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Forest floor leachate biogeochemistry and decomposition dynamics

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FOREST FLOOR LEACHATE BIOGEOCHEMISTRY AND DECOMPOSITION DYNAMICS

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xi
INTRODUCTION	1
Background	3
Sample Collection for Analysis of Soluble Organics	3
Measurement of Soluble Organics in Forest Solutions	5
Chemical Characteristics of DOC	6
Formation and Structure of Humic Substances	11
Solubility of Soil Organics	15
Biogeochemistry of DOC in Forest Ecosystems	16
Summary of DOC Characteristics and Controls	18
Nitrogen Retention and Dissolved Organic Nitrogen	19
Field Study Objectives	22
CHAPTER	
I. DISSOLVED ORGANICS IN FOREST-FLOOR LEACHATE AT HARVARD FOREST	23
Introduction	23
Materials and Methods	24
The Harvard Forest Study Site	24
Experiment Design and Installation	25
Sample Collection and Preservation	28
Laboratory Analysis	30
Statistical Analysis	31
Volume Weighting and Flux Calculations	32
Results	33
Precipitation	33
Throughfall Chemistry	34
Throughfall Chemical Fluxes	40
Oa Leachate Chemistry	41

TABLE OF CONTENTS
(continued)

Discussion 58
Dissolved Organics in Throughfall 58
Sampling of Forest Floor Leachate 59
Differences Between Year 1 and Year 2 Results 60
Disturbance Effect Mechanisms 62
Decreased DOM in the Second Year 64
Significance for Ecosystem Functioning 65

II. ASPECTS OF INORGANIC CHEMISTRY OF THROUGHFALL AND FOREST-FLOOR LEACHATE AT HARVARD FOREST 67
Introduction 67
Materials and Methods 68
Calculations and Statistical Analyses 69
Results 71
Precipitation and Throughfall Chemistry 71
Oa-Leachate Hydrology 76
Oa-Leachate Chemistry 77
Discussion 97
Soil Solution Acidification and Base Cation Leaching 97
Stand Differences 98
Oa Leachate Chemistry Differences Between Years 100
Site Base Status 101

III. A PROCESS MODEL-BASED EXTRAPOLATION OF FOREST-FLOOR DECOMPOSITION DYNAMICS TO COVER A HETEROGENEOUS LANDSCAPE 103
Introduction to the Modeling Project 103
The White Mountains of New Hampshire 105
Vegetation 105
Disturbance and Land Use History 106
Climate 107
Soils 107
Background 108
Methods 110
Model Description 110
Model Tests Against Parameterization Datasets 123
Annual Litter Inputs and Climate Driver 127
Model Validation 131
GIS Application of DocMod 135

TABLE OF CONTENTS
(continued)

Results 137
Ecosystem-Level Dynamics 137
Landscape-Scale Patterns 138
Discussion 143
Model Mechanisms 143
GIS Environment 145
Dynamics in Forest Floor Mass 146
Limitations and Future Work 148

LIST OF REFERENCES 152

APPENDIX 166

LIST OF TABLES

Page

I.1. DOC characterization by molecular weight 9

I.2. Summary of DOC Fractionation Analysis results 9

I.3. Structural composition of an average humic acid 12

1.1 Throughfall chemistry 34

1.2 Throughfall DOC and DON fluxes 40

1.3 (A). DOC and DON concentrations in red pine stand Oa leachate 46

1.3 (B). DOC and DON concentrations in hardwood stand Oa leachate 47

2.1. Aspects of inorganic chemistry in precipitation, TF and Oa leachate 74

2.2. Oa-leachate sample numbers and amounts collected 76

2.3. Stand, year and N treatment differences in Oa-leachate chemistry 96

3.1. Basic litter mass-loss equations used in DocMod 112

3.2. DocMod forest floor mass and N capital comparisons with measurements... 134

3.3. Modeled steady-state forest-floor mass by cover type in the WMNF 143

LIST OF FIGURES

Page

1.1. Zero-tension lysimeter (ZTL) installation 26

1.2. Precipitation amount by month at the Harvard Forest 35

1.3. Seasonal patterns in pine stand throughfall DOC concentrations 36

1.4. Seasonal patterns in pine stand throughfall DON concentrations 37

1.5. Seasonal patterns in hardwood stand throughfall DOC concentrations 38

1.6. Seasonal patterns in hardwood stand throughfall DON concentrations 39

1.7. Seasonal patterns in pine stand Oa-leachate DOC concentrations 42

1.8. Seasonal patterns in pine stand Oa-leachate DON concentrations 43

1.9. Seasonal patterns in hardwood stand Oa-leachate DOC concentrations 44

1.10. Seasonal patterns in hardwood stand Oa-leachate DON concentrations 45

1.11. DOC concentrations versus Oa-leachate sample amount collected 48

1.12. DON versus DOC in Oa-leachate samples 49

1.13. Time series of DOC:DON mass ratios in pine stand Oa-leachate 53

1.14. Time series of DOC:DON mass ratios in hardwood stand Oa-leachate 54

1.15. Forms of N in Oa leachate in the pine and hardwood stands 55

1.16. Single collection Oa-leachate DON fluxes 56

2.1 (A). Time series of pine stand throughfall pH levels 72

2.1 (B). Time series of hardwood stand throughfall pH levels 73

2.2. Nitrate concentrations in Oa leachate by stand, year and N treatment 80

2.3. Ammonium concentrations in Oa leachate by stand, year and N treatment ... 81

LIST OF FIGURES
(continued)

Page

2.4. Hydrogen ion concentrations in Oa leachate by stand, year and N treatment.. 82

2.5. Calcium concentrations in Oa leachate by stand, year and N treatment 83

2.6. Magnesium concentrations in Oa leachate by stand, year and N treatment ... 84

2.7. Potassium concentrations in Oa leachate by stand, year and N treatment 85

2.8. Sodium concentrations in Oa leachate by stand, year and N treatment 86

2.9. Sulfate concentrations in Oa leachate by stand, year and N treatment 87

2.10. Pine stand Oa-leachate chemistry from a single collection set 88

2.11. Hardwood stand Oa-leachate chemistry from a single collection set 89

2.12. Nitrate versus calcium concentrations in Oa leachate 90

2.13. Pine stand nitrate-N versus DOC concentrations in Oa leachate 91

2.14. Hardwood stand nitrate-N versus DOC concentrations in Oa leachate 92

3.1. DocMod mass pools and transfers 114

3.2. AET effect on mass loss for all mass compartments in DocMod 115

3.3. DocMod nitrogen pools and transfers 121

3.4. DocMod LC pool nitrogen immobilization algorithm 122

3.5. DocMod fresh foliar litter mass and N dynamics over two years 125

3.6. DocMod N dynamics in five litters used during model development 126

3.7. DocMod litter inputs during forest aggradation 128

3.8. DocMod simulation of forest-floor mass recovering from clear-cutting 139

LIST OF FIGURES
(continued)

Page

3.9. DocMod image of steady-state forest-floor mass in the WMNF 141

3.10. DocMod forest-floor mass versus elevation in the WMNF 142

ABSTRACT
(continued)

Site-level data from previous studies were used to construct a process model of forest-floor decomposition and N dynamics. After validation through blind predictions, the model was used to simulate forest-floor mass and N capital during recovery from clear-cutting in northern hardwood forests. The model was also applied in 10-ha patches across a heterogeneous landscape to predict patterns of forest floor mass and N capital in the White Mountain National Forest.

INTRODUCTION

The forest floor is a dynamic center of carbon and nutrient processing. Forest-floor processes affect ecosystem storage, transformation, retention or loss of carbon and nutrients. Inputs occur each year in litterfall and throughfall. Outputs from the organic soil horizons occur through plant uptake, efflux of gases and leaching of material to lower soil horizons.

Current, dramatic changes in global and regional cycling of nitrogen could affect forest production, decomposition, community structure and biodiversity (Vitousek et al., 1994). Nitrogen deposition to forests at regional scales may exhibit complex interactions and feedbacks with other aspects of global change such as increased atmospheric CO_2 and temperature changes; forest floor and soil organic matter processes mediate such interactions (Rastetter et al., 1991; Schindler and Bayley, 1993). In addition, nitrogen deposition in regional watersheds accounts for 11 to 100% of the nitrogen loading to coastal waters such as Chesapeake Bay, Narragansett Bay and the New York Bight (Hinga et al., 1991). Large uncertainties are due partly to the lack of understanding of processes responsible for N retention in and loss from terrestrial ecosystems.

Increasing nitrogen deposition in a gradient across New England and New York has been positively correlated with increasing forest floor percent nitrogen and with increasing rates of nitrification (McNulty et al., 1990; McNulty et al., 1991). Time series

analysis has indicated recent increases in leaching losses of nitrate in forests in the Adirondack Park, New York (Driscoll and van Dreason, 1993).

Manipulation studies in which nitrogen has been added to the forest floor have shown great variability in ecosystem responses. With low levels of N addition to the Bear Brooks Watershed in Maine (2.5 g N m^{-2} yr^{-1}), nitrate leaching occurred rapidly (Kahl et al., 1993). In contrast, in two forest stands at the Harvard Forest in Massachusetts, essentially all of the nitrogen in larger additions (5 and 15 g N m^{-2} yr^{-1}) over the course of six years was retained in most treatments (Magill et al., *in preparation*). The exception was a high-N addition red pine plot, which began leaching high levels of nitrate in the third year of treatment (Aber et al., 1993).

A strategy for addressing the complex process of N retention by terrestrial ecosystems is to integrate long-term biogeochemical studies with process-based modeling efforts (Boring et al., 1988; Mitchell et al., 1994). In this dissertation I present the results of field research and computer modeling research. The modeling involved development and regional application of a process-based model of forest-floor decomposition focusing on C and N dynamics. The modeling work and field projects are related through the topic of biogeochemistry of decomposition processes in terrestrial ecosystems, and could lead to a future synthesis.

My field and laboratory work quantified biogeochemical responses of forest-floor solution chemistry to chronically elevated nitrogen inputs to two forest stands. I collected and analyzed solution entering the forest floor in throughfall and leaving the forest floor

in leachate. I worked in the Chronic N Addition plots at the Harvard Forest, a site in the U.S. Long Term Ecological Research (LTER) network. My fieldwork comprised part of a long-term, integrated study to test hypotheses concerning the effects of nitrogen inputs in acid deposition to forests of northeastern North America.

Background

Sample Collection for Analysis of Soluble Organics

Zero-tension lysimeters (ZTL's), which collect primarily gravitational or high-flow water, are commonly used to collect soil solution from forest organic horizons for chemical analysis (David and Driscoll, 1984; Qualls et al., 1991). Tension lysimeters are a standard means of collecting mineral-soil solution for chemical analysis (Dawson et al., 1978; McDowell and Likens, 1988), though zero-tension lysimeters are sometimes used in mineral soil as well.

DOC sources and sinks are also studied in laboratory soil columns. Columns have been leached with DIW, with simulated throughfall and with salt solutions. Soil columns in the laboratory or soil horizons in the field have been treated with acid (Cronan, 1985; Vance and David, 1989). Other workers have add acid and shaken soil for a long period of time to solubilize DOC. Additionally, KCl has been used to extract DOC from soil cores (Foster et al., 1985).

The extraction of soluble C from soil cores in the laboratory has some similarities to analysis of field-collected DOC and some similarities to analysis of soil organic

extracts. Cold and hot water extractions are the most common, but the use of salts such as KCl and $SrCl_2$ have also been reported. Ideal extraction techniques remain to be found (Schnitzer, 1991). Different investigators study DOC and/or soluble SOM for quite different purposes. Some investigators may want to characterize the fluxes of C, N and other element movements in soil solution; some want to determine the character of soil organics as microbial substrates or products; others may want to extract organics selectively to study the nature of soil organic matter (SOM).

Another technique is simply to centrifuge field-wet soil samples to obtain soil solution (Seto and Yui, 1983). Cold water has also been added and cores shaken for a short time prior to centrifuging (Davidson et al., 1987), or stored for 24 hours prior to analysis (Cronan et al., 1992). In the latter study, the water-extraction method produced DOC levels of 240 mg L^{-1}, approximately 5 to 15 times higher than average concentrations usually observed in forest-floor leachate. Water-extractions have yielded much higher DOC concentrations from O and A horizons than from those with less SOM (Dethier et al., 1988) and increasing DOC levels with age in a chronosequence (Zak et al., 1990).

Some workers have studied water-soluble organics leached from leaf litter (McClaugherty, 1983; Qualls et al., 1991). This overlaps with studies of carbon quality in forest litter, as leaching with hot water is used to separate out polar extractives (simple sugars and water-soluble phenolics) in proximate-carbon-fractionation analysis of forest litters (Ryan et al., 1989).

Obviously, the organic character of samples collected through these various means may differ significantly. The amounts of Total DOC and the nature of the compounds comprising DOC may differ from laboratory solubilization studies versus field studies, and the use of different lysimeter types and collection procedures in the field makes even comparisons among field studies problematic.

Measurement of Soluble Organics in Forest Solutions

A variety of compounds contribute to the spectrum of organics in solution, impeding isolation and identification of particular compounds (Stumm and Morgan, 1981). Bulk measurement of total organic carbon (TOC) is often measured through combustion or chemical oxidation of all organics present in a liquid sample, followed by measurement of CO_2 produced. Measurements of TOC thus obtained, in themselves, yield no information on sizes, charges, molar concentrations or structures of the organics.

A cation-anion deficit is sometimes used as a means to quantify organic anion charge in solution (Eshleman and Hemond, 1988; Vance and David, 1991a). Investigators measuring quantities of DOC directly do so with an operational approach, measuring the quantity of organic carbon that passes through filters of a certain size. The use of various pore sizes in filters complicates the reporting of DOC in literature. For measuring DOC in soil solution, workers have used filter pore sizes of 0.45 um (Cronan and Aiken, 1985; Yavitt and Fahey, 1986; Trumbore et al., 1992), 0.7 um (Vance and David, 1991a; Qualls and Haines, 1992), 0.8 um (Dunnivant et al., 1992) and 1.2 um (Cole et al., 1984; David and Driscoll, 1984; McDowell and Likens, 1988).

Chemists may consider anything larger than 1000 g mol^{-1} to be colloidal material, but soil biogeochemists include much larger particles in bulk measurements of "dissolved" organic carbon. Many of the organics of interest are humic materials, which can attain molecular weights of up to 30,000 g mol^{-1}. Colloidal humic substances may be highly dispersed, if chemically stabilized, and may pass through a 0.45 um filter (Stumm and Morgan, 1981). Some workers consider particles larger in diameter than .021 um to be colloidal, and have found this colloidal fraction to include up to half of the organic carbon in streamwater samples passed through a 0.45 um filter (Lock et al., 1977). Soil biogeochemists, by using the operational definition of DOC, thus include humic substances and may often include even larger particles; a significant fraction of organics passing through a 1.2 um filter were found to be larger than 100,000 g mol^{-1} (table I.1; Cole et al., 1984). Polymeric organics containing enough hydrophilic functional groups (--COO-, --NH_2, R_2NH, --RS^-, ROH, RO^-) can remain in solution in spite of large molecular size (Stumm and Morgan, 1981).

Chemical Characteristics of DOC

Molecular weight. Characterization of dissolved organics from the B horizon at Hubbard Brook, NH by molecular weight class showed that the bulk of dissolved organics were molecules in the 1,000 to 10,000 g mol^{-1} range (table I.1). The O-horizon-leached organic acids from a Durohumult soil on the Olympic Peninsula and a Cryandept in the Central Cascades, Washington, were measured by gel filtration to have molecular weights in the range of 810 to 930 g mol^{-1} (Dawson et al., 1981). Homman and Grigal (1992) found the major fraction (47 to 71%) of $SrCl_2$-extracted soluble organic

matter to be in the > 14,000 g mol^{-1} class. The latter authors found the soluble organic matter to vary significantly with location on a soil catena, with horizon, and with treatment to simulate disturbance.

Fractionation analysis. A widely used method of analytically partitioning DOC into components, called DOC Fractionation Analysis (DOC-FA), was originated and standardized by Leenheer (1981). The method was developed as a combination of various techniques that together would recover 90% of the organics, isolate them from the solution matrix, separate them into interpretable and reproducible fractions and apply across a variety of waters (Leenheer, 1981). Samples are acidified to pH 2 with HCl and passed through various resin that adsorb different components of the dissolved organic matrix based on acidic, basic or neutral character and hydrophobic or hydrophilic behavior. The choice of pH 2 as the initial acidification point is an optimization between the need for low pH in order to protonate and precipitate organics and the concern that very low pH values disrupt organic molecules. In the reporting of results, all of the bases are often grouped together with the understanding that they are predominantly hydrophilic. Classes of organic compounds considered to comprise each of the five DOC-FA fractions are listed in table I.2. When subject to DOC-FA, oxalic, succinic and citric acids were classified as HPI-A, while benzoic and salicylic acids were determined to be HPO-A (David et al., 1989).

DOC fractionation analysis techniques vary; workers use different procedures similar to that formalized by Leenheer (1981) but with variations (Qualls et al., 1991;

Vance and David, 1991). Qualls et al. (1991) used a variation that distinguished phenols (weak hydrophilic acids) from the rest of the hydrophilic acids; the phenols included flavonids and tannins lacking carboxylic acid groups. In their definition, the rest of the hydrophilic acids (non-'weak') are lower in molecular weight and higher in carboxyl group content.

A pertinent question concerns the biogeochemical significance of DOC fractions. In characterizing DOC from different locations and different types of samples, uniformity is often observed in the DOC-fractionation-analysis results. Differences in total DOC can be seen easily; it has a great range. But even where total DOC varies by a factor of ten (between throughfall and forest floor leachate, for example), DOC-FA results may show no significant differences. For example, DOC-FA results did not differ significantly over old fields of varying age, community composition, distribution and amount of plant biomass, C and N storage, potential CO_2-C and net-N mineralization (Cook and Allan, 1992). Fractions also remained constant during a lab decomposition incubation (Cook and Allan, 1992).

