS:

Occluded_to_Labile_3 = IF(Occluded_P_3=Labile_P_3*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P_3-Labile_P_3*((1-NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

PO4_Leachate_Shallow (Not in a sector)

OUTFLOWS:

Labile_to_Occluded_3 = Labile_P_3*0.9873170203

PO4_Leachate_to_Deep (Not in a sector)

Occluded_P_3(t) = Occluded_P_3(t - dt) + (Labile_to_Occluded_3 - Occluded_to_Labile_3) * dt

INIT Occluded_P_3 = 0.4056270127

INFLOWS:

Labile_to_Occluded_3 = Labile_P_3*0.9873170203

OUTFLOWS:

Occluded_to_Labile_3 = IF(Occluded_P_3=Labile_P_3*((1-NP_Interaction)/NP_Interaction))

THEN(0)

ELSE(0.1*((Occluded_P_3-Labile_P_3*((1-

NP_Interaction)/NP_Interaction)))*EXP(0.115*Temperature-2.88)*Precip)

PO4 - Throughfall

Aambient_PO4 = 1

Ambient_PO4_Deposion = 0

Increased_PO4 = 1.43

PO4_Deposion =

(Aambient_PO4*Ambient_PO4_Deposion)+(Increased_PO4*Predicted_PO4_Deposion)

PO4_Input = (PO4_by_Month)*PO4_Deposion

Predicted_PO4_Deposion = 0

PO4_by_Month = GRAPH(TIME)

(4.00, 0.0363), (5.00, 0.0363), (6.00, 0.0363), (7.00, 0.0363), (8.00, 0.0363), (9.00, 0.0363), (10.0, 0.00191), (11.0, 0.00191)

Temperature and Moisture

Ambient_Temperature = 0

Increased_Temp = Ambient_Temp+5

NP_Interaction = (0.00378503948973332/1000)*0.24+2.9

Predicticed_Temperature = 0

Ambient_Temp = GRAPH(TIME)

(1.00, 3.20), (2.00, 1.30), (3.00, 7.20), (4.00, 14.6), (5.00, 18.7), (6.00, 22.8), (7.00, 23.7), (8.00, 23.9), (9.00, 19.0), (10.0, 12.7), (11.0, 8.40), (12.0, -0.6), (13.0, 3.20), (14.0, 4.50), (15.0, 9.50), (16.0, 13.1), (17.0, 18.0), (18.0, 22.1), (19.0, 20.7), (20.0, 21.9), (21.0, 19.2), (22.0, 13.0), (23.0, 9.80), (24.0, 9.00)

Precip = GRAPH(TIME)

(1.00, 17.0), (2.00, 11.7), (3.00, 17.2), (4.00, 15.8), (5.00, 27.4), (6.00, 6.10), (7.00, 15.8), (8.00, 12.6), (9.00, 37.7), (10.0, 25.9), (11.0, 19.6), (12.0, 30.7), (13.0, 18.9), (14.0, 14.8), (15.0, 11.5), (16.0, 11.4), (17.0, 13.3), (18.0, 8.76), (19.0, 6.63), (20.0, 9.50), (21.0, 13.7), (22.0, 12.0), (23.0, 19.1), (24.0, 8.00)

Temperature =

GRAPH((Ambient_Temp*Ambient_Temperature)+(Increased_Temp*Predicticed_Temperature))

(0.00, 3.78), (0.112, 6.56), (0.224, 7.67), (0.336, 12.1), (0.449, 15.1), (0.561, 19.1), (0.673, 22.1), (0.785, 20.0), (0.897, 19.0), (1.01, 11.8), (1.12, 8.28), (1.23, 4.06), (1.35, 6.50), (1.46, 3.56), (1.57, 5.67), (1.68, 10.9), (1.79, 16.9), (1.91, 20.9), (2.02, 23.8), (2.13, 22.3), (2.24, 19.3), (2.36, 12.9), (2.47, 7.50), (2.58, 2.83), (2.69, 0.389), (2.80, 4.89), (2.92, 8.94), (3.03, 14.0), (3.14, 15.3), (3.25, 21.1), (3.36, 21.6), (3.48, 20.8), (3.59, 17.6), (3.70, 12.9), (3.81, 9.78), (3.93, 6.06), (4.04, 3.72), (4.15, 2.89), (4.26, 10.4), (4.37, 13.7), (4.49, 17.1), (4.60, 19.6), (4.71, 22.5), (4.82, 22.8), (4.93, 18.3), (5.05, 13.1), (5.16, 6.06), (5.27, 2.83), (5.38, 1.17), (5.50, 4.33), (5.61, 5.44), (5.72, 11.7), (5.83, 18.1), (5.94, 20.1), (6.06, 22.1), (6.17, 21.3), (6.28, 17.4), (6.39, 13.2), (6.50, 6.28), (6.62, 4.67), (6.73, 3.28), (6.84, 6.28), (6.95, 11.4), (7.07, 10.9), (7.18, 14.9), (7.29, 19.3), (7.40, 22.6), (7.51, 20.3), (7.63, 18.6), (7.74, 13.4), (7.85, 5.78), (7.96, 3.44), (8.07, 5.33), (8.19, 6.11), (8.30, 7.89), (8.41, 12.9), (8.52, 19.2), (8.64, 21.7), (8.75, 22.9), (8.86, 22.0), (8.97, 20.3), (9.08, 14.6), (9.20, 9.39), (9.31, 7.28), (9.42, 5.39), (9.53, 6.06), (9.64, 6.78), (9.76, 15.4), (9.87, 16.8), (9.98, 20.9), (10.1, 23.6), (10.2, 23.2), (10.3, 18.6), (10.4, 13.8), (10.5, 10.6), (10.7, 4.89), (10.8, 3.94), (10.9, 6.67), (11.0, 10.6), (11.1, 12.9), (11.2, 19.1), (11.3, 21.2), (11.4, 22.7), (11.6, 22.2), (11.7, 19.1), (11.8, 13.9), (11.9, 7.61), (12.0, 0.611)

Min_Denitrificaiton = Min_NO3*Denitrification

OUTFLOW FROM: Min_NO3 (IN SECTOR: N - 10 cm into Mineral Layer)

NH4_Deep_Leachate = GRAPH(Min_NH4)

(4.00, 0.008), (5.60, 0.003), (7.20, 0.002), (8.80, 0.016), (10.4, 0.004), (12.0, 0.002)

OUTFLOW FROM: Min_NH4 (IN SECTOR: N - 10 cm into Mineral Layer)

NO3_Deep_Leachate = GRAPH(Min_NO3)

(4.00, 0.002), (5.60, 0.00), (7.20, 0.006), (8.80, 0.004), (10.4, 0.001), (12.0, 0.00)

OUTFLOW FROM: Min_NO3 (IN SECTOR: N - 10 cm into Mineral Layer)

O_Denitrification = O_NO3*Denitrification

OUTFLOW FROM: O_NO3   (IN SECTOR: N - Organic Layer)

PO4_Leachate_Shallow = GRAPH(Labile_P_2)

(4.00, 0.01), (5.14, 0.014), (6.29, 0.027), (7.43, 0.018), (8.57, 0.01), (9.71, 0.007), (10.9, 0.053), (12.0, 0.015)

OUTFLOW FROM: Labile_P_2   (IN SECTOR: P - 10cm - 30cm into Soil)

INFLOW TO: Labile_P_3   (IN SECTOR: P - 30+cm into Soil)

PO4_Leachate_to_Deep = GRAPH(Labile_P_3)

(4.00, 0.01), (5.60, 0.009), (7.20, 0.015), (8.80, 0.022), (10.4, 0.021), (12.0, 0.026)

OUTFLOW FROM: Labile_P_3   (IN SECTOR: P - 30+cm into Soil)

PO4_Throughfall = PULSE(PO4_Input)