Table I.1

Molecular weight class [g mol^{-1}]	Percent of total
> 100,000	6.9 ± 5.6
10,000 to 100,000	4.6 ± 4.1
1,000 to 10,000	81.6 ± 3.1
< 1,000	6.9 ± 2.9

Table I.1. DOC characterization by molecular weight. Samples were collected from soil B horizon at 30 cm. depth at Hubbard Brook, NH. Total DOC defined as compounds passing through a GF/C 1.2 um filter. (Cole et al., 1984)

Table I.2

DOC fraction	Compound Class	Percent of Total
Hydrophobic		
Acids	simple aromatic acids; mixture of aromatic, polyfunctional acids and phenols; complex aliphatic carboxylic acids	30 - 70% of DOC
Bases	polynuclear amines, ethers and quinones; porphyrins	< 1% of DOC
Neutrals	hydrocarbons; complex alcohols, amides, esters and ketones	up to 15% of DOC
Hydrophilic		
Acids	simple aliphatic acids; mixture of aliphatic and aromatic polyfunctional acids and phenols	30 - 50% of DOC
Bases	amphoteric proteinaceous compounds; amino acids and sugars	consistent 5 - 10% of DOC
Neutrals	carbohydrates; polyfunctional alcohols	up to 12% of DOC

Table I.2. Summary of DOC Fractionation Analysis results. Characteristics listed are primarily from forested ecosystem samples. Results are from Leenheer, 1981; David et al., 1989; Vance and David, 1989; Vance and David, 1991.

There are differences among DOC-FA fractions that relate to chemical properties of the organics in each fraction. The HPI-A component has greater charge per unit weight of organic C than the HPO-A component. Elemental analysis has revealed that though HPI- and HPO-acids have approximately equivalent C:N ratios, HPI-acids contain more oxygen per unit carbon, suggesting a greater number of COOH groups (Vance and David, 1991a). These relationships underscore the importance, for solubility of the organics, of functional groups that are anions in the pH range of soil solutions.

Humic substances. Humic substances comprise fulvic acid, humic acid and humin, all of which can be obtained from soil organic matter (Stevenson, 1982; David et al., 1990). Fulvic acid is yellow or yellow-brown in color, whereas humic acid is dark brown or grey-black. Humic acid is more highly polymerized, has greater molecular weight and carbon content, with lower oxygen content and lower exchange acidity than fulvic acid (Stevenson, 1982).

The terms 'humic acid' and 'fulvic acid' are also used in referring to organics as they occur in natural soil solution. Yavitt and Fahey (1986) considered polymerics in forest floor leachate to be similar to fulvic and humic acids. Vance and David (1991) found DOC in forest-floor leachate from a Northern Hardwood stand to be similar in chemistry to fulvic acids. Cronan et al. (1992) acidified soil solution samples to pH 1, centrifuged, then dried and weighed the precipitate, which they considered to be humic acid.

The fractions identified in DOC-FA bear ambiguous relations to the classifications of organic acids as 'humic' and 'fulvic'. However, work has been done to discover the relationships. DOC-FA classified both humic and fulvic acids as 70 to 80% hydrophobic (David et al., 1989). DOC-FA of a fulvic acid revealed it to comprise primarily organic acids, 70% HPO-A and 19% HPI-A. Analysis of a humic acid revealed it also to comprise primarily organic acids, 43% HPO-A, 27% HPI-A, 12% HPO-B and 13% HPO-N (David et al., 1989). Hydrophobic acids as determined by Qualls et al. (1991) in a variation of the DOC fractionation analysis were considered to be 'aquatic humic substances' by the International Humic Substances Society (Qualls et al., 1991).

Formation and Structure of Humic Substances

In recent years a number of spectroscopic techniques have come into use for characterizing soil organic matter in both the solid and liquid phases. These include Synchronous-Scan Flourescence spectroscopy (SSFS), Fourier-Transform Infrared spectroscopy (FT-IR), UV absorption spectroscopy and ^{13}C-NMR (Nuclear Magnetic Resonance) spectroscopy.

Other spectral methods are often used to identify dissolved organic molecules of homogeneous structure, such as monosaccharides or polysaccharides (McDowell and Likens, 1988; Vance and David, 1991). Spectroscopic techniques can also be used to estimate DOC concentration by focusing on one representative wavelength (e.g., UV absorption at 254, 360, or 400 nm) (Dawson et al., 1981; Grieve, 1991; Koprivnjak and Moore, 1992). Cronan et al. (1992) have suggested that SSFS might be used to reveal a

taxonomic influence on spectra of forest floor leachates. The most significant applications of absorption spectra might be their use in probing for the presence of various structural groups in humic substances, which have eluded chemical characterization. Humic substances (humic acid, fulvic acid, and humin) appear to be random polycondensates of various organic components. They are believed to contain phenolics and partially oxidized lignins as a basic structure onto which biopolymers and other organics are adsorbed (Stevenson, 1982).

There is a generally well-accepted view of the formation of humic substances (Stevenson, 1986). Soil microbial biomass increases as microbes metabolize plant detrital materials, including lignin. Chemically activated intermediates are produced; there may be enzymatic conversion of polyphenols to quinones, for example, which are especially subject to condensation reactions (Stevenson, 1982; Haynes, 1986). Reactive molecules polymerize (into complex, high-molecular-weight compounds) with other organics. These include proteinaceous material, carbohydrates, other alkanes, fatty acids, long-chain alcohols, waxes and sterols (table I.3).

Table I.3

Phenols, mono- and di-lignins	45%
Aliphatics	30%
Polysaccharides	10%
Proteinaceous compounds	5%
Other N-containing compounds	10%

Table I.3. Structural composition of an average humic acid. Analysis by ^{13}C-NMR (Schnitzer, 1991).

Other spectral analyses have provided information about humic substances as well. HPO-A and HPI-A fractions have been observed, via FT-IR, to have strong absorption peaks in the carboxyl absorption band, in agreement with the established view that these fractions derive much of their acidity from COOH groups. Another strong absorption band corresponded to associated OH groups, also in agreement with the view that these fractions contain phenolic structural and functional groups (Vance and David, 1991).

Much recent effort has been directed toward identifying model functional groups or model compounds that represent fractions of DOC or types of humic substances. Spectral studies have contributed to this trend. The ^{13}C-NMR technique can distinguish between carboxylic, aromatic, phenolic, amino-acid and other structures (Schnitzer, 1991). Cronan et al. (1992) observed an SSFS peak in Oa-leachate samples that appeared similar to salycilic acid, a single-carboxyl single-phenolic compound. The peak occurred at approximately 350 nm (UV), and its intensity was linearly related to sample carboxyl content. These workers identified three model compound wavelengths -- 350, 395 and 470 nm -- absorption at which behaved similarly to fulvic and humic acid standards and model aromatic compounds. The percent aromatic carbon in dissolved humic substances has been measured by comparing relative UV absorption at three wavelengths (Novak et al., 1992) or by dividing the ^{13}C-NMR spectrum in two, the two fractions representing aromatics (including phenols) and aliphatics. Aromaticity of humic acids have thus been calculated to range from 20 to 60% (Schnitzer, 1991).

Spectral analyses have been used to probe the results of DOC fractionation analysis. Much of the evidence for assigning various compound types to each fraction (table I.2 above) is in this form. There are obvious FT-IR spectral differences among fractions (Leenheer, 1981); HPO-N and HPO-A fractions show strong aliphatic-C absorption bands, and acid fractions show carboxyl content. HPO-A and HPI-A fractions also show strong carboxyl absorption in ^{13}C-NMR spectra (Vance and David, 1991a). These spectra indicate that the chief difference between HPO-A and HPI-A is that the former have slightly more absorption in the band of aromatics (among other compounds) -- 36 vs. 29% -- while the latter have slightly more absorption in the band of carboxylic groups (among other compounds), 23 vs. 18% (Vance and David, 1991).

Emphasis in DOC analysis lately has been placed on carboxylic content, aromatic content, phenolic content, and relative content of these groups in dissolved organics and in DOC-FA fractions. Carboxylics are often quantified as a fraction of total C. In the Adirondacks, NY and in Bear Brook Watershed, ME the soil solution DOC was found to have a carboxylic content of approximately 4 to 7 meq COOH per gram carbon (Cronan and Aiken, 1985; Cronan et al., 1992). Cronan and Aiken (1985) used the average or model compound concept to characterize the general acid-base characteristics of dissolved humic material in watersheds of the Adirondack park. They described a model compound with a pK_a of 3.85.

Solubility of soil organics

The relation of DOC to acid-base chemistry of soils and streams has received much study. DOC affects and is affected by solution acidity and pH. Much of what is known concerning DOC biogeochemistry has come from studies concerned with the impacts of acid deposition, in which soils or solutions have been treated with acids or bases. Leenheer fractionation describes DOC components based partly on acid-base characteristics (Leenheer, 1981).

Solubilities of O horizon organics decrease as H^+ concentration increases. Hydrophobic acids decrease and hydrophilic acids increase in relative solubility with greater acid inputs (Vance and David, 1989). Since the B horizon selectively adsorbs HPO-A to a greater extent than HPI-A, B-horizon soil solution contains a greater relative amount of HPI-A (Vance and David, 1989, 1991). As pH decreases in forest floor leachates over the pH range of 5.1 to 3.9, organic anions calculated by charge balance decrease as well, supporting the idea that DOC contains weak acids with dissociation constants over a broad pH range (Vance and David, 1991).

The lowering of pH in simulated throughfall from 5.7 to 3.5 did not appear to make a substantial difference in the DOC concentration leached from Spodosol cores. Lowering the pH further to 2.0, however, decreased concentrations of soluble organic C dramatically (to 20 mg L^{-1} from values in the range of 60 to 120 mg L^{-1}) (Hay et al., 1985). Similarly, the concentration and amount of sulfuric acid used in a column leaching study of forest-floor material had no effect on DOC solubilized when elevated

3.5x over controls, but decreased DOC solubility significantly when elevated much higher over controls (Vance and David, 1991).

Whether strong acid is nitric or sulfuric appears to make a difference to solubility of soil-solution organics only at pH values lower than 3.0 (David et al., 1989) and low ionic strength (Evans et al., 1988), in which case nitric acid solubilizes less DOC. At higher ionic strength (0.004 to 0.01 M), the ionic strength decreases the solubility of organics (Evans et al., 1988; Vance and David, 1989).

Biogeochemistry of DOC in Forest Ecosystems

Precipitation DOC may be in the range of 1 to 2 mg C L^{-1} (McDowell and Likens, 1988; Schiff et al., 1990; Koprivnjak and Moore, 1992; Moore et al., 1992). Organics leach from canopy surfaces; DOC in throughfall, studied in several locations and under several canopy species, has been observed in the range from < 1 to 15 mg C L^{-1}, with most reports in the 5-10 mg C L^{-1} range. Dissolved organics in soil solution derive primarily from plant detritus in various stages of decomposition (Qualls et al., 1991). Field studies have focused largely on DOC concentrations; few studies have been conducted to estimate annual fluxes of DOC through systems because of the need for year-round sampling and the need for estimation of hydrologic fluxes. DOC concentrations are often highest in forest floor solution, decreasing in mineral soil solution because organics sorb to mineral surfaces (Seto and Yui, 1983; Cronan and Aiken, 1985; McDowell and Likens, 1988). DOC can increase in concentration,

however, in mineral soil horizons containing organic matter (Guggenberger and Zech, 1992; Moore et al., 1992).

In the northeastern U.S., seasonally-averaged Oa-leachate DOC concentrations in coniferous stands have ranged from ca. 25 to 70 mg C L^{-1} (Cronan and Aiken, 1985; Dalva and Moore, 1991). Under hardwood forests in the East, seasonally averaged DOC concentrations in Oa-leachate have ranged from 14 to 38 mg C L^{-1} while fluxes have measured ca. 20 to 40 g C m^{-2} yr^{-1} (Cronan and Aiken, 1985; McDowell and Likens, 1988; Qualls et al., 1991). In other regions, total DOC in forest-floor leachate has been reported to range from 4 mg C L^{-1} in a control watershed at H.J. Andrews to 110 mg C L^{-1} during snowmelt near Laramie, WY in a *Pinus contorta* forest (Sollins and McCorison, 1981; Antweiler and Drever, 1983).

The contribution that root exudates may make to soil solution DOC has not been well quantified for mature forest vegetation. In cropland species, grasses or seedlings, root exudates can amount to 8 to 20% or more of photosynthetically-fixed carbon. Root exudates also deposit nitrogen into the soil (Biondini et al., 1988; Uren and Reisenauer, 1988). Root exudates influence nutrient solubility indirectly through affecting microbial activity, root growth, and rhizosphere physical properties. Exudates affect nutrient solubility directly through acidification, chelation, precipitation and oxidation-reduction reactions. Chemical analysis of exudates has revealed carbohydrates, amino acids, vitamins, organic acids, nucleotides, enzymes, and unidentified compounds (Feldman,

1988). Other sources of soil carbon from roots include root litter, root caps, cortical tissue sheets, tissue fragments and individual cells sloughed from roots (Tate, 1987).

The age of the carbon in dissolved organics (the time since its fixation in photosynthesis) has been studied in a forested catchment in Ontario, Canada (Schiff et al., 1990; Trumbore et al., 1992). In laboratory studies in which DIW-soluble DOC was compared with residual (that fraction that was not solubilized) SOM carbon, there was little difference in average age between the two in the organic horizon (both classes were significantly less than 30 years old on average). At 10-25 cm depth, however, residual carbon had a much greater age than the DIW-soluble fraction.

Summary of DOC Characteristics and Controls

The focus in characterizing dissolved organics in literature has been to invoke model classes of compounds, each with properties representing a part of the spectrum of disparate organics in solution. Focus has been placed primarily across three dimensions: structural makeup, acid-base characteristics, and hydrophobic-hydrophilic behavior. Interestingly, these three dimensions are related through one parameter, the ratio of carboxylic to phenolic structural/functional groups. A greater relative fraction of carboxyl groups makes dissolved organics more acidic and at the same time more hydrophilic at all but very low pH. The significance of the ratio is that it embodies a solubility difference and acidity difference distinguishing the two predominant fractions of DOC, hydrophilic and hydrophobic acids.

There appear to be few simple trends in DOC concentrations or fluxes found among field studies to date. The use of different filter types and different collection techniques makes comparisons problematic. Comparisons can best be made when results within one study are considered. Cronan et al. (1992) have provided an excellent summary of factors relevant to DOC variation under different conditions. The authors summarized that DOC concentrations can vary ten-fold in forest floor leachates among different ecosystems, three-fold among sampling dates and two-fold among disturbance treatments within a given system. They concluded that Oa-leachate DOC is controlled by unknown, complex interactions among several environmental variables.

Nitrogen Retention and Dissolved Organic Nitrogen

Organic N compounds account for 90% of the N in soils (Haynes, 1986). Though at least 50% of soil-organic-matter N exists in forms not yet identified, much occurs as amino acid N (33% to 42% of total soil N) (Schnitzer, 1991). In plant leaves and stems, approximately 60% of the N is enzyme or membrane protein; the remainder is water-soluble free amino acid N (Parsons and Tinsley, 1975). Much N in microbial cells is in the form of protein; most of the remainder is present in cell walls as highly polymerized heteropolymers comprising amino acids and amino sugars. Amino sugars, found in significant quantities in soils (2-8% of total humic acid N), provide evidence that much soil N is of microbial origin; amino sugars (such as chitin) are major structural components of the cell walls of bacteria and fungi, but are present only in trace amounts in plant tissue (Haynes, 1986).

Results of a study of DOC and DON conducted at Coweeta (Qualls et al., 1991) provide clues about DON production. In throughfall the distribution of N between inorganic and organic forms was approximately equal. In Oa leachate, DON accounted for 90% of the N flux. DON fluxes in HPO-A and HPI-A fractions in Oa leachate were much too high to be accounted for by DON in these fractions in throughfall and leaf-litter leachate. Also, the DOC:DON mass ratio of the HPO-A fraction narrowed from over 100 in leaf litter to the range of 43 to 73 in O-horizon leachate. Clearly, in the organic horizon, N was somehow incorporated into soluble humic substances. DON production in the forest floor at Coweeta largely occurred through incorporation of N into existing (from leaf-litter leachate) fractions of dissolved organics (Qualls et al., 1991).

In current views of forest soil N-cycle responses to N inputs (Tietema, 1992), nitrogen in dissolved organics (DON) does not appear explicitly in conceptual models. The traditional view of decomposition (leading to humification) has stressed N turnover by microbial biomass in soils. Tracer (^{15}N) studies have shown that gross N immobilization rates are 10-20 times greater than net cycling rates (Davidson et al., 1990; Aber, 1992). Observations of CO_2 efflux after nitrogen additions to forested plots at the Harvard Forest, however, suggest that although high levels of nitrogen are being retained in nonexchangeable form in the soil, the mechanism may not be through microbial uptake (P. Micks et al., *unpublished data*). Nitrogen additions did not enhance net CO_2 efflux from soils (contributions to CO_2 efflux from microbial activity and root respiration were not distinguished).

Understanding processes of DON formation and illuviation may be important for understanding N retention in forest soils. It has been suggested that the "nonbiological incorporation of N into humus" is potentially an important mechanism of system N retention (Axelsson and Berg, 1988; Johnson, 1992). The oxidative coupling of phenolics to one another and to N-containing compounds appears to be catalyzed by indigenous soil enzymes (Berry and Boyd, 1984). The fixation of inorganic N, amino acids or amino sugars into humic substances by enzymes or by condensation with reactive intermediates produced in the decomposition process (Stevenson, 1986) could potentially be an enhanced N sink without increasing CO_2 efflux. Nitrogen could potentially enter into a non-extractable pool through incorporation into hydrophobic acids and subsequent illuviation from the O horizon and sorption in mineral soil.

Field Study Objectives

The objectives for my field research in the Chronic N Addition plots at the Harvard Forest were as follows:

(1) To quantify dissolved organic carbon and nitrogen (DOC and DON) concentrations in throughfall and Oa leachate in reference plots over a period spanning two 'litterfall years', 1 October 1992 to 30 September 1994 (Chapter I);

(2) To quantify changes in DOC and DON concentrations in Oa leachate under chronic N amendments and to characterize differences in responses between the red pine and mixed hardwood stands (Chapter I);

(3) To characterize selected aspects of inorganic chemistry including pH and concentrations of NH_4, NO_3, Ca, Mg, K, Na, Cl, SO_4 in throughfall and Oa leachate in reference plots over the two year period (Chapter II);

(4) To quantify changes in these selected aspects of inorganic chemistry under chronic N amendments and to characterize differences in chemical responses between the two stands (Chapter II).

My objectives for the modeling research are listed in Chapter III.