INFLOW TO: Labile_P   (IN SECTOR: P - 10cm into Soil)

PO4_to_10cm_to_30cm = GRAPH(Labile_P)

(4.00, 0.047), (5.00, 0.084), (6.00, 0.052), (7.00, 0.039), (8.00, 0.044), (9.00, 0.012), (10.0, 0.019), (11.0, 0.024), (12.0, 0.012)

OUTFLOW FROM: Labile_P   (IN SECTOR: P - 10cm into Soil)

INFLOW TO: Labile_P_2   (IN SECTOR: P - 10cm - 30cm into Soil)

CHAPTER 5

CONCLUSION

Global climate change is expected to affect temperature, precipitation, nutrient availability, and species distributions (Schlesinger 1997, Iverson & Prasad 1998) and thus affect nitrogen (N) and phosphorus (P) dynamics in southern Appalachian forests. Though there is some evidence of this when comparing trends observed in previous studies and trends observed in 2010 in the Coweeta gradient plots, it is important to emphasize the value of continuing data collection. While the previous trends and 2010 trends are similar, there is some variability between the previous years and 2010, which might be explained by year-to-year variability.

THROUGHFALL

Looking at overall throughfall trends for the previous gradient-plot-work by Knoepp et al. (2008), ammonium (NH_4) concentrations were greater in the MO-H plot and the NH plot. However, this was not observed in the 2010 throughfall data. Analysis comparing mean monthly NH_4 concentrations for the growing season (April-September) and the fall season (October-December), showed that there was significantly greater mean throughfall concentrations of NH_4 in the growing season for both the low and MO-H plots. In contrast, though it was not significant, the two lowest elevation plots tended to have greater mean monthly concentrations of NH_4 in throughfall during the fall. Nitrate (NO_3) concentrations in throughfall were greatest in the NH and the MO-L plot based on the previous throughfall measurements (Knoepp et al. 2008). The 2010 throughfall measurements of NO_3 found a similar pattern for the NH plot, but not for the mixed oak plots, supporting the initial hypothesis that the highest elevation plot would receive the greatest N input. Mean monthly NO_3 concentrations in throughfall were significantly greater during the fall season for all plots. This may be explained by canopy presence and uptake of throughfall NO_3 during the growing season (Potter et al. 1993).

In addition to predicted increases in anthropogenic N deposition there is significant N deposition variability along elevational gradients in the southern Appalachian Mountains. Lovett and Lindberg (1993) looked at N deposition in the Great Smokey Mountains and found that in high elevations N deposition could be as high as 28 kg of N/ha per year, while in low elevations N deposition was about 10 kg of N/ha per year. This phenomenon has often been attributed to greater dry deposition and greater wet deposition from fog and clouds (Cai et al. 2010, Lovett and Lindberg 1993). Both the previous throughfall measurements and the 2010 measurements for NH_4 could be explained by this, as in both cases it is the highest elevation plots with significantly greater NH_4 concentrations in throughfall. The 2010 NO_3 throughfall measurements may also be explained by this phenomenon, as the highest elevation plot also had significantly greater NO_3 concentrations in throughfall. The previous data supports this to an extent, but the high NO_3 concentrations in throughfall for the mid-elevation plot may need to be explained by another factor such as species composition or spatial variability (Cai et al. 2010, Finzi et al. 1998a, Finzi et al. 1998b, Lovett and Lindberg 1993).