CHAPTER I

DISSOLVED ORGANICS IN FOREST-FLOOR LEACHATE AT HARVARD FOREST

Introduction

The illuviation of dissolved organic matter (DOM) from the forest floor into mineral soil and its sorption in organo-mineral complexes could account for much of the plant nutrients and humic material in mineral soil (Fahey et al., 1985; Schoenau and Bettany, 1987; Qualls et al., 1991). Humic substances can form complexes with, illuviate and precipitate weathering products, heavy metals and organic pollutants in mineral soil (Schnitzer, 1991). The movement of dissolved organic carbon and nitrogen (DOC and DON) from organic to mineral soil has amounted to approximately 5% to 24% of leaf litter C flux and 15% to 37% of leaf litter N flux in the few temperate forests studied (Cole and Rapp, 1981; McDowell and Likens, 1988; Qualls et al., 1991; Vance and David, 1991a). Qualls (1991) has pointed out that these percentages are close to the proportions of litter that eventually become humus.

The Chronic N Study at the Harvard Forest provided an opportunity to study leaching of DOC and DON from the forest floor in two stands subject to long-term N amendment. The reasons for studying dissolved organics range from the desire to understand of the roles of leaching in decomposition processes (Schlesinger and Hasey,

1981; Yavitt and Fahey, 1986; Harmon et al., 1990) to the desire to better understand mechanisms of ecosystem N retention and C and N interactions.

Various hypotheses were advanced at the outset of my field research. It was suggested that increased N availabilities would show decreases in DOC concentrations due to increased use of DOC as a microbial substrate, indicating increased rates of microbial N cycling in the forest floor. Alternatively, it was hypothesized that DON concentrations in Oa-leachate would increase with N treatment, providing a mechanism of increased transport of N to mineral soil in nonexchangeable form. DON has been observed to compose from 70% to over 95% of the N leaching from forest organic horizons (Sollins and McCorison, 1981; Fahey et al., 1985; Qualls et al., 1991). Qualls et al. (1991) concluded that leaching of DON from the forest floor at Coweeta, NC was a significant source of N to the A horizon, while transport of inorganic N was not because inorganic N was removed by immobilization or other forest-floor processes.

Materials and Methods

The Harvard Forest Study Site

Site description. Located in the Central Highlands of Massachusetts, the Harvard Forest ranges in elevation from 220 to 410 m, with a mean temperature in January of -7° C and in July of 19° C. Average precipitation is approximately 110 cm yr^{-1}, distributed fairly evenly throughout the year (Van Cleve and Martin, 1991). A snowpack may begin to form in the forest in December and last until early April, or it may melt completely and re-form in midwinter (*personal observation*). Soils in the stands considered here are

Entic Haplorthods; they are rocky, well-drained fine sandy to sandy loams formed from glacial till.

Nitrogen additions. Nitrogen amendments have been made since 1988 to two forest stands: an even-aged red pine (*Pinus resinosa*) stand planted in 1926 and a mixed hardwood stand approximately 50 years old, naturally regenerating from clear-cutting (Aber et al., 1993; Magill et al., *in preparation*). Nitrogen has been added in six equal applications per year, approximately once per month from early May through late September. The treatment plots considered here are each 30 m *x* 30 m, comprising one reference (no N addition), low-N-addition (50 kg N ha^{-1} yr^{-1}) and high-N-addition (150 kg N ha^{-1} yr^{-1}) plot in each stand. Backpack sprayers are used to apply the fertilizer onto the forest floor as 4.0 mol L^{-1} NH_4NO_3 for the high-N-addition plots and 1.3 mol L^{-1} NH_4NO_3 on the low-N-addition plots.

Experiment design and installation

Zero-tension lysimeters. For collection of water leaching from the Oa horizon, 30 zero-tension lysimeters (ZTL's) were installed, five in each treatment per stand. Placement within each subplot was random apart from the stipulations that each ZTL be at least 1 m from a tree stem and that the forest floor above the ZTL be free of large rocks. A new type of ZTL and sample-bottle assembly was designed that allowed access to the collection bottle for retrieval (figure 1.1). The ZTL body was cut from a rectangular polyethylene container in such a way that one corner pointed downward, acting as a drain. Each ZTL drained a surface area of 154 cm^2. Each ZTL was packed

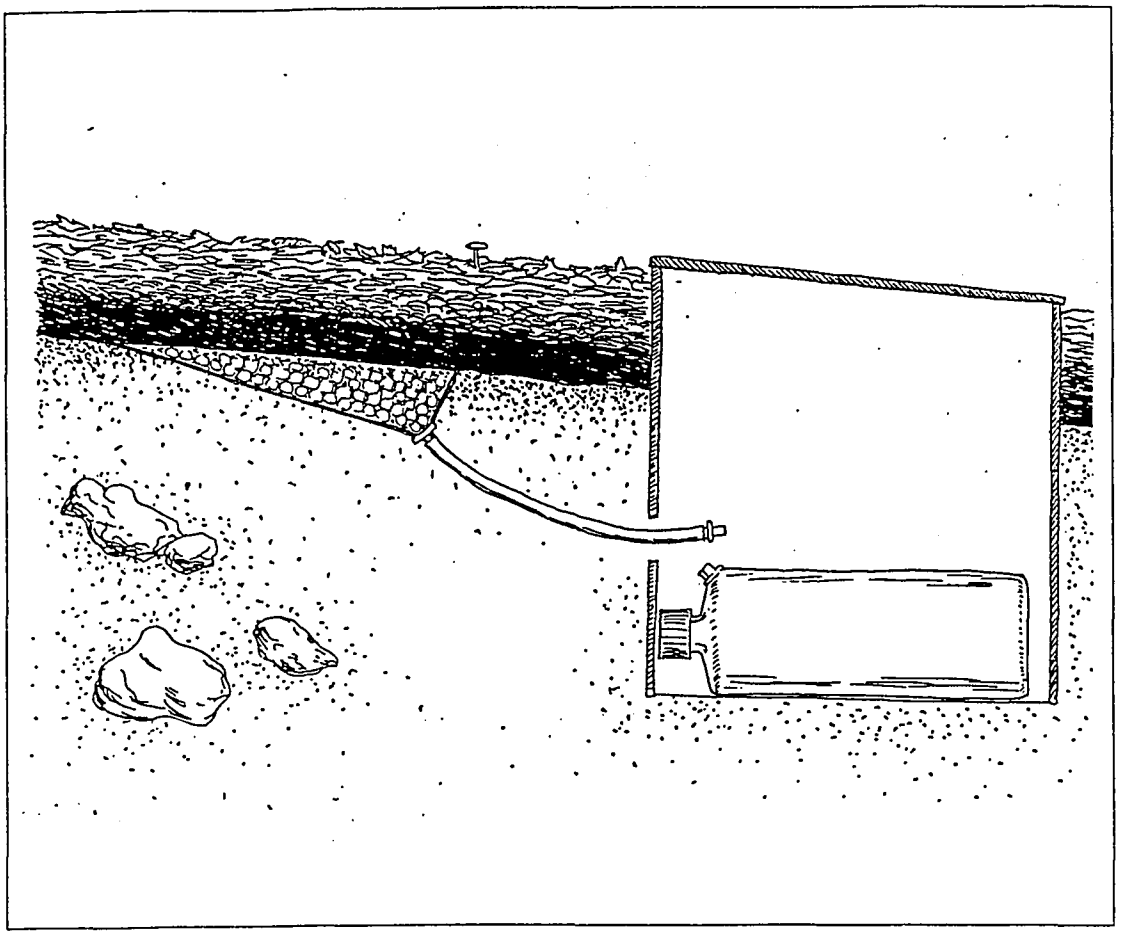

Figure 1.1. Zero-tension lysimeter (ZTL) installation. The wedge-shaped ZTL body is shown on the left, filled with glass beads and silica gravel. A tube leads downslope from the drain to the bottle well shown on the right. The tube can be quickly disconnected from the collection bottle as shown for retrieval of the entire bottle to the laboratory.

with a mixture of sizes of glass beads (0.6 to 1.5 cm diam.) and acid-washed, DIW-rinsed silica gravel (0.3 to 1.0 cm). Flexible vinyl tubing was fitted onto a hose barb at the drain and run downward at a 45° angle to the collection bottle. Each ZTL collection bottle lay on its side in an accessible well, connected to the vinyl tubing from the lysimeter. ZTL collection bottles were 1 L polyethylene bottles each with a hole drilled at the rim and a

high-density polyethylene connect-disconnect fitting glued at a 45° angle. For sampling, a worker opened the well cover, reached in and disconnected the tubing at the point of the collection bottle, retrieved the entire bottle, replaced it with a clean collection bottle and reconnected the tubing.

During installation, disturbance to the Oa horizon above the ZTL was minimized as follows. First, a hole for the bottle well was made downslope of the ZTL site. A horizontal tunnel 40 cm in length in the upper mineral soil was then carefully excavated upslope from the well. Mineral soil was gently scraped from the roof of the tunnel to expose the bottom of the Oa horizon, which transitioned abruptly to the upper mineral horizon in these soils (< 1 cm). The ZTL was then installed at the farthest reach of the tunnel. Soil and small rocks were used to pack the ZTL firmly in place from below, and the excavation tunnel refilled with mineral soil. A plywood well housing with a hinged cover was then fitted tightly into the well hole in order to preserve surrounding soil structure.

Throughfall and precipitation collectors. A throughfall (TF) collector was placed within 1 m of each ZTL collector (30 total). Each TF collector consisted of a bottle, a funnel, and liners. Dark, opaque 1 L polyethylene bottles were used, staked firmly in place on the ground. Polyethylene funnels (14 cm. diam.) were fitted with 2 mm nylon mesh to exclude debris. Funnels rested in bottle mouths and liners were placed inside bottles. Precipitation was collected in an acid-washed, DIW-rinsed polyethylene bucket set in a wooden stand in a clearing at Harvard Forest, approximately 1 km from the

Chronic N Plots. No vegetation or buildings were present within a cone 20° from horizontal surrounding the precipitation collector (Galloway and Likens 1978).

Sample collection and preservation

ZTL installation was complete in mid-August 1992. Sampling of TF and ZTL collectors covered two "litterfall years," beginning in October 1992 and continuing until October 1994, with breaks in sampling from December to mid-April due to snow cover. For sampling of Oa-leachate, ZTL collection bottles were retrieved and replaced in the field with acid-washed bottles after each collection. Two sets of ZTL collection bottles made it possible to sample continuously. The unpredictability of forest-floor hydrology coupled with my scheme of using clean bottles for each sample set made it impractical to sample exclusively on an event basis. I installed clean collection bottles for predicted rain events and collected on an event basis where possible, with an event collection defined as retrieval of samples within 36 hours of the onset of rain. Otherwise I left the collection bottles in the field attached to the lysimeter tubing for longer periods until enough sample was present for analysis. Excluding event collections, the average time that samples remained in the field prior to collection was 9.3 d. I refer to these as 'biweekly' samples for simplicity even though the sampling periods were irregular. Retrieval of one set of ZTL snowmelt samples was accomplished in 1994 by digging through the 40 cm snowpack to install clean collection bottles in late March. Collection was made 21 d later after the snowpack had completely melted.

Throughfall funnels were returned to the laboratory for cleaning at the start of the collection season each spring and approximately every 6 weeks thereafter. TF funnels and bottles were either removed from the field or covered with plastic bags when plots were fertilized. For each TF collection, a new, DIW-rinsed and air-dried polyethylene liner was placed inside each bottle. As with ZTL sample sets, TF sample sets were collected on an event basis in some cases and over longer periods in other cases. Event samples were collected within 36 hours of the onset of rainfall. Otherwise, sample was allowed to accumulate for up to 8 days. The average time that non-event TF samples remained in the field before collection was 5.5 d; I refer to these as 'weekly' samples for simplicity. Precipitation samples were collected within 24 hours of the start of rain events.

Over the two-year period, 33 ZTL sample sets were collected (11 of them 'event' sets), 29 TF sample sets (16 of them 'event' sets) and 10 precipitation event samples. In all but four sets, ZTL or TF samples were bulked by stand and treatment leaving 6 bulked ZTL samples (pine reference, low-N, high-N, and hardwood reference, low-N, high-N) or 6 bulked TF samples. On three occasions, all 30 ZTL samples were kept unbulked for analysis. Since this type of collection produced 5 Oa-leachate samples per treatment in each stand, it gave me the ability to quantify within-treatment variability among lysimeters. On one occasion, all 30 TF samples were kept unbulked for analysis.

All samples were placed on ice within 1 hour of collection and transported on ice to the Aber laboratory at the University of New Hampshire, where they were filtered

immediately or refrigerated at 4°C overnight. Within 36 hours of collection, all samples were vacuum-filtered through ashed (1 hour at 425°C) Whatman GF/F glass-fiber filters (nominal pore size 0.7 um) and frozen in high-density polyethylene storage bottles. Samples remained frozen for 1 to 18 months prior to analysis.

Laboratory analysis

I measured pH potentiometrically on each sample as it entered the laboratory. Other analyses were performed on frozen samples after thawing. Flocculation of organics during freezing of post-filtered samples was not visible and was not considered significant; G. Qualls had quantified flocculation as $\leq 2\%$ of DOC in similar samples (*personal communication*). For measurement of DOC I quantified total organic carbon, in filtered samples, through catalytic oxidation at 680°C with a Shimadzu TOC 5000 unit.

Nitrate-N was measured by the automated hydrazine reduction method and ammonium-N by the automated Berthelot reaction method (Bran Lubbe 1978; Markus et al. 1985). Zinc sulfate was added to the working reductor in the hydrazine reduction method (10 mL of 3% $ZnSO_4$ in 500 mL working reductor) to alleviate humic-acid interference.

Total dissolved nitrogen (TDN) was measured by alkaline persulfate digestion converting all nitrogen to nitrate (Solorzano and Sharp 1980), with subsequent measurement of nitrate by automated hydrazine reduction. This method for TDN measurement is described in detail in Merriam et al. (*in preparation*). Nitrite-N was negligible, as revealed by High Pressure Liquid Chromotography analysis of these

samples as part of a parallel research project, and in agreement with the findings of Qualls et al. (1991). Dissolved organic N (DON) was then calculated as shown in equation (1).

$$DON = TDN - NO_3\text{-}N - NH_4\text{-}N \quad (1)$$

Unfortunately, in the third unbulked ZTL collection set (September 28, 1994), inorganic N concentrations in treatment plots were highly elevated (up to 106 mg N L^{-1}) due to plot fertilization. This made the calculation of DON by difference from TDN impossible to carry out with accuracy for that sample set.

Statistical analysis

For each unbulked set of ZTL or TF samples, two steps were taken. First, statistical analyses were performed within the unbulked set. The second step was designed to combine the data from the unbulked collection dates with those of the bulked sets. To avoid giving excess weight to the unbulked sets, means in each variable were calculated within each stand and treatment. The resulting means were then entered into the two-year database as representing individual 'bulked' samples.

All data were tested for normality of distribution using the Shapiro-Wilk test (Stata Corporation, 1993). For Oa-leachate chemistry, DOC:DON ratio was found to be normally distributed, while DOC and DON concentration data were non-normal. A simple log transform of [DOC] data to remove skewness transformed the data to a normal distribution, so statistical analyses were performed on ln([DOC]). DON was separated

into pine and hardwood stand subsets and separate log transforms found for each subset that converted the data to normal distributions. Statistical tests were performed on transformed data. All data were separated by stand type for further statistical analyses. Within each stand, analysis of variance by season (as defined below) showed significant effects of season on the DOC:DON ratio and on the log-transformed DOC and DON data. T-tests for significant differences among means grouped by N-treatment (reference, low-N and high-N addition) were then performed within each stand/season combination for DOC:DON and log-transformed DOC and DON data. Differences at the $p \leq 0.05$ level are reported as significant.

Volume Weighting and Flux Calculations

Samples were grouped by season, based on collection date, for reporting volume-weighted chemistry by season. Those collected in April, May and June were classified as spring samples; July, August and September as summer; and October and November classified as fall. For throughfall, samples were grouped within each season irrespective of year because differences were not apparent between the first and second years of the study. For Oa-leachate, however, samples were grouped by season in separate years because differences between years were apparent.

Chemical Fluxes. My quantification of throughfall collected in 14 event sets, together with simultaneous precipitation measurements made by myself and by Harvard Forest staff allowed me to derive regressions of throughfall quantity versus precipitation quantity. These regressions were then applied to monthly total precipitation levels for

October 1992 through September 1994, excluding December through March (Harvard Forest weather station data). Monthly chemical fluxes were estimated by multiplying monthly throughfall hydrologic fluxes within each stand by mean throughfall chemistry that had been volume-weighted within each stand and season.

For calculation of Oa-leachate chemical fluxes for individual event collections, concentration data for each sample were simply multiplied by the amount of Oa leachate collected.

Results

Precipitation

Precipitation at Harvard Forest amounted to 120 cm (water equivalent) in the first litterfall year of the study (1 October 1992 to 30 September 1993) and 144 cm in the second litterfall year (1 October 1993 to 30 September 1994; Harvard Forest weather station data). One aspect of the monthly distribution of the precipitation in this period deserves mention: as shown in figure 1.2, rainfall at the start of the growing season in May of 1993 was very low relative to the long-term average.

Ten rainfall samples spanning the first litterfall year (excluding December through March) were collected for chemical analysis. Collections ranged from 0.2 to 3 cm rainfall with pH ranging from 3.4 to 4.6. DON in rainfall was below detection (detection estimated as 0.15 mg L^{-1}). Volume-weighted DOC in rainfall measured 1.0 mg C L^{-1}. Multiplied by the levels of precipitation this would amount to a wet-deposition flux into

the ecosystem of 1.2 g DOC m^{-2} yr^{-1} the first litterfall year and 1.4 g DOC m^{-2} yr^{-1} the second.

Throughfall Chemistry

Time series for throughfall (TF) DOC and DON are shown in figures 1.3 through 1.6. No effects related to N amendment were noted in summary statistics of throughfall chemistry, however the June DON peak as a single event may be an exception. Seasonal trends were apparent in both stands. Concentrations of dissolved organics in throughfall (TF) peaked in June in both years in both the pine and hardwood stands, followed by decreases through the growing season (table 1.1).

Table 1.1.

	DOC [mg L^{-1}]	DON [mg L^{-1}]	DOC:DON
Red pine			
Spring	23.4 ± 18(24)	0.606 ± 0.58(24)	36.8 ± 7.4(24)
Summer	17.6 ± 9.4(39)	0.435 ± 0.30(39)	41.1 ± 9.7(37)
Fall	12.3 ± 5.1(21)	0.294 ± 0.20(21)	45.0 ± 15(19)
Hardwood			
Spring	24.0 ± 40(24)	.508 ± .68(23)	38.4 ± 20(19)
Summer	13.1 ± 12(39)	0.371 ± 0.29(39)	39.5 ± 23(36)
Fall	10.7 ± 6.9(21)	0.199 ± 0.15(21)	56.7 ± 30(13)

Table 1.1. Throughfall chemistry. Data are shown volume-weighted within each season, irrespective of year collected. Mean and standard deviation are shown, with number of samples in parentheses. Each sample was bulked from 5 TF collectors. Samples from references and N treatments were grouped together for this analysis.

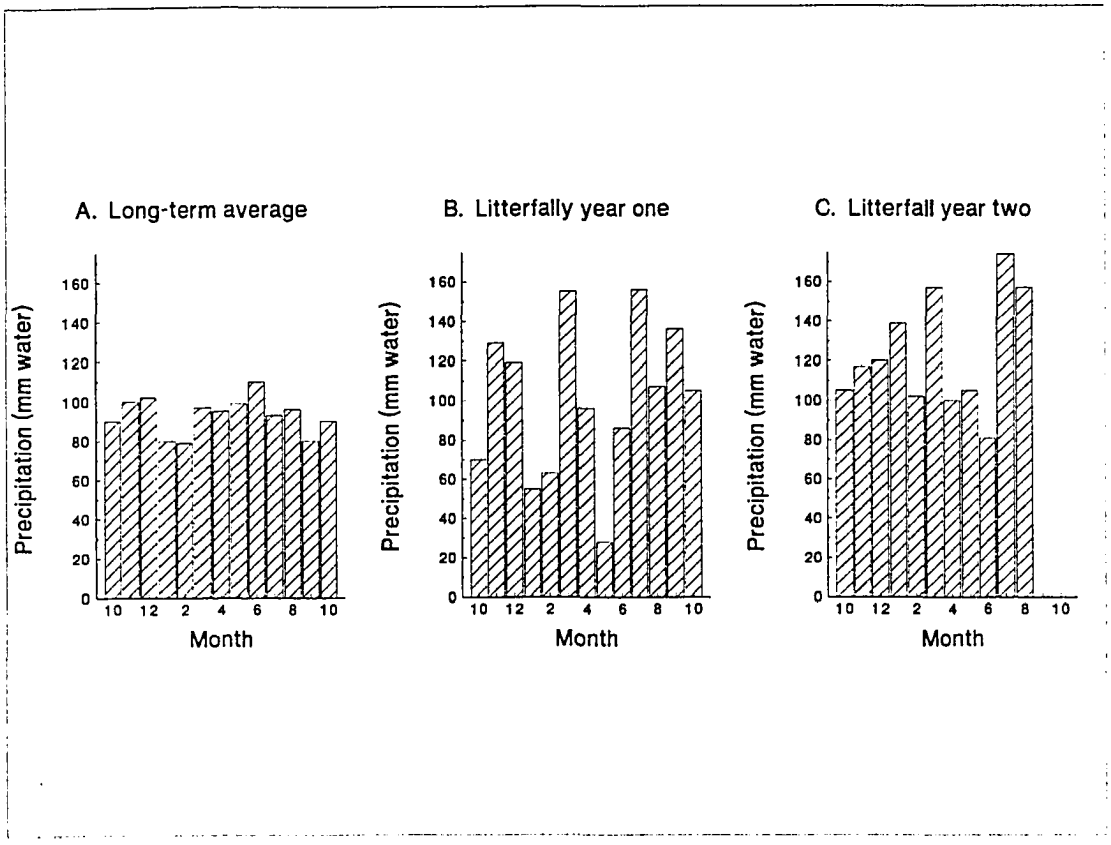

Figure 1.2. Precipitation amount by month at the Harvard Forest. Values are given in water equivalent [mm]. (A). Averages 1970-1989. (B). Litterfall year 1. (C). Litterfall year 2. (September and October 1994 are not shown; gaps exist in the observations. Harvard Forest weather station data.)

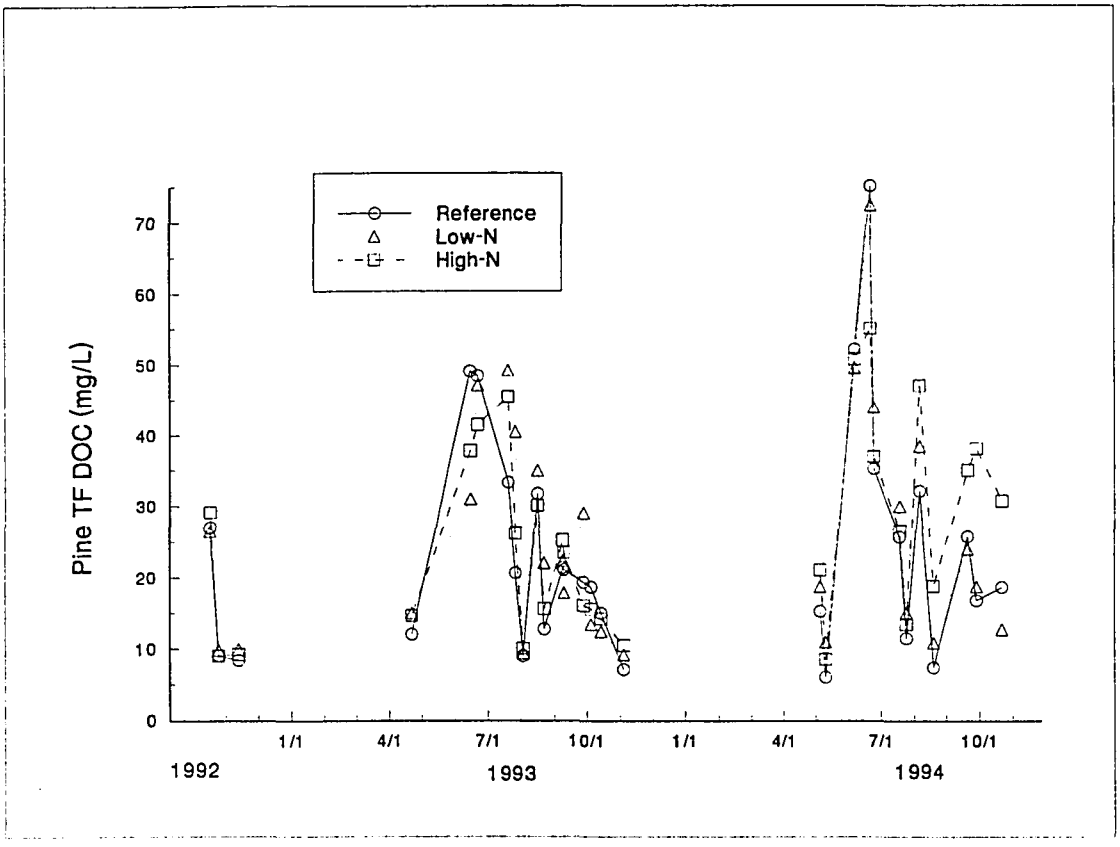

Figure 1.3. Seasonal patterns in pine stand throughfall DOC concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

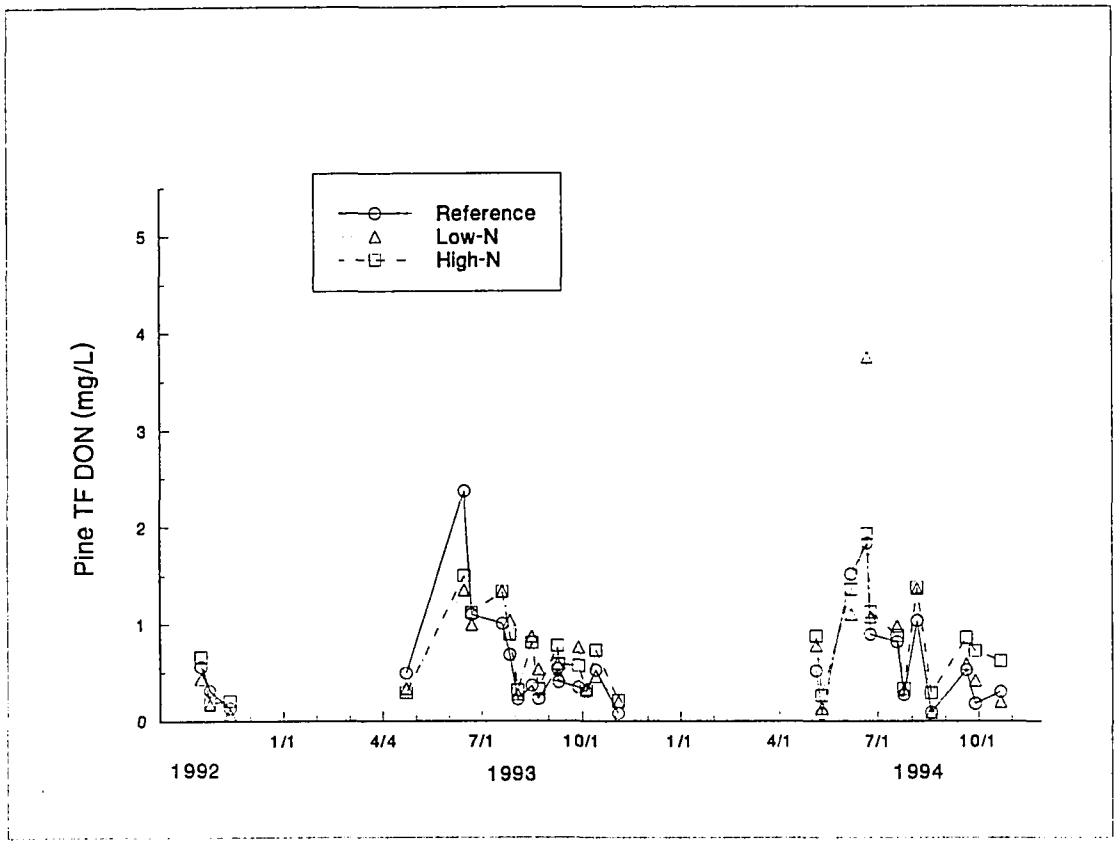

Figure 1.4. Seasonal patterns in pine stand throughfall DON concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

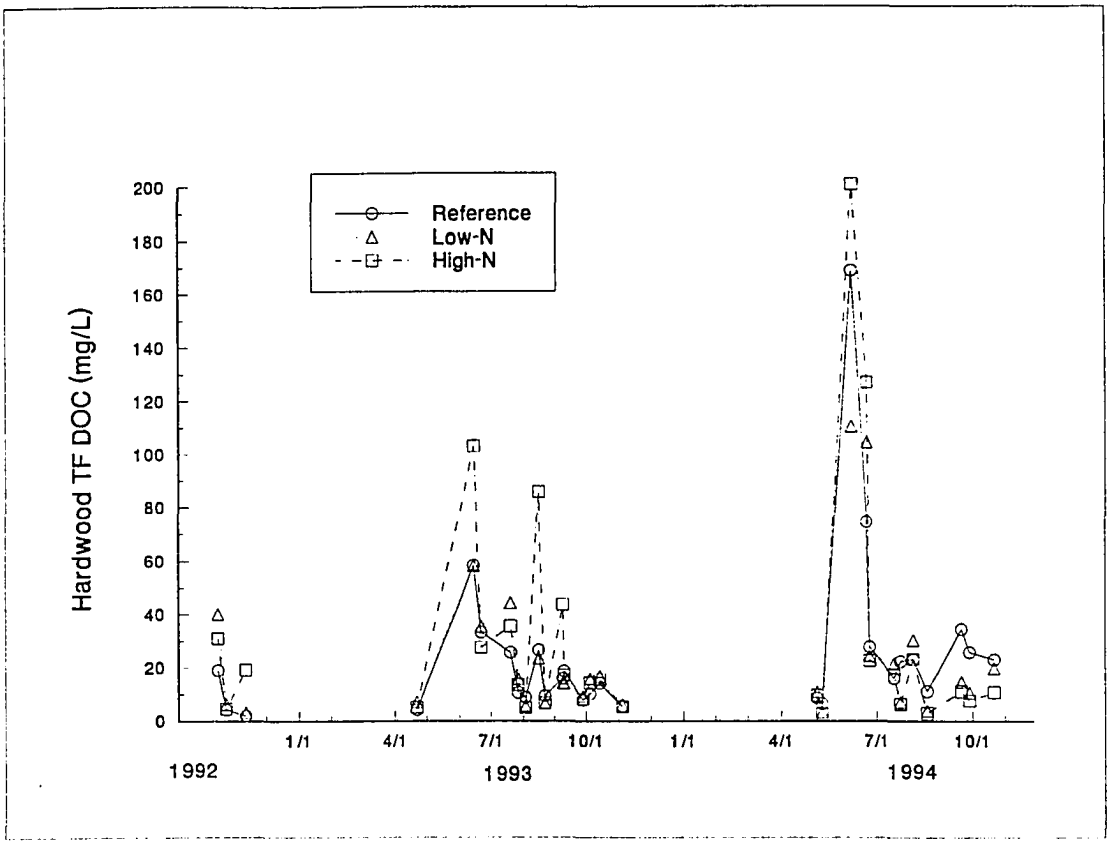

Figure 1.5. Seasonal patterns in hardwood stand throughfall DOC concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

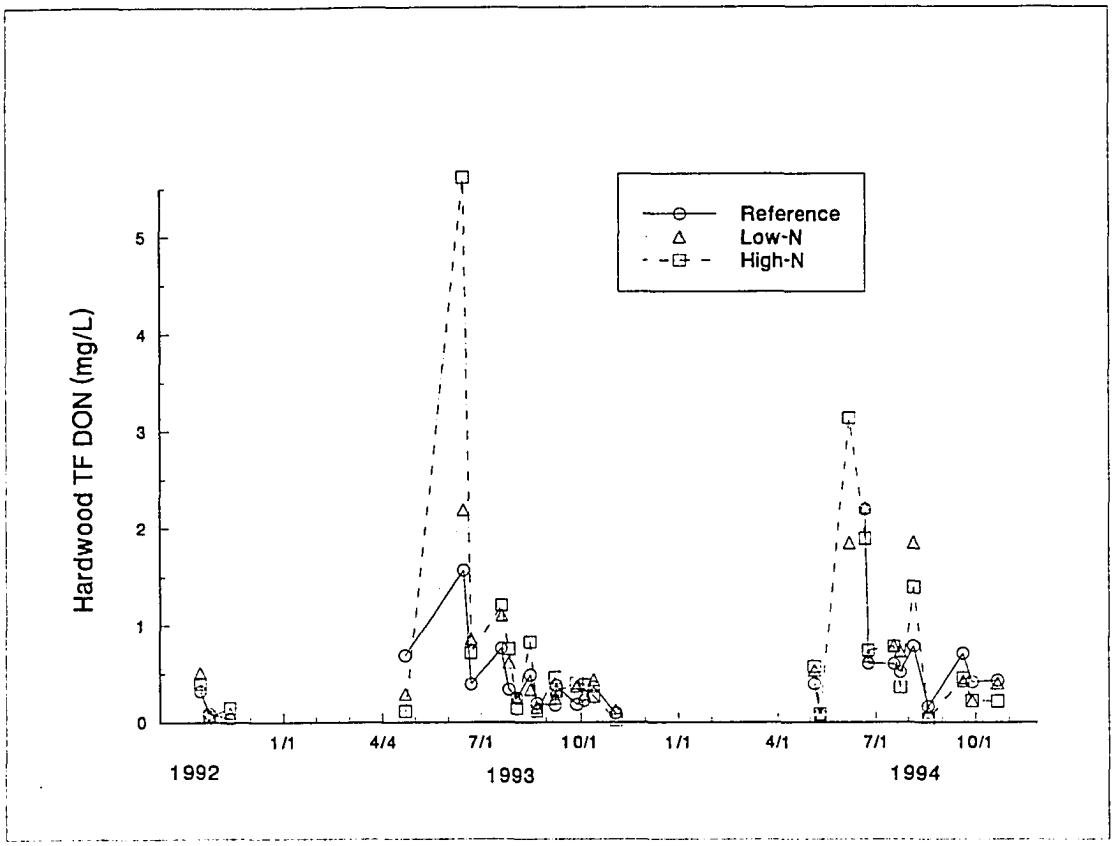

Figure 1.6. Seasonal patterns in hardwood stand throughfall DON concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

Throughfall Chemical Fluxes

Regressions of throughfall quantity versus precipitation quantity are shown in equation (2) for the red pine stand and equation (3) for the hardwood stand. Each regression is based on 14 events in which data from 15 throughfall collectors were combined per stand. TF refers to throughfall and PPT to rainfall, where both are in equivalent units such as [mm].

$$TF = (0.801 \cdot PPT) - 0.120 \qquad r^2 = 0.91 \qquad (2)$$

$$TF = (0.759 \cdot PPT) - 0.059 \qquad r^2 = 0.93 \qquad (3)$$

Table 1.2

	DOC [g m^{-2} $month^{-1}$]	DON [g m^{-2} $month^{-1}$]
Red pine stand		
Spring	1.52	0.039
Summer	1.88	0.046
Fall	1.02	0.024
Hardwood stand		
Spring	1.49	0.032
Summer	1.33	0.038
Fall	0.85	0.016

Table 1.2. Throughfall DOC and DON fluxes. Data are summarized by season and normalized to a monthly basis. Results are averages over two years, based on throughfall hydrology calculated through regressions against precipitation.

Throughfall DOC and DON fluxes (table 1.2) extrapolated to an annual basis, excluding winter, would amount to the following totals: 13.3 g DOC m^{-2} yr^{-1} in the pine stand and 11.0 g DOC m^{-2} yr^{-1} in the hardwoods; 0.327 g DON m^{-2} yr^{-1} in the pine stand and 0.255 g DON m^{-2} yr^{-1} in the hardwood stand.

Oa leachate chemistry

Reference plots and general patterns. Time series of DOC concentrations in each stand through the two-year study are shown in figures 1.7 (red pine stand) and 1.9 (hardwood stand). DOC concentrations in reference plots exhibited a general seasonal pattern of rising as midsummer approached, peaking some time from July through the end of September, and decreasing into fall. Similar seasonal trends in Oa-leachate DOC concentrations have been reported by Cronan and Aiken (1985) and McDowell and Likens (1988) in similar forests with soils and climate similar to Harvard Forest, and by Grieve (1990) in a Scottish peatland. In spring DOC concentrations were much lower in 1994 than in 1993. This pattern was inversely related to the levels of spring rainfall in the two years. Time series of DON concentrations (figures 1.8 and 1.10) followed similar seasonal patterns to DOC concentrations. DON concentrations were also slightly elevated in spring 1993 relative to 1994. Peaks of DON concentration occurred in mid-July to late August.