When comparing trends in throughfall input of phosphate (PO_4), both the previous measurements (Knoepp et al. unpublished data) and the 2010 measurements observed that significantly greater PO_4 concentrations occurred during the growing season (April through September) in the low elevation plots. In previous measurements this trend was also exhibited in the high elevation plots, but this was not the case in the 2010 measurements. The 2010 throughfall measurements showed significantly more PO_4 in throughfall from the mid elevation site during the growing season, and in the highest elevation site only during the fall. Though the previous throughfall measurements of PO_4 do have strong overall trends, there is still important variability from year to year (Knoepp et al. unpublished data). It is also possible that the changes observed when comparing the previous PO_4 measurements and the 2010 measurements can be attributed to significant changes to measurement methods. Based on these observations it seems that to get a better understanding of PO_4 input to the system from throughfall, measurements must be done with consistent methodologies, on a yearly basis, in order to account for year-to-year variability. In addition to throughfall measurements, deposition measurements would also be helpful in determining if there is an increase of PO_4 deposition and if so can it be linked to anthropogenic sources based on time and location (Mahowald et al. 2008), or if PO_4 is leached by the canopy into throughfall (Potter 1992 , Potter et al. 1993, Norden 1991). This would help determine if the greater concentrations of PO_4 in throughfall during the growing season are the result of anthropogenic or canopy sources.

There is much research suggesting that it is difficult to use throughfall to estimate bulk deposition (Barker et al. 2002, Raat et al. 2002, Shubzda et al. 1995). Though throughfall is a useful index for determining input of nutrients to a system below the canopy, it is not always useful in determining inputs strictly from deposition, as the canopy can play a crucial role in throughfall chemistry (Garten et al. 1999). For example, work by Potter et al. (1993), found that PO_4 was consistently added to throughfall by the canopy, while NH_4 and NO_3, were usually absorbed by the canopy.To fully understand nutrient deposition dynamics it would be important to measure deposition, along with throughfall and canopy-leaf chemistry. This would give an idea of what nutrients are coming into the system via deposition, what nutrients are being taken-up or leached in the canopy, and what nutrients are finally making their way into the soil.

SOIL POOLS AND TRANSFORMATIONS

N deposition is relatively high in the southern Appalachians highlighting the need to better understand soil N transformations. Cai et al. (2010) found that NH_4 was significantly greater in throughfall when compared to NH_4 in the A soil horizon. However, Cai et al. (2010) found the opposite relationship between NO_3 in throughfall and NO_3 in the A soil horizon.

Previous studies suggest the greatest mineralization rates to occur during the summer months and in the highest elevation plot, the NH plot, and in the mid-elevation plot and the cove hardwood plot

(Knoepp and Swank 1998, Knoepp and Vose 2007, Knoepp et al. 2008). In the 2010 N transformation measurements, this trend was only observed for the highest elevation plot, which was expected as the highest elevation plot would have the greatest effect on N transformations, based on increased N deposition and temperature and moisture effects. Garten (2000) found greater N mineralization and nitrification rates in coves than mineralization and nitrification rates found on ridges, which might explain the high mineralization rates found in the cove hardwood plot in previous measurements. It is also possible that species compositionmay be partly driving the soil N transformations (Finzi et al. 1998a, Finzi et al. 1998b). In 2010 measurements were done on the organic and the mineral layers separatelyand it was determined that significantly greater N transformations in the organic layer across all plots.

S Soil NO_3 and NH_4 concentrations tend to vary both spatially and temporally (Cain et al. 1999, Kay et al. 2006, & Robertson et al. 1988). Kay et al. (2006) found that both weather and time of year can significantly affect plant available N. Furthermore, other forms of N might also be available to plants via N-fixation by lightning or by free-living and symbiotic microbes (Schlesinger 1997). If measurements of soil NO_3 and NH_4 concentrations are done over space and time, taking into account variability, soil NO_3 and NH_4 concentrations could then be used a base index for plant available N. To more fully understand plant available forms of N, it will be important to examine N in soil solution.