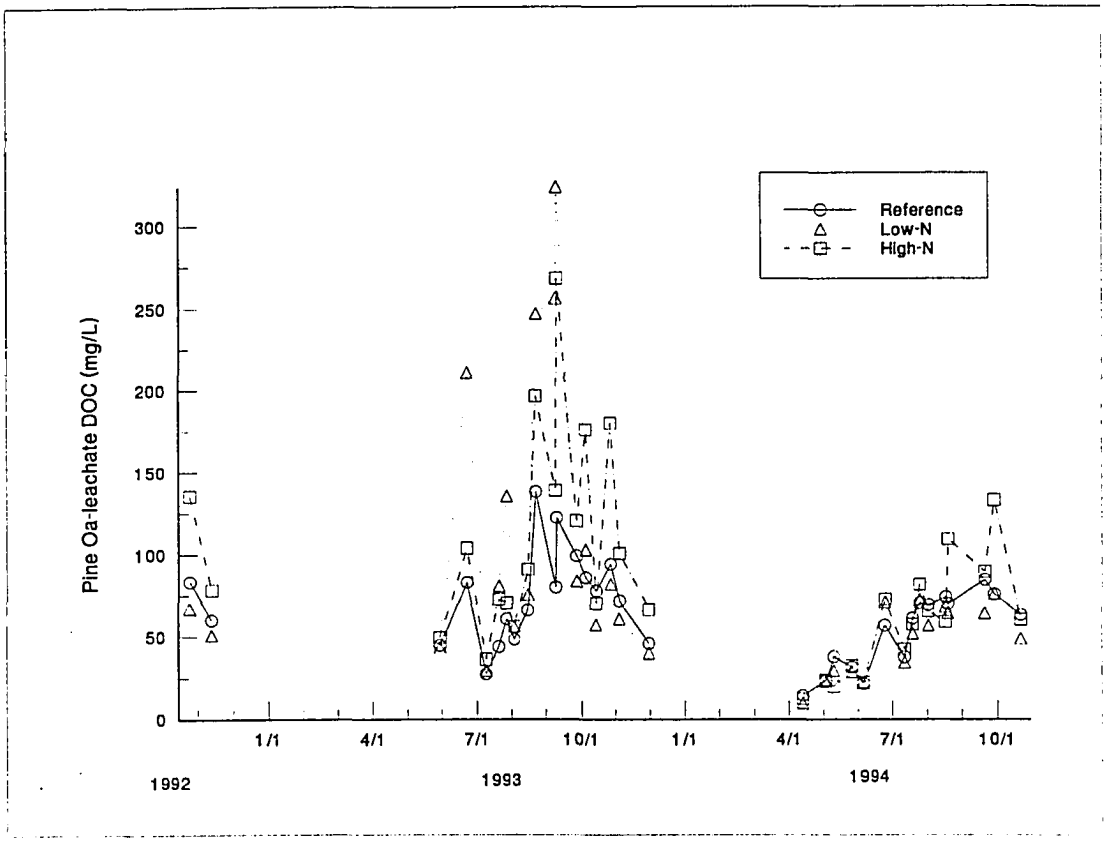

Figure 1.7. Seasonal patterns in pine stand Oa-leachate DOC concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

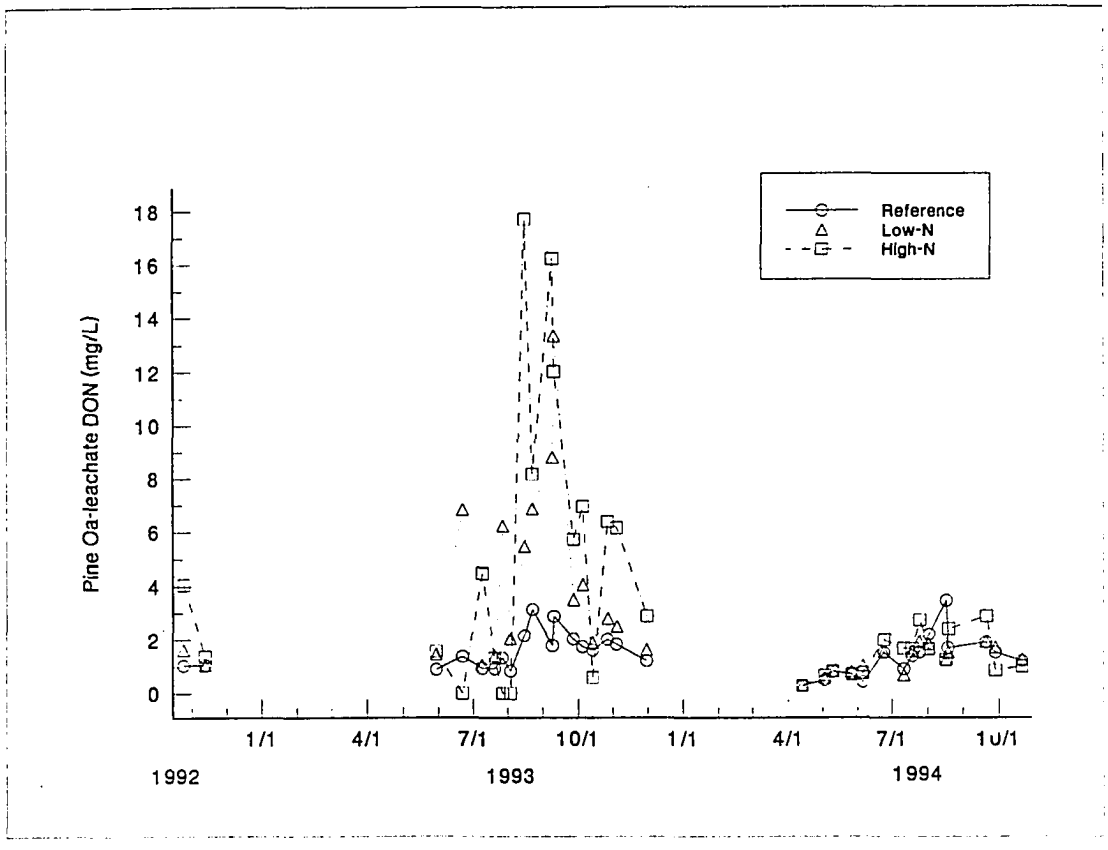

Figure 1.8. Seasonal patterns in pine stand Oa-leachate DON concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

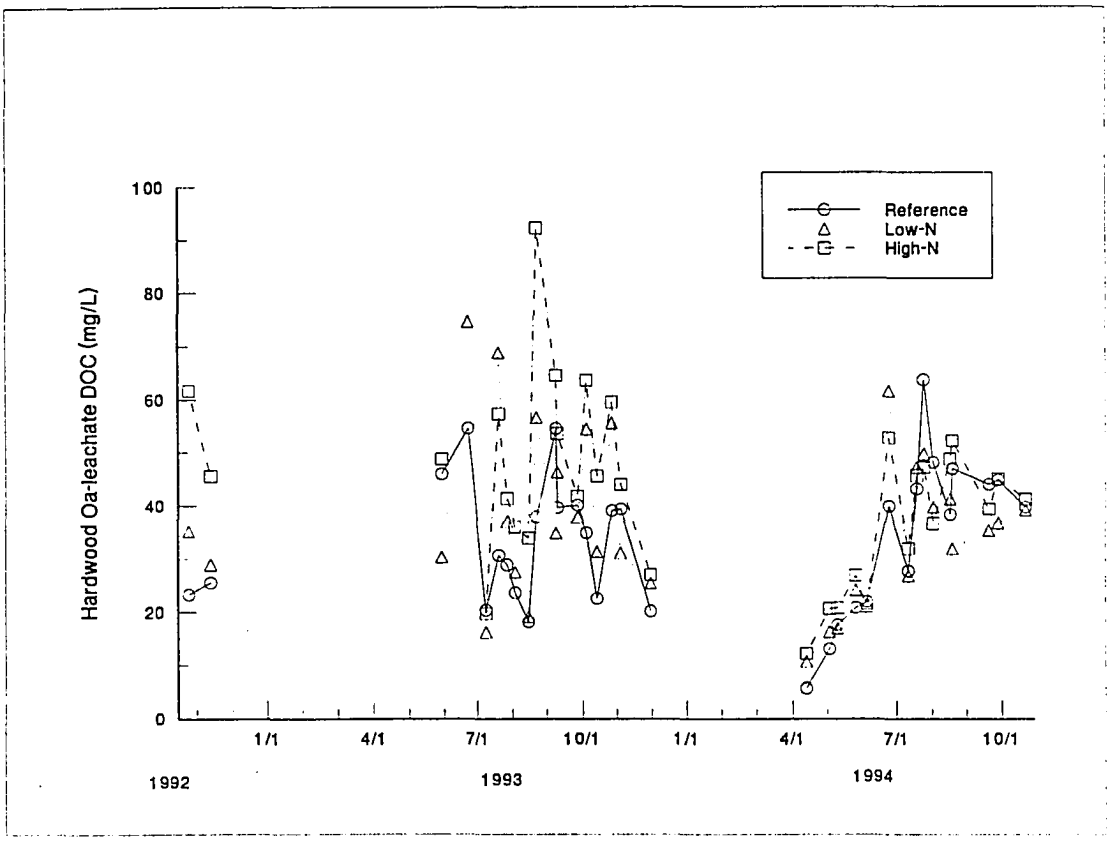

Figure 1.9. Seasonal patterns in hardwood stand Oa-leachate DOC concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

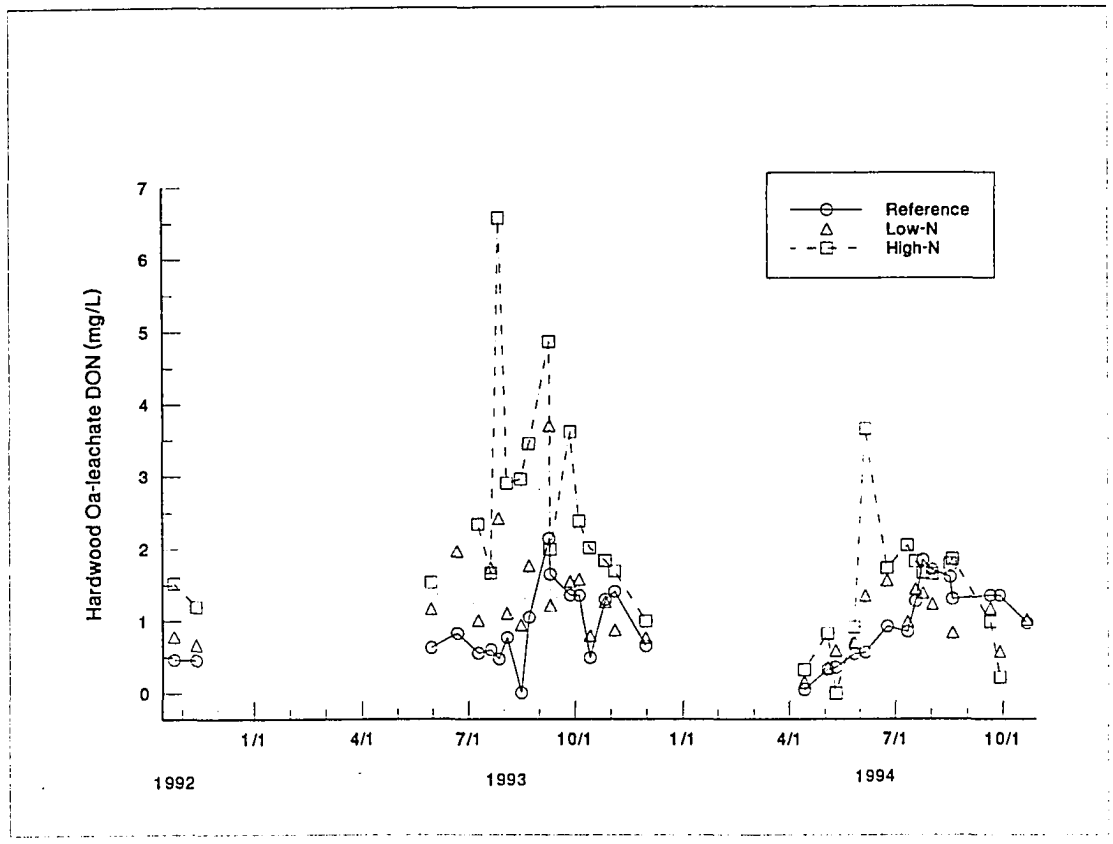

Figure 1.10. Seasonal patterns in hardwood stand Oa-leachate DON concentrations. Reference, Low-N and High-N treatments are shown. Values indicated represent chemistry of bulked samples from 5 replicate collections within each treatment.

Table 1.3 (A).

Season	Treatment	DOC [mg L^{-1}]	DON [mg L^{-1}]	DOC:DON mass ratio
1992 Fall:	Reference	64± 12(2)	1.1 ± .01(2)	60 ± 13(2)
	Low-N addition	55 ± 10(2)	1.2 ± .34(2)	46 ± 3.8(2)
	High-N addition	91 ± 33(2)	2.0 ± 1.6(2)	51 ± 13(2)
1993 Spring:	Reference	56 ± 25(2)	1.0 ± .31(2)	53 ± 6.7(2)
	Low-N addition	72 ± 90(2)	2.4 ± 2.9(2)	30 ± 0.7(2)
	High-N addition	59 ± 30(2)	1.6 (1)	32 (1)
1993 Summer:	Reference	60 ± 34(9)a	1.4 ± .72(9)a	44 ± 11(9)a
	Low-N addition	94 ± 81(9)b	3.5 ± 2.7(9)b	29 ± 10(9)b
	High-N addition	74 ± 48(9)b	4.7 ± 5.3(8)ab	14 ± 5.3(5)c
1993 Fall:	Reference	58 ± 18(5)ab	1.4 ± .31(5)a	40 ± 4.7(5)a
	Low-N addition	54 ± 18(5)a	2.0 ± .59(5)b	27 ± 3.0(5)b
	High-N addition	88 ± 43(5)b	3.4 ± 2.3(5)ab	23 ± 3.8(4)b
1994 Spring:	Reference	34 ± 15(6)	0.81 ± .47(6)	45 ± 5.3(6)
	Low-N addition	42 ± 25(6)	1.1 ± .41(6)	36 ± 11(6)
	High-N addition	36 ± 25(6)	1.1 ± .62(6)	37 ± 3.7(4)
1994 Summer:	Reference	65 ± 14(8)a	1.6 ± .55(8)	41 ± 7.1(8)
	Low-N addition	59 ± 16(8)b	1.5 ± .50(8)	40 ± 7.4(8)
	High-N addition	80 ± 32(8)a	1.9 ± .67(8)	39 ± 6.8(5)

Table 1.3 (A). DOC and DON concentrations in red pine stand Oa leachate. Concentration and ratio values are volume weighted, reported as mean ± standard deviations (number of observations in parentheses) within each season and treatment. Letters (a,b,c) denote results of tests for significance of treatment effects, shown in columns, tested within each season and stand. Different letters denote a significant difference at the 0.05 level.

Table 1.3 (B).

Season	Treatment	DOC [mg L^{-1}]	DON [mg L^{-1}]	DOC:DON mass ratio
1992 Fall:	Reference	25 ± 1.2(2)	0.46 ± .005(2)	55 ± 3.2(2)ab
	Low-N addition	30 ± 3.1(2)	0.68 ± .06(2)	44 ± 0.81(2)a
	High-N addition	49 ± 8.8(2)	1.3 ± .18(2)	38 ± 1.3(2)b
1993 Spring:	Reference	47 ± 4.4(2)	0.66 ± .10(2)	72 ± 3.8(2)
	Low-N addition	59 ± 30(2)	1.7 ± .54(2)	34 ± 8.1(2)
	High-N addition	49 (1)	1.5 (1)	32 (1)
1993 Summer:	Reference	32 ± 12(9)a	0.95 ± .62(9)a	37 ± 12(8)a
	Low-N addition	32 ± 13(9)a	1.6 ± .84(9)b	21 ± 7.2(9)a
	High-N addition	42 ± 22(9)b	3.3 ± 1.2(9)c	16 ± 6.9(5)b
1993 Fall:	Reference	24 ± 7.3(5)a	0.72 ± .33(5)a	35 ± 8.3(5)ab
	Low-N addition	32 ± 11(5)a	0.88 ± .26(5)a	37 ± 4.0(5)a
	High-N addition	38 ± 13(5)b	1.5 ± .53(5)b	26 ± 3.1(5)b
1994 Spring:	Reference	22 ± 11(6)a	0.53 ± .26(6)a	42 ± 4.4(5)a
	Low-N addition	35 ± 23(6)ab	1.1 ± .54(6)b	39 ± 6.3(5)ab
	High-N addition	27 ± 14(6)b	1.3 ± 1.3(6)ab	27 ± 3.1(3)b
1994 Summer:	Reference	47 ± 12(8)a	1.5 ± .35(8)	33 ± 3.5(8)
	Low-N addition	37 ± 8.3(8)b	1.0 ± .29(7)	35 ± 5.2(7)
	High-N addition	43 ± 7.8(8)ab	1.6 ± .52(8)	25 ± 7.4(7)

Table 1.3 (B). DOC and DON concentrations in hardwood stand Oa leachate. Concentration and ratio values are volume weighted, reported as mean ± standard deviations (number of observations in parentheses) within season and treatment. Letters denoting statistical differences are as in (A).