Knoepp et al. (unpublished data) found that soil PO_4-P concentrations tended to be greater in the high elevation plots in the 1992, 1994, and 1995 measurements, which was similar to the overall P concentrations in the January 2008 soils. It was also observed that PO_4-P concentrations increased significantly from the August 1992 measurement to the January 1994 measurement. These concentrations dropped in the January 1995 measurement, but remained significantly greater than the 1992 measurements for the cove hardwood, low elevation mixed oak, and NH plots. This observation could not be made for the recent P fractionation measurement, as it was done on one-time sampled soils (Knoepp et al. unpublished data). Walbridge et al. (1991) found that P adsorption capacity was closely linked to Al and Fe concentrations in Coweeta soils, due to observations of PO_4 being tightly bound to Al and Fe hydroxide surfaces. This goes along with what was observed in the 2008, reducible Fe-P pool and the "Al and some Fe-P." Walbridge et al. (1991) also observed the greatest P concentrations in the forest floor near the surface of the mineral soil that in turn, declined significantly with depth. This was not observed with the P pools extracted in the 2008 soils at three different depths, but the forest floor was not fractionated for P pools. In contrast to the P concentrations by depth Walbridge et al. (1991) found that there was no significant variation of Al and Fe concentrations by depth. There is also strong evidence to suggest that along with abundance of Al and Fe, the role of pH is very important in the immobilization of P via adsorption in to oxides and clays (Havlin et al. 2005, Stevenson 1986). The gradient plot soils have an average pH of 4. This explains the large "Al and some Fe-P" pool fractionated from the gradient soils. Though the previous soil P measurements cannot be directly compared to the 2008 fractionated P soil measurements, however, it is important to recognize that to really understand what is going on with the soil P pools analysis must be conducted yearly to account for year-to-year variability observed with the previous soil P measurements. It is also important to investigate P pools at different soil depths along the gradient plots, as phosphate availability, particularly in mineral soils, has been shown to increase as altitude decreases (Dighton and Coleman 1992).

Based on the P pool fractionation showing little plant available P and and low PO_4 concentrations in throughfall, it is likely that the gradient plot soils are P limited. The P pool fractionation displayed very low P concentrations in the most plant available pools, the "labile P" and "reducible Fe-P" pools. One argument that could be made with the labile P extraction would be as to why the extraction was done with NH_4Cl buffered to a pH of 7 rather than that of the soil pH of ~4. This step in modified Psenner fractionation was used by SanClements et al. (2009) as a means to control method inconsistencies (varying soil pH), as this step was originally done with H_2O (SanClements 2009, Personal Communication with SanClements). However, it is likely that the buffered labile P extraction is underestimating available P by as much as double the recorded concentrations (Personal Communication with SanClements). This would still be considerably low, averaging 0.5 mg/kg. While P concentrations were high in the “Al and some Fe-P” pool, due to low soil pH and high Al and Fe concentrations, this pool is occluded, thus not plant available (see table 3.2, and figures 3.3 and 3.10). This is largely in part due to the metamorphic parent material found in the Coweeta gradient plot soils, which tend to be high in Al and Fe (Qualls et al. 2002, Vitousek et al. 2010, Walbridge et al. 1991).

SOIL SOLUTION LEACHATE

Previous measurements by Knoepp et al. found high concentrations of NO_3 in soil solution in the highest elevation plot, the NH plot, which suggested that there was N saturation occurring in this plot (Knoepp et al 2000, Knoepp et al. 2008). The same pattern was seen with the 2010 measurements for in-soil solution leachate in the NH plot, as it was expected that N dynamics would be significantly greater in this highest-elevation plot. Previous soil solution NH_4 concentrations were found to be high the mid-elevation plot, the low mixed oak plot, and the high elevation plot;however, this trend was not observed in 2010. It is possible that the variation in significance for soil solution NH_4 concentrations between the previous measurements and the 2010 measurements is due to changes in N dynamics due to global climate change, but it is also possible that the change in measurement methods maybe be the cause. A study done in high-elevation spruce and fir forests of the Great Smoky Mountains National Park, found evidence to suggest that N availability in soils and NO_3 leaching will increase in response to warming and acid deposition (increased soil pH), which is supported by both the previous and the 2010 soil solution measurements (Garten 2000, Johnson et al. 1999). Though different from what is observed on the gradient plots, Ross and Hales (2003) found that NO_3 and NH_4 leaching followed the same patterns as one another in Camels Hump State Forest in Huntington and Duxbury, VT.

Overall, most of the trends seen in previous measurements were observed in the 2010 measurements. The slight differences may be attributed to global change, but it is also possible that changes in measurement methodologies are the cause of slight differences between previous and 2010 measurements. Only by continuing these measurements under the condition of changing change and deposition rates will we gain a better understanding of southern Appalachian forest biogeochemical dynamics. Further, with advances in measurement techniques and technology it is likely that we will gain a more realistic view of what is occurring in N processes in forests.

In previous soil solution measurements, O-PO_4 concentrations were observed to be greatest in the shallow lysimeters, when compared to the deep lysimeters. The soil solution O-PO_4 concentration in leachate tended to be greater in the deep lysimeters during the winter months (November through March), with the greatest O-PO_4 concentrations commonly observed in the high elevation plots year round (Knoepp et al. unpublished data). The 2010 soil solution measurements on TP followed the same trend as the previous soil measurements, with the greatest O-PO_4 concentrations observed during the winter months (November through March) and in the high elevation plots year round. While the O-PO_4 concentrations in the 2010 measurements tended to be greater in the high elevation plots, the seasonal trend was observed to be the inverse of the previous O-PO_4 soil solution measurements, particularly in the shallow lysimeters. Qualls et al. (2002) looked at dissolved organic P (DOP) in soil solution in watershed 2 at the Coweeta Hydrologic Laboratory and found significantly more DOP in soil solutions from the Oa layer, when compared to deeper soil horizons which had negligible DOP concentrations. Qualls et al. (2002), like Walbridge et al. (1991), attributed this phenomenon to DOP adsorption into the highly Fe and Al rich mineral soils.

It was expected that the highest elevation site would receive the most PO_4 deposition into the system measured via throughfall, and as one of the most extreme sites also have the greatest response to increased N and P deposition and moisture dynamics. Though previous PO_4 throughfall measurements observed greater PO_4 concentrations in the highest elevation plot, the 2010 measurements did not observe a similar significant trend. Despite this, the highest elevation plot did have the largest total soil P pool, though most of the P was unavailable in Fe and Al phosphates, due to low pH and high Fe and Al concentrations in parent soil material. In addition to a greater overall soil pool, the highest elevation plot also had the most TP leachate at both lysimeter depths, and the greatest PO_4 leachate for the deep lysimeters. In all cases plant available P tended to be low, especially with increasing soil depth. This suggests, that PO_4 deposition is not significantly affecting P processes in these southern Appalachian forests, however it is possible that increased N deposition is increasing the systems demand for plant available P.

MODEL PREDICTIONS

It was predicted that increased temperature and increased N deposition would lead to increase N mineralization and thus contribute to a P limited system, which is supported based on the P outputs from the model. It was hypothesized that 1) under global change, southern Appalachian forests will become P limited due to increased N mineralization, resulting from increased N deposition. Based on the model outputs there was not a significant increase in mineralization (NH_4 and NO_3) for any sites except the cove hardwood and the MO-H plots. Though not significant the other plots did have a slight increase in NH_4 and NO_3 soil pools, which most likely drive P limitation based on N and P stoichiometric relations. While the model did show an increase of NO_3 in throughfall, this was not enough to shift the system to saturation and exhibit an increase of NO_3 leachate; thus, our hypothesis was not supported. It was also hypothesized that with increased temperatures and 2) despite increased PO_4 deposition, southern Appalachian forests will still be P limited due to occlusion of P into Al and Fe phosphates, as a result of high concentrations of Al and Fe along with low soil pH. This hypothesis was supported, primarily by the decrease in plant available P in all soil pools and the significant increase of unavailable P in all pools based. This could be further explained by an increase in N availability that drove the system to P limitation. Further, although there was an increase of throughfall PO_4 into the system, the input was not enough to prevent system limitation of plant available P. Currently, precipitation predictions are less certain than those for temperature under global climate change. Perhaps with more certain precipitation predictions the model could be better parameterized to predict moisture effects on N and P processes.