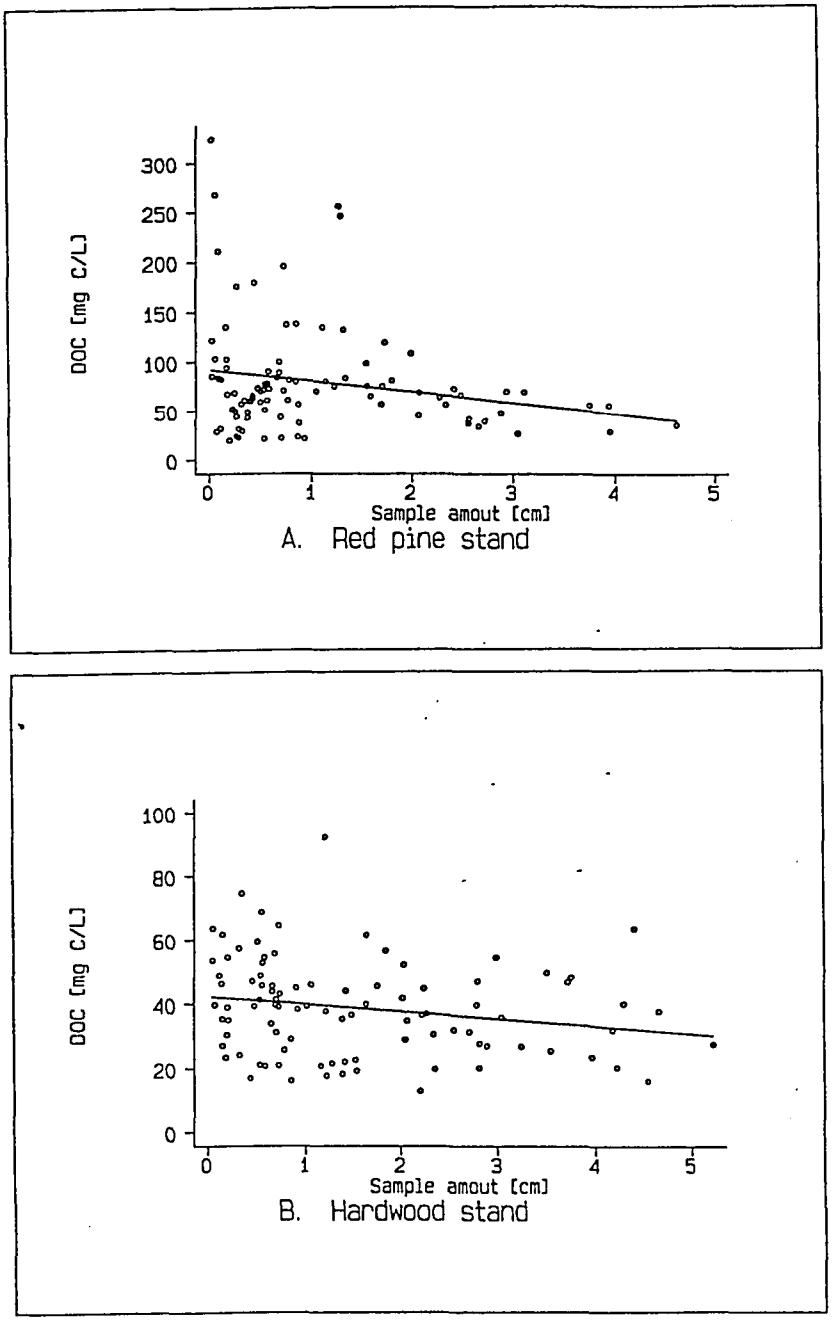

Figure 1.11. DOC concentration versus Oa-leachate sample amount collected. DOC data are reported in [mg C L^{-1}]. Sample amount refers to hydrologic flux through the Oa horizon in [cm] during the sampling period. Data from reference plots and low and high N treatments are shown. (A). Red pine stand. Regression shown is significant at p = 0.04 with $r^2 = 0.04$. (B). Hardwood stand. Regression shown is significant at p = 0.0499 with $r^2 = 0.04$.

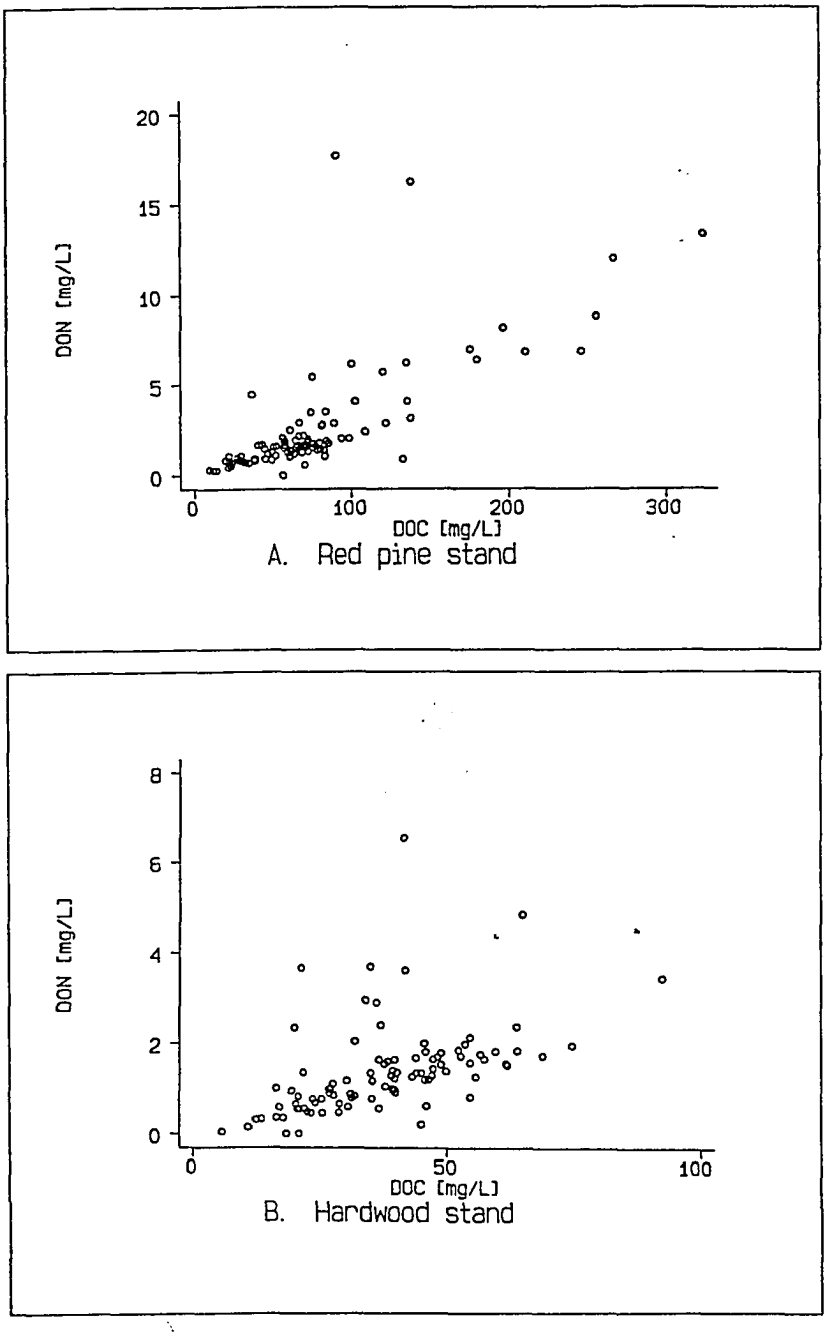

Figure 1.12. DON versus DOC in Oa-leachate samples. DON concentration data are reported in [mg N L^{-1}], DOC concentration data in [mg C L^{-1}]. Data from reference plots and low and high N treatment plots are combined in these figures. (A). Red pine stand. DON and DOC concentrations were highly correlated with $p < 0.001$ and $r^2 = 0.53$. (B). Hardwood stand. DON and DOC concentrations were correlated with $p < 0.001$ and $r^2 = 0.23$.

DOC and DON concentration data by stand and season are summarized in table 1.3 A (pine stand) and B (hardwood stand). Volume-weighted DOC seasonal means in the reference plots ranged from 34 to 64 mg C L^{-1} in the red pine stand and from 22 to 47 mg C L^{-1} in the mixed hardwood stand. For DON, volume-weighted seasonal means ranged from 0.81 to 1.6 mg N L^{-1} in the pine stand and from 0.46 to 1.5 mg N L^{-1}, corresponding to DOC:DON mass ratios of 40 to 60 in the pines and 33 to 72 in the hardwoods.

Significant but highly scattered relationships were observed between DOC concentrations and amounts of sample collected (figure 1.11). Relationships were stronger between DON and DOC concentrations within each stand, as depicted in figure 1.12.

Effects of Nitrogen Treatment. In the first year of the study there was a striking difference in DOC concentrations in the N addition treatments relative to references in both stands. As shown in table 1.3, the higher DOC concentrations were statistically significant ($p \leq 0.05$) in both stands in the summer of 1993 and in the hardwood stand in fall 1993. In the rest of the first litterfall year (fall of 1992 and spring of 1993), the trend of higher DOC with treatment was potentially present but samples were few and variability was high. The level of N addition, 50 kg ha^{-1} yr^{-1} versus 150 kg ha^{-1} yr^{-1}, was not as important as the comparison of either level with reference plots. I thus use the phrase 'N addition effect' to refer to a comparison of either low-N-addition plot data or high-N-addition plot data versus reference plot data.

Increases in DOC with N treatment in 1993 occurred roughly from June through September (pines) or October (hardwoods). During this time frame, there were a number of relevant factors: it was the growing season; fertilization of the plots was being conducted; and temperatures were higher. Through time, DOC concentrations in N-amended plots tended to increase and decrease in step with increases and decreases in reference plot DOC concentrations. This pattern suggests that processes controlling concentrations of DOC in Oa-leachate may have been modified as to rate or extent but not changed in terms of mechanisms. The patterns of simultaneous increases and decreases in DOC concentration were not present, however, in summer 1994.

The second year of the study produced quite different results. DOC concentrations in N-amended plots not only diminished, but did so to such an extent that N addition effects actually reversed. As late as spring 1994 in the hardwood stand, 21 months after lysimeter installation, DOC concentrations were still significantly elevated with N treatment. But in the summer of 1994 the low-N treatment DOC concentrations were significantly lower than those in reference plots in both forest stands.

Responses of DON concentrations to N treatment were similar to DOC responses. In the first year of the study DON concentrations were significantly higher in the pine stand low-N addition plots; the trend was also present in the high-N addition plots but variability was high. In the hardwood stand there were also significantly elevated DON concentrations resulting from N addition. The second year of the study showed no significant treatment effects in DON concentration in the pine stand. In the hardwood

stand DON concentrations were still significantly elevated over references in spring 1994 (as were DOC concentrations). By summer 1994 concentrations were no longer elevated; DON concentrations trended toward a decrease in the low-N plot relative to reference.

The ratio of C to N in forest detritus is an important parameter, potentially indicating the degree of decomposition along a 'decay continuum' from litter to humus or soil organic matter (Melillo et al. 1989). Fresh foliar and root litter at Harvard Forest exhibits C:N ratios of ca. 30 to 50 and woody litter on the order of 300. Humus and mineral soil organic matter, in advanced stages of decay, exhibit C:N ratios of ca. 15 to 20 (Magill et al., *in preparation*). The Oa-leachate DOC:DON ratio measures the C:N ratio of the dissolved organic matter leaching from the bottom of the forest floor, potentially providing information about its degree of decomposition.

Volume-weighted seasonal averages in DOC:DON mass ratio are depicted in figures 1.13 (red pine stand) and 1.14 (hardwood stand). Levels of significance among N treatment effects are shown in table 1.3. In the first year of the study, DOC:DON mass ratios were significantly lower in N-amended plots in both stands. Although DOC concentrations increased in N-treated plots, DON concentrations increased to a greater extent and the DOC:DON mass ratio decreased.

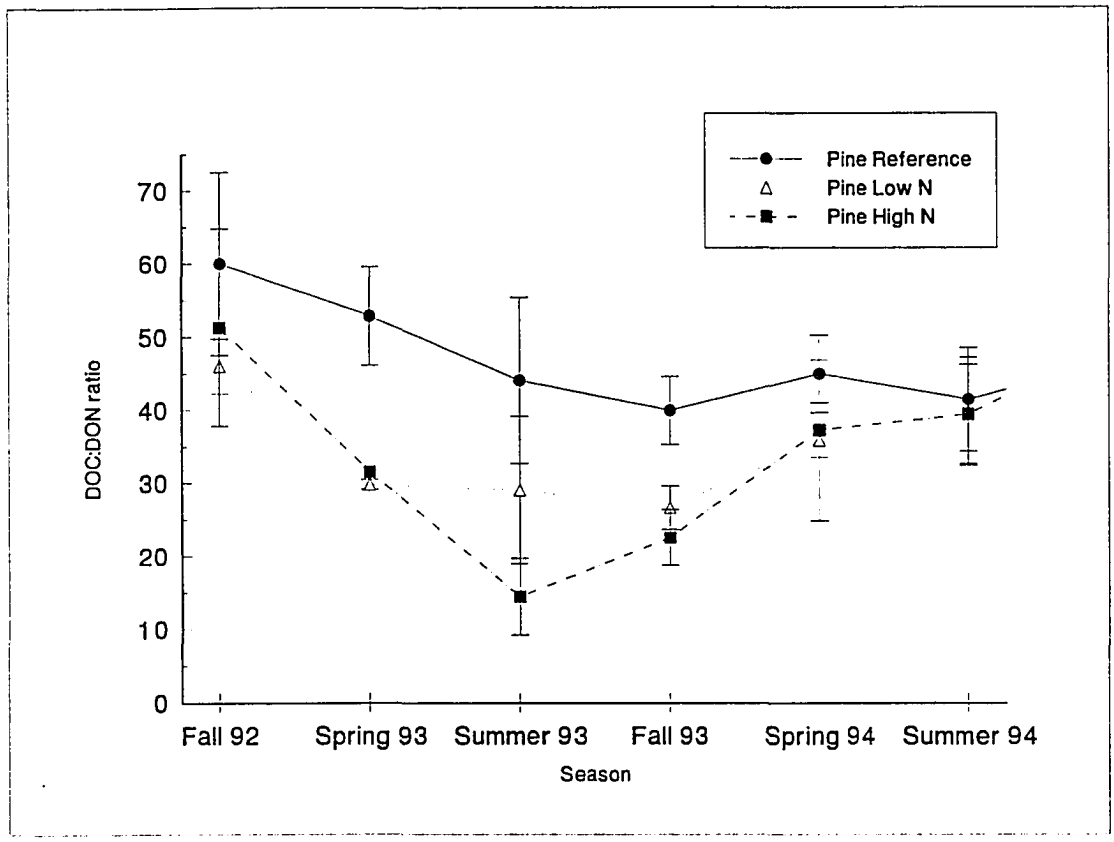

Figure 1.13. Time series of DOC:DON mass ratios in pine stand Oa-leachate. Volume-weighted seasonal means are shown for reference, low-N and high-N treatments. Error bars represent standard deviation among samples within each season in each treatment.

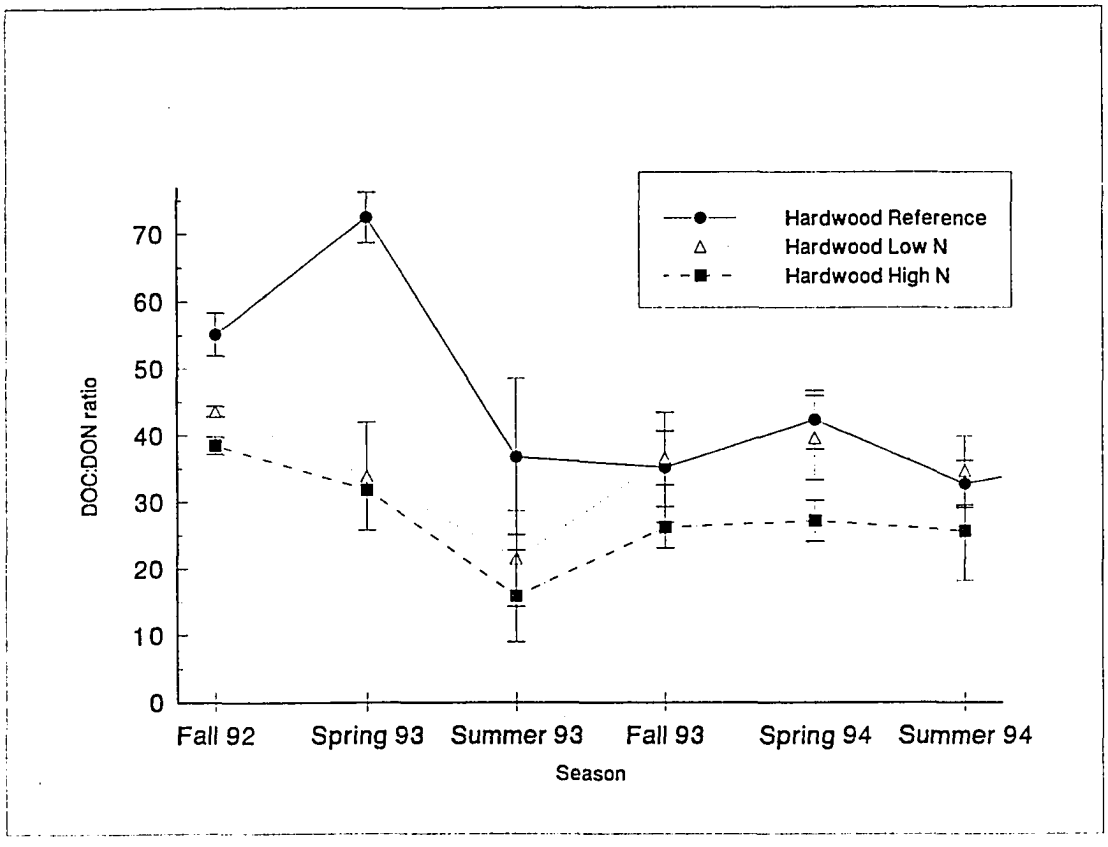

Figure 1.14. Time series of DOC:DON mass ratios in hardwood stand Oa-leachate. Volume-weighted seasonal means are shown for reference, low-N and high-N treatments. Error bars are as in figure 1.13.