In addition to improved predicted values, the model may have more P effects from predicted values if N and P were better linked within the model. Time could also be a crucial component. The recent data was collected over one year. Parts of the model, such as P soil dynamics, relied on data from a one-time only measurement. It is possible that the single year did not account for enough variability in the system. More research is needed to better understand the N and P linkage mechanisms. In light of a better understanding of N and P linkages, the model could be adjusted, making P more susceptible to N deposition. Ultimately this model can be used as a step toward predicting future nutrient cycling in the southern Appalachians. With a better understanding of nutrient cycling, particularly of N and P, there will be a better understanding of overall forest function including C dynamics in both the past and the future.

ACKNOWLEDGEMENTS

The author would like to acknowledge Jennifer D. Knoepp for in-depth descriptions of N and P measurement methods used on the Coweeta LTER gradient plots. The author would also like to acknowledge Michael D. SanClements for clarification of the modified Psenner P fractionation methods.

LITERATURE CITED

Barker, M., Helga Van Miegroet, N. S. Nicholas, and I. F. Creed. 2002. Variation in overstory nitrogen uptake in a small, high-elevation southern Appalachian spruce–fir watershed. Canadian Journal of Forest Research 32: 1741-1752.

Cai, Meijun, John S. Schwartz, R. Bruce Robinson, Stephen E. Moore, and Matt A. Kulp. 2010. Long-Term Effects of Acidic Deposition on Water Quality in a High-Elevation Great Smoky Mountains National Park Watershed: Use of an Ion Input–Output Budget. Water, Air, and Soil Pollution 209(1-4): 143-156.

Cain, Michael L., Scott Subler, Jonathan P. Evans, & Marie-Josée Fortin. 1999. Sampling spatial and temporal variation in soil nitrogen availability. Oecologia 118: 397-404.

Dighton, John, and David C. Coleman. 1992. Phosphorus relations of roots and mycorrhizas of Rhododendron maximum L. in the southern Appalachians, North Carolina. Mycorrhiza 1: 175-184.

Finzi, Adrien C., Charles D. Canham, and Nico Van Breeman. 1998b. Canopy Tree-Soil Interactions within Temperate Forests: Species Effects on pH and Cations. Ecological Applications 8(2): 447-454.

Finzi, Adrien C., Nico Van Breeman, and Charles D. Canham. 1998a. Canopy Tree-Soil Interactions within Temperate Forests: Species Effects on Soil Carbon and Nitrogen. Ecological Applications 8(2): 440-446.

Garten, C. T., Jr. 2000. Nitrogen Saturation and Soil N Availability in a High-Elevation Spruce and Fir Forest. Water, Air, and Soil Pollution 120: 295-313.

Havlin, John L., James D. Beaton, Samuel L. Tisdale, Wener L. Nelson. 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Upper Saddle River, New Jersey: Peason Education Inc.

Iverson, Louis R., and Anantha Prasad. 1998. Predicting abundance of 80 species following climate change in the Eastern United States. Ecological Monographs 68(4): 465-485.

Johnson, D. W., R. B. Susfalk, P. F. Brewer, and Wayne T. Swank. 1999. Simulated Effects of Reduced Sulfur, Nitrogen, and Base Cation Deposition on Soils and Solutions in Southern Appalachian Forests. Journal of Environmental Quality 28: 1336-1346.

Kay, B.D., A.A. Mahboubi, E.G. Beauchamp, & R.S. Dharmakeerthi. 2006. Integrating Soil and Weather Data to Describe Variability in Plant Available Nitrogen. Soil Science Society of America Journal 70: 1210-1221.

Knoepp, Jennifer D. and James M. Vose. 2007. Regulation of nitrogen mineralization and nitrification in Southern Appalachian ecosystems: Separating the relative importance of biotic vs. abiotic controls. Pedobiologia 51: 89-97.

Knoepp, Jennifer D., and Wayne T. Swank. 1998. Rates of Nitrogen Mineralization across an Elevation and Vegetation Gradient in the Southern Appalachians. Plant and Soil 204: 235-241.

Knoepp, Jennifer D., David C. Coleman, D.A. Crossley Jr., and James S. Clark. 2000. Biological indices of soil quality: an ecosystem case study of their use. Forest Ecology and Management 138: 357-368.

Knoepp, Jennifer D., James M. Vose, and Wayne T. Swank. 2008. Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests. International Journal of Environmental Studies 65: 389-408.

Lovett, Gray M., and Steven E. Lindberg. 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. Canadian Journal of Forest Research 23(8): 1603–1616.

Mahowald, Natalie, Timothy D. Jickells, Alex R. Baker, Paulo Artaxo, Claudia R. Benitez-Nelson, Gilles Bergametti, Tami C. Bond, Ying Chen, David D. Cohen, Barak Herut, Nilgun Kubilay, Remi Losno, Chao Luo, Willy Maenhaut, Kenneth A. McGee, Gregory S. Okin, Ronald L. Siefert, and Seigen Tsukuda. 2008. Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts. Global Biogeochemical Cycles 22.

Norden, U. 1991. Acid Deposition and Throughfall Fluxes of Elements as Related to Tree Species in Deciduous Forest of South Sweden. Water, Air, and Soil Pollution 60(3-4): 209-230.

Potter, Christopher S. 1992. Stemflow Nutrient Inputs to Soil in a Successional Hardwood Forest. Plant and Soil 140(2): 249-254.

Potter, Christopher S., Harvey L. Ragsdale, and Wayne T. Swank. 1991. Atmospheric Deposition and Foliar Leaching in Regenerating southern Appalachain Forest Canopy. Journal of Ecology 79: 97-115.

Psenner, R., B. Bostrom, M. Dinka, K. Petterson, R. Pucsko, and M. Sager. 1988 Fractionation of phosphorus in suspended matter and sediment. Arch Hydrobiol Beih Ergebn Limnol 30: 98-103.

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

Raat, K. J., G. P. J. Draaijers, M. G. Schaap, A. Tietema, and J. M. Verstraten. 2002. Spatial variability of throughfall water and chemistry and forest floor water content in a Douglas fir forest stand. Hydrology and Earth System Sciences 6(3): 363-374.

Robertson, G. Philip, Michael A. Hutson, Francis C. Evans, & James M. Tiedje. 1988. Spatial Variability in a Successional Plant Community: Patterns of Nitrogen Availability. Ecology 69(5): 1517-1524.

SanClements, Michael D. 2009. The Chemistry of Acidic Soils in Humid, Temperate Forested Watersheds with Emphasis on Phosphorus, Aluminum, and Iron. University of Maine, Orono, ME.

SanClements, Michael D., Ivan Fernadndez, and Stephen A. Norton. 2009. Forest Ecology and Management 258: 2318-2325.

Schlesinger, William H. 1997.Biogeochemistry: An Analysis of Global Change. New York: Academic Press.

Shubzda, J., Steven E. Lindberg, C. T. Garten, and S. C. Nodvin. 1995. Elevational trends in the fluxes of sulphur and nitrogen in throughfall in the southern Appalachian mountains: Some surprising results. Water, Air, and Soil Pollution 85(4): 2265-2270.

Stevenson, F.J. 1986. Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients. New York: John Wiley & Sons.

Vitousek, P.M., S. Porder, Benjamin Z. Houlton, and Oliver A. Chadwick 2010. Terrestrial phosphorus limitation: mechanisms, implications, and nitrogen-phosphorus interactions. Ecological Applications 20(1): 5-15.

Walbridge, Mark R., C.J. Richardson, and Wayne T. Swank. 1991. Vertical distribution of biological and geochemical phosphorus subcycles in two southern Appalachian forest soils. Biogeochemistry 13: 61-85.