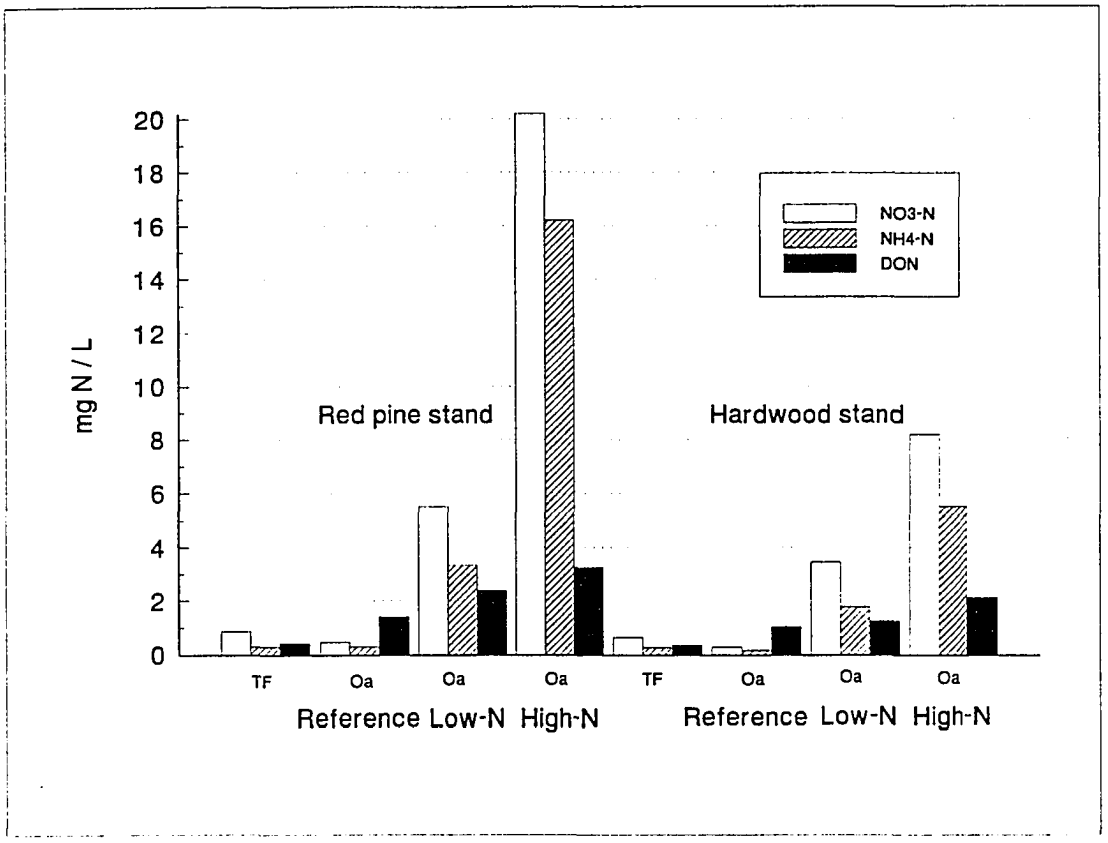

Figure 1.15. Forms of N in Oa leachate in the pine and hardwood stands. Nitrate-N, ammonium-N and DON are shown as volume-weighted mean concentrations [mg N L^{-1}] over the entire two-year study. Bars are grouped for throughfall (TF) and for Oa-horizon leachate by treatment for each stand.

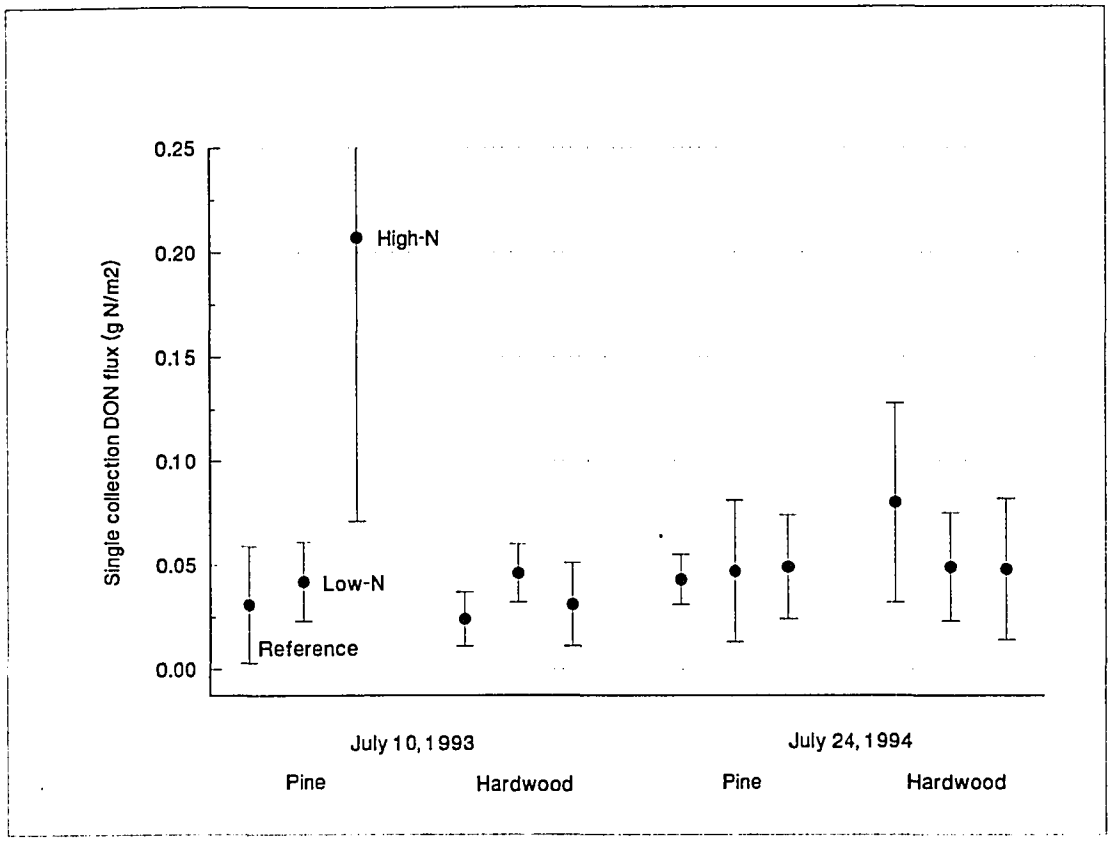

Figure 1.16. Single collection Oa-leachate DON fluxes. Results from two unbulked collection sets are shown. Each point and set of error bars represents mean and standard deviation in a set of five samples collected simultaneously from each of five lysimeters. Results within each stand are grouped in order of reference, low-N addition and high-N addition plots.

Forms of N in Oa leachate. As summarized above, when DON has been measured leaching from forest organic horizons, it has uniformly been measured as the major form of N in solution. My results from the reference plots at Harvard Forest exhibit this pattern as well (figure 1.15). Averaging over the entire two-year study, DON comprised 66% and 68% of total dissolved N in Oa-leachate in the pine and hardwood reference plots respectively. Mean DON concentrations, when averaged over the entire study, showed a general increase with N treatment. The volume-weighted fraction of total dissolved nitrogen (TDN) that was in organic form decreased in high-N addition treatments to 11% in the pine stand and 34% in the hardwood stand. When volume-weighted means were calculated within the first litterfall year and second litterfall year separately (not shown), the DON concentration increases with treatment were much more dramatic in the first year of sample collection.

Unbulked sets. Single-collection DON fluxes for two of the unbulked sets are shown in figure 1.16. In the third unbulked collection set of Oa-leachate samples, collected on September 28, 1994, inorganic N and TDN concentrations were so high (Methods section) that only the reference-plot concentrations can be reported for DON: the single-collection DON fluxes were 0.026 ± 0.018 g m^{-2} in the pine reference and 0.032 ± 0.024 g m^{-2} in the hardwood reference plot.

In figure 1.16, DON flux shows a strong response to fertilization in the pine stand in July of the first year. Such a response is not apparent in the unbulked set taken in July of the second year or in the hardwood stand in either year. It should be noted that the July

1993 set was taken 11 days after plot fertilization, whereas the July 1994 set was taken 29 days after fertilization. The much higher inorganic-N concentrations in the July 1993 samples contributed to the large uncertainty in the calculation of DON concentrations, as shown by the error bars on the flux calculations in figure 1.16. Still, the results show two longer-term patterns. First, the 1993 single-collection pine-stand DON fluxes responded to treatment to a greater degree than did hardwood-stand fluxes. Second, in 1994 the single-collection hardwood-stand DON fluxes showed an apparent decrease in the N treatment plots relative to the reference plot.

Discussion

Dissolved Organics in Throughfall

Concentrations of throughfall DOC observed at Harvard Forest were similar in range to concentrations observed in TF event collections made at Hubbard Brook, NH under various tree species: growing-season averages of 12 to 34 mg L^{-1} (McDowell and Likens, 1988). In the cited study, however, DOC concentrations peaked in October. An important factor in the Harvard Forest June peak in TF may have been pollen, which was visibly high in the collectors of both stands in June. Pollen itself was removed during filtering, but may have leached organics into solution, also contributing to the June DON peak. Leaching of dissolved organics from pollen could be considered a legitimate influx to the forest floor of dissolved organics in throughfall. However, it is unclear whether the collectors used here would accurately measure such a flux.

Calculated fluxes of dissolved organics in TF were very close to the values calculated by Qualls et al. (1991) at Coweeta, North Carolina: 12.5 g DOC m^{-2} yr^{-1} and 0.36 g DON m^{-2} yr^{-1}. For comparison to other forest floor inputs, the Harvard Forest dissolved organic fluxes in throughfall corresponded approximately to 7% of the foliar litter C flux in the pine stand, 8% in the hardwood stand and 7% of the foliar litter N flux to the forest floor in each stand (Aber et al. 1993).

Sampling of Forest Floor Leachate

Forest soil structure and processes are heterogeneous in space and time. Soil solution in the forest floor epitomizes this heterogeneity. Preferred flowpaths exist on the centimeter scale and smaller in the form of tunnels left by decayed roots or twigs, and on the meter scale and larger in the form of mounds and depressions. Hydrologic flow varies under rainfall ranging from drizzle that moistens but does not pass through the humus, to intense rain events on already wet soils. Chemistry of water held at differing tensions varies (Haines et al., 1982); chemistry of soil solutions are highly affected by soil heterogeneity (Litaor, 1988). Precise locations sampled with lysimeters and precise time periods sampled are important sources of random variation in solution chemistry results (David and Gertner, 1987). Investigators collecting soil solution for chemical analysis for the purpose of characterizing stand or ecosystem-level chemistry must confront these problems as best as possible in the field and then assess the results critically.

In this study I analyzed bulked samples from 5 lysimeters in most cases in an effort to obtain spatially representative results. I analyzed unbulked collection sets on

three occasions to assess the differences among samples collected by the widely separated lysimeters. I found standard deviations within each set of 5, in volume-weighted chemistry, were often 50% of the mean or larger (figure 1.16). I collected a large number of sample sets (33) over a two-year period in order to obtain temporally representative results. Differences in solution chemistry from one sampling period to the next were tractable in reference plots, but highly variable in nitrogen-treated plots in the first year of the study. I reported results for solution chemistry by season, because there were seasonal patterns, and because grouping samples together in this manner afforded a means of performing statistical tests of treatment effects.

Zero-tension lysimeters collect gravitational water, or saturated flow. The sample chemistry probably over-represents the chemistry of high-flow hydrologic events. This is especially true of the unbulked collection sets in the current study, in which particularly high-flow events were collected so that enough sample from each collector would be present for chemical analysis. (More information concerning hydrology in ZTL collections is provided in Chapter II.) In the two-year dataset overall, only weak relationships were present between DOC concentrations and sample amounts collected (figure 1.11). The possibility still exists that a stronger relationship would exist between DOC concentration and hydrologic flux if water held at greater tensions were included.

Differences Between Year 1 and Year 2 Results

The presence of significantly elevated concentrations of DOC and DON in forest-floor leachate under N amendment in the first year of this study was a substantial

finding. The second-year results, disappearance of the effect in the pine stand and an apparent reversal of the effect in the hardwood stand, were also substantial findings. The second year results answer some questions and raise others.

If the effects of the first year had been duplicated in the second, numerous possibilities would suggest themselves to explain the rise in dissolved organic C and N under nitrogen amendment: increased rate of formation of dissolved organics as decomposition products, increased root exudation or fine root turnover, increased microbial grazing by microfauna, and direct chemical changes to humic substances or dissolved organic matter that increased solubility or rates of formation. These possibilities remain. However, an additional level of complexity must be present.

Whatever the factors that led to significantly higher concentrations of DOC and DON with N treatment in the first year, they must have interacted with at least one other factor present in 1993 but not 1994. The fact that this result held true in both the red pine and the mixed hardwood stand suggests that the same interannual factor was at work in both stands. The two most obvious possibilities are these: differences in the distribution of rainfall, or disturbance of the soil during lysimeter installation.

The period of low rainfall in late spring of 1993 (figure 1.2) lasted approximately 5 weeks from late April to the last day in May. This followed a spring in which March precipitation was high above average and April precipitation was average. Mean May temperature at Harvard Forest is 12° C (Van Cleve and Martin, 1991). Melting of the snowpack ordinarily occurs in mid April, and leaf-out in the hardwood stand occurs

approximately mid-May; oaks, the dominant overstory species, leaf-out later than the others present (*personal observation*). It may be reasonable to suspect that reduced rainfall in May after a wet spring and followed by an average June and wet July was not severe enough to be the dominant interannual difference affecting soil solution chemistry.

A more likely explanation of the first year results may be small-scale disturbance resulting from lysimeter installation. It is important to emphasize what the results do *not* show: that disturbance caused higher concentrations of DOM leaching from the forest floor. Lysimeters were installed in reference plots, yet differences in DOC and DON seasonal patterns were not evident between two years in the reference plots. If disturbance was the cause of the elevated DON and DOC concentrations in the first year, then it was the interaction of disturbance with elevated levels of N availability or inorganic N leaching.

Disturbance Effect Mechanisms

This raises the question, what aspects of small-scale disturbance could interact with elevated levels of inorganic N to produce elevated concentrations of soluble organic C and N? Lysimeter installation probably causes fine root breakage and disruption of the humus mass. A possible explanation could be increased fine root growth or turnover, spurred not by disturbance alone but by the combination of disturbance and high levels of N availability. In that case the observed increases in DOM could be exudates from living or senescing roots. The root exudates, however, would have to have a very low C:N ratio in order to lower the average C:N ratio of all DOM significantly as shown in table 1.3. In

addition, I noted earlier that DOC and DON in treated plots, though at higher concentrations than references, showed temporal patterns in the first year of rising and falling in step with reference-plot DOC and DON concentrations. This suggests that the essential mechanisms causing the production or solubilization of Oa-leachate organic C and N were not changed but were enhanced with N treatment. The predominant compounds in Oa-solution DOM ordinarily are not root exudates, they are humic substances (Introduction section).

Fine root breakage and humus disruption could produce temporarily higher quantities of labile C at the bottom of the Oa horizon. Perhaps labile C, increased by the disruption, provided fuel for increased microbial activity (Lynch, 1982; Paul and Clark, 1989), occurring in both reference plots and N treated plots. Though increased activity could lead to N immobilization in litter where C:N ratios are higher, in the Oa horizon where C:N ratios are lower it is conceivable that labile C could stimulate NH_4^+ mineralization. If true, I would expect to see this effect in the reference plots. In fact, NH_4^+ in Oa leachate in the red pine reference plot was significantly higher in the first year compared to the second (Chapter II).

Where higher levels of inorganic N were present, together with labile C, increased microbial enzyme activities could have increased the rates of humic substance formation. Microbial enzymes such as peroxidases, phenoloxidases, and laccases are considered to be important in oxidative polymerization processes that produce humic substances in soils (Nelson et al., 1979; Sjoblad and Bollag, 1981; Liu et al., 1985; Tate, 1987). The

fungus *Coriolus versicolor*, which produces a ligninase enzyme system, is thought to require labile C (other than lignins) as an energy source (Paul and Clark, 1989). This would account for temporal patterns being similar in treated plots and references, since DOM production in all cases would be subject to the same temperature and moisture controls. Correlations between DOC and DON content across all Oa-leachate samples (figure 1.12) support this interpretation. If humic substances formed under higher N availability and higher rates of N cycling (Magill et al., *in preparation*) have higher N content, the increased-humic-substance-formation interpretation would also explain the decreased DOC:DON ratios observed in Oa leachate from treated plots

If this interpretation is correct, I suggest that increased rates of humic substance formation occurred after the small scale disturbances, during the first litterfall year. The alternative would be that my observations represent flushing of humic substances formed at an increased rate throughout the previous five years of N amendment, and that by spring in the second litterfall year (1994) the flushing of the excess soluble organic C and N was complete. In that case I would have expected to see reference-plot flushing of DOM also decrease in the second year, but such a trend is not apparent.

Decreased DOM in the Second Year

I view the primary cause in differences in DOM leaching between the two years as lysimeter-installation disturbance. I view the second year, especially summer 1994, as beyond the period when disturbance effects operated. Significant declines in

seasonally-averaged DOC concentrations occurred in both the pine and hardwood stands under N treatment, with no significant effects on DON or DOC:DON ratios.

If DOC functioned largely as a microbial substrate, and if microbes in the O horizon were nitrogen-limited, then reductions in DOC concentrations once disturbance effects had passed could be viewed as increases in microbial consumption of soluble organics. As noted above, however, no increases in CO_2 efflux with N treatment were observed in these plots. In addition, organics that comprise the bulk of DOC are not easily biodegradable. Only 14 to 33% of Oa-solution DOM was biodegradable in 134-day laboratory incubations (Qualls and Haines, 1992).

A more likely explanation is that decreasing pH levels in Oa-leachate with N treatment (Chapter II) decreased the solubility of organics (Introduction Chapter). The fact that the decreases in leached DOM in the second year were more pronounced in hardwood stands support this interpretation (Chapter II).

Significance for Ecosystem Functioning

If small-scale disturbances in the upper mineral horizons and Oa horizons never occurred in nature, then the effects I attribute to disturbance would simply be experimental artifacts. But the forest floor is subject to myriad disturbances at various scales. Rodents (voles, chipmunks and squirrels) dig tunnels or bury objects in the soil; Hymenoptera (ants, wasps) nest in the upper soil horizons. Earthworms mix organic and mineral soil in some forest ecosystems (not Harvard Forest). Dramatic disturbance to the forest floor occurs during windthrow; pits and mounds from past events are widely

evident at Harvard Forest. During lysimeter installation when 30 small pits were excavated for housing the ZTL bottle wells, measurements of forest floor and A horizon thickness were taken at four points in each small pit. Overall, 3.5% of the O horizon points and 16% of the A horizon points were too disturbed for measurement.

Logging operations can have heavy impacts on the forest floor; an estimate of the extent of heavy impacts to the forest floor may be 20% (Stone, 1973). Bormann and Likens (1979) speculated that following clearcutting, a large N transfer to mineral soil from the O horizon occurred at Hubbard Brook, NH. Qualls et al. (1991) suggested that the process responsible may have been DOM leaching from the O horizon and sorbing in mineral soil. If my hypotheses are correct, then increased N availability following clear-cutting would significantly contribute to the formation of DON leaching from the O horizon. Illuviation of DON to mineral soil, where much of it would be sorbed, could be an important mechanism of ecosystem N retention following large-scale disturbance.

If my interpretations of the decreased DOM concentrations in the second year are correct, then acidification of soil solution would have the opposite effects of mechanical disturbance; DOM leaching would be decreased and more organic matter would accumulate in the forest floor.

CHAPTER II

ASPECTS OF INORGANIC CHEMISTRY OF THROUGHFALL AND FOREST-FLOOR LEACHATE AT HARVARD FOREST

Introduction

Models of acid-deposition effects on forest soils and surface waters, including acidification and leaching of nutrient cations, focused on the effects of sulfate deposition prior to a recent 'paradigm shift' in conceptual models of temperate forest nitrogen cycling (Aber, 1992; Johnson, 1992; Aber et al., 1993). It is now recognized that nitrogen inputs to a forest-soil system with a high nitrogen demand can result in nonlinear responses when the retention capacity of the system is surpassed, a phenomenon known as nitrogen saturation (Agren and Bosatta, 1988; Aber et al., 1989). One nonlinear response can be the onset of nitrate leaching from the system (Mitchell et al., 1992; Aber et al., 1993).

In northeastern North America, watershed nitrate retention may be an important source of alkalinity for surface water (Eshleman and Hemond, 1988), and nitrate leaching can contribute significantly to surface-water acidification (Murdoch and Stoddard, 1992).

In forests subject to acid deposition and where nitrate is taken up by plants or retained in the forest floor and mineral soil, sulfate has been observed to leach base cations from the forest floor (Johnson et al., 1985). In forests where nitrate leaches from the forest floor, nitrate concentrations have been shown to correlate with calcium and

magnesium concentrations in soil solution and with calcium concentrations in stream water, suggesting a strong control on cation movement (Foster et al., 1989; Morrison et al., 1992).

In this chapter I present selected aspects of the inorganic chemistry of throughfall and forest-floor leachate in the red pine and mixed hardwood stands of the Chronic N plots at the Harvard Forest. Analyses reported here were conducted on the same samples described in Chapter I. Here I consider stand differences, interannual differences and effects of N amendment on NO_3, NH_4, SO_4, pH, Ca, K, Mg, Na and Cl in solution.

Materials and Methods

Methods of nitrate and ammonium measurement were described in Chapter I. I measured pH potentiometrically on each sample as it entered the laboratory. After filtering, frozen storage and thawing, subsamples were taken for the additional cation and anion analyses. Cation subsamples were acidified to pH < 2 by addition of 100 microliters of 5 N H_2SO_4 and stored in tightly capped plastic vials at room temperature for up to one year (Greenberg et al. 1992). Anion subsamples were refrozen in plastic vials for up to one year prior to analysis. After thawing, anion samples were refiltered through filters of nominal pore size 0.2 um.

Analyses for Ca, K, Mg and Na were performed on a direct-coupled plasma (DCP) arc spectrophotometer at the US Forest Service Northeast Experiment Station in Durham, NH. A prepared stock solution (USDA) was used for standardization, and standards were also measured as samples in each run. Blind duplicates were also

included in each run. Independent check standards made in the Aber laboratory and analyzed as samples measured within 11% of expected values. Since the DCP ionizes samples and measures total content for each element, my results should be considered total elemental profiles.

Chloride and SO_4 were quantified through high-pressure liquid chromatography (HPLC) with conductivity detection in the McDowell laboratory at the University of New Hampshire. The instrument comprised an IONPAC AS4A (10-32) Analytical Column from Dionex Corp., a Waters 431 Conductivity Detector, a Waters Model 510 pump and an autosampler. I used a nominal pressure of 1400 psi, a flow rate of 2 mL min^{-1} and an eluent of 162 mM Na_2CO_3 plus 153 mM $NaHCO_3$. Software used for peak acquisition and analysis was Maxima 820 Chromatography Workstation (Millipore, 1988). Each analytical run included blind duplicates and standards run as samples. An ULTRAcheck certified standard (ULTRA Scientific, North Kingston, RI) was run as an independent check standard. Chloride concentrations measured within an average of 12% of the certified value and sulfate concentrations within an average of 3%.

Calculations and Statistical Analyses

Concentrations of H^+ in ueq L^{-1} were calculated from pH measurements with a slight correction for ionic strength (γ_{H^+} = 0.98; Stumm and Morgan, 1981). The average ionic strengths of my samples were 0.0003 for throughfall and 0.0007 for Oa-leachate.

As with the data analysis reported in Chapter I, two steps were taken for each unbulked set of 30 TF or ZTL samples collected on the same date. First, summary

statistics were calculated within the unbulked set. Second, mean concentrations for each chemical species within each stand and treatment were entered into the main database so as not to assign undue weight to the unbulked collection dates during analysis of the two-year dataset.

As outlined in Chapter I, the field collections spanned 25 months: two litterfall years, October to September, with one final sample set collected in October of the third year for closure. The final sample is not included in the statistical analyses reported here, but is shown on time series diagrams. Summary data reported here are either analyzed over the entire study or separated by litterfall year. Year 1 covered from 1 October 1992 to 30 September 1993; Year 2 from 1 October 1993 to 30 September 1994.

Most aspects of throughfall chemistry showed no trends among N treatments. Those that did show potential treatment effects were tested for normality of distribution. Logarithmic transformations were found that produced normal distributions in each, and analyses of variance performed on volume-weighted and transformed data. Differences at the confidence level $p \leq 0.05$ are reported as significant.

All Oa-leachate data were tested for normality of distribution, and logarithmic transforms found where necessary to produced normal distributions. For Ca, K, Mg, SO_4, NO_3, NH_4 and H, nitrogen treatment effects were tested with analysis of variance (volume-weighted; Stata Corp., 1993). Analyses of variance (volume-weighted) were also used to test for the following specific effects: (1) differences between the pine and hardwood reference plots; (2) interannual differences in reference plots in each stand

considered separately; (3) interannual differences when both references and treatments were included, in each stand considered separately; (4) an interaction effect between N treatment and stand type (over the entire two-year dataset). Test results with a p-value of 0.10 or less are reported, with values of 0.05 or lower considered significant.

Results

Precipitation and Throughfall Chemistry

Some trends were present to suggest a potential effect of nitrogen treatment on aspects of throughfall chemistry. In the hardwood stand there was a highly significant decrease in Ca in N treatment plots relative to reference plots ($p < 0.001$). Though the trend was significant, the data were quite scattered; correlation of Ca concentrations with N addition levels had an r^2 value of 0.18. In the red pine stand, ammonium concentrations were significantly higher in N treatments relative to references. Again the relationship was not highly explanative of measured concentrations ($r^2 = 0.12$). Nitrate showed a trend toward an increase in N-treated plots relative to references in the two stands. Both trends were significant at the $p = 0.10$ level, but not at the 0.05 level. In sum, relationships with N treatment were few, and highly scattered even when significant. For these reasons I report throughfall chemistry averaged over the three treatments within each stand and collection date.

A difference in throughfall chemistry between litterfall years one and two was evident. The second year of collection showed pH levels elevated in both forest stands relative to the first year. The differences in volume-weighted H^+ concentrations were

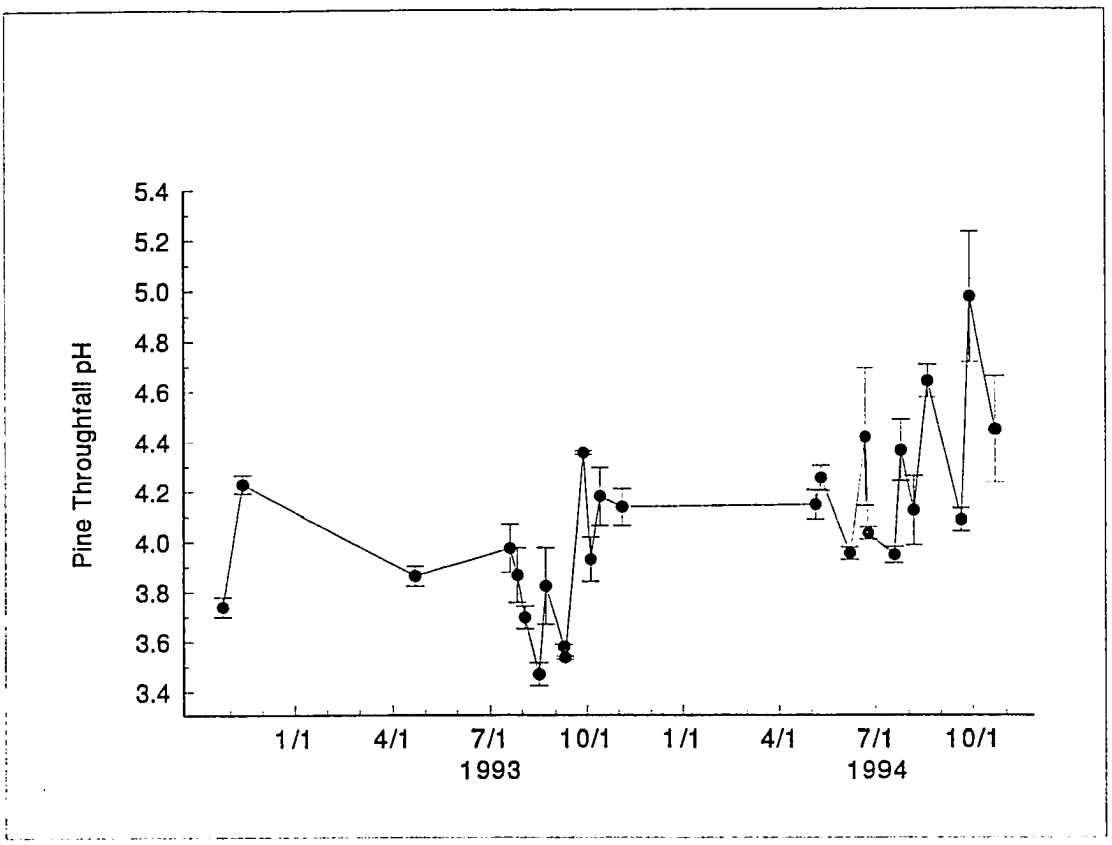

Figure 2.1 (A). Time series of pine stand throughfall pH levels. Means and standard deviations are shown within each set of three measurements per stand (reference and two N treatment plots) grouped for this analysis.

highly significant ($p < 0.001$) in both stands. Time series of throughfall pH levels over the two-year collection period are shown in figures 2.1 (A) and (B). Similar interannual differences in throughfall pH have been noted elsewhere (Edmonds et al., 1991). A likely contributing factor in the present case was higher rainfall in the second year. Higher rainfall levels could cause dilution of canopy wash of dry-deposited H^- and NO_3^-

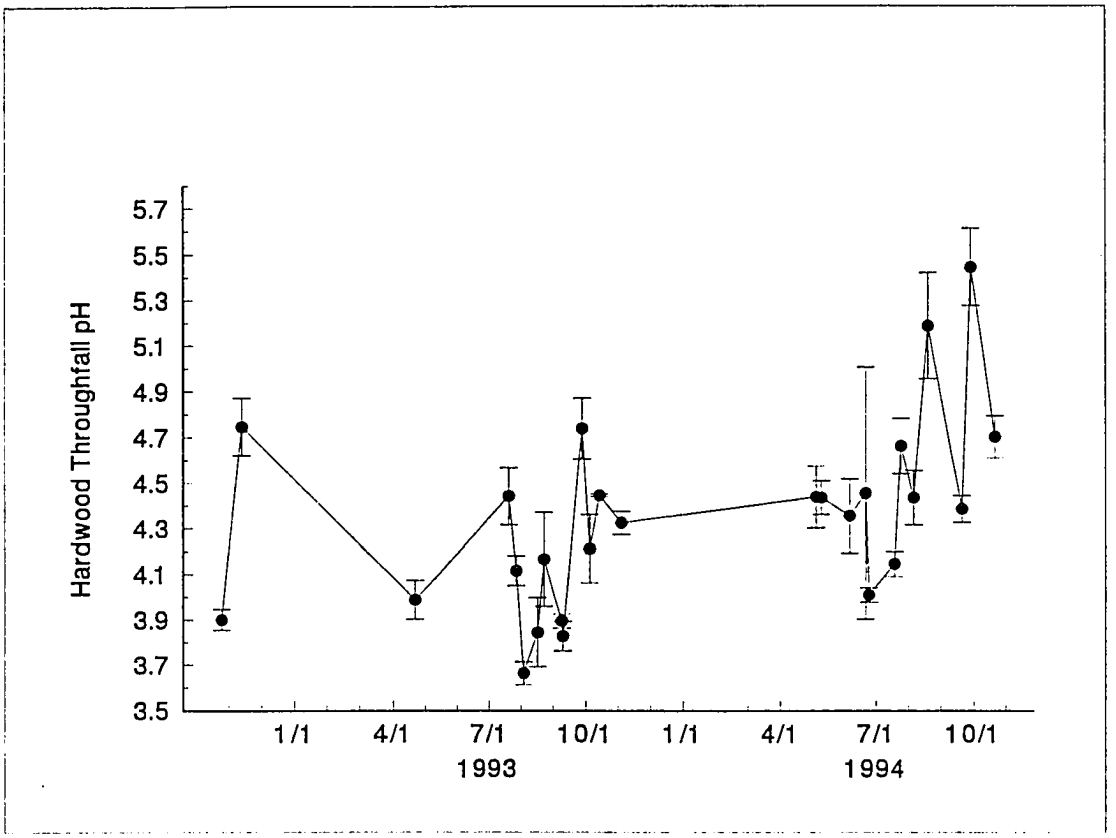

Figure 2.1 (B). Time series of hardwood stand throughfall pH levels. Means and standard deviations are shown within each set of three measurements per stand (reference and two N treatment plots) grouped for this analysis.

(Lindberg et al., 1986). Throughfall results were thus analyzed separately for each litterfall year.

Table 2.1

Sample set	Ca	Mg	K	Na	Cl	SO_4	NO_3	NH_4	H^+
Precipitation year 1	1.6	0.84	4.3	6.4	9.2	39.5	26.8	18.0	111
Red pine									
TF year 1	60.7	25.4	48.5	17.4	19.6	121	69.9	22.1	182
TF year 2	48.8	21.2	50.7	13.8	12.1	90.8	55.9	19.9	61.3
Oa year 1	110	47.8	66.7	45.9	38	107	36.3	32.6	182
Oa year 2	116	49	50.8	30.9	24.2	109	32.4	14	107
Hardwood									
TF year 1	33.9	20.3	56.5	15.4	11.7	92.1	52.1	17.5	131
TF year 2	35.8	17.2	51.2	6.7	2.7	65.4	40.8	19.3	36.8
Oa year 1	52.7	36.1	79.6	23.5	15.3	83.5	19	11.6	118
Oa year 2	59.1	41.9	41	18.7	8.1	86.3	21.1	10	97.8

Table 2.1. Aspects of inorganic chemistry in precipitation, TF and Oa leachate. Volume-weighted averages within each litterfall year are listed. TF (throughfall) concentrations are averaged among all three nitrogen treatments. Oa (forest floor) leachate chemistry shown here is from reference (no N addition) plots only. All values are in microequivalents L^{-1}.

Of the anions studied, volume-weighted charge concentrations [ueq L^{-1}] in TF occurred in the order $SO_4^{2-} > NO_3^- > Cl^-$ in both stands (table 2.1). Volume-weighted charge concentrations on cations were present in the order $H^+ > Ca^{2+} > K^+ > Mg^{2+} > NH_4^+ > Na^+$ in the pine stand. In the hardwood stand the order was $H^+ > K^- > Ca^{2+} > Mg^{2+} > NH_4^+ > Na^+$ in the first year and $K^+ > H^+ > Ca^{2+} > NH_4^+ > Mg^{2+} > Na^+$ in the second year. The only species that appeared unchanged in TF from concentrations in precipitation was ammonium (table 2.1). Sulfate, nitrate and hydrogen ion increased in TF over precipitation the first year, perhaps partly due to evaporative concentration and canopy wash of dry deposition. Calcium, potassium and magnesium were all highly elevated in TF relative to precipitation, presumably from canopy wash of dry deposition and from canopy leaching (Lindberg et al., 1986). When converted into mg L^{-1} units, potassium in TF dominated over calcium by a factor of 2 and over magnesium by a factor of 8.

The sizable decrease in H^+ concentration in TF in the second year (relative to the first year) was accompanied in both stands by decreases in TF sulfate and nitrate. This suggests a decrease in the acidity of precipitation in the second year. This change correlated with lower concentrations of Ca, K and Mg entering TF from the pine stand canopy. In the hardwood stand, only K and Mg concentrations appeared to be reduced under substantial decreases in H^+ inputs.

Table 2.2

Stand, treatment and year	Average amount [cm]	*n*	A
Red pine			
Reference year 1	0.89	18	2
Low-N year 1	1.25	18	2
High-N year 1	1.12	18	2
Reference year 2	1.13	29	5
Low-N year 2	1.08	29	5
High-N year 2	0.93	29	2
Hardwood			
Reference year 1	1.90	18	6
Low-N year 1	1.87	18	5
High-N year 1	0.99	17	3
Reference year 2	1.74	29	7
Low-N year 2	1.67	29	7
High-N year 2	1.12	29	4

Table 2.2. Oa-leachate sample numbers and amounts collected. The average amounts of solution collected by zero-tension lysimeters per collection are shown for each stand, treatment and litterfall-year combination. The number *n* refers not to the number of collection dates but to the number of samples analyzed for chemistry, including bulked and unbulked collection sets. In column A are listed the numbers of collections in which the average sample amounts exceeded 2 cm.

Oa-Leachate Hydrology

The total Oa-leachate hydrologic fluxes collected in this study amounted to ca. 20% to 32% of precipitation that fell during the collection periods, and 12% to 20% of annual precipitation in these two years. Collection amounts by stand, treatment and litterfall year are shown in table 2.2. Differences among these results should be

interpreted with caution, because of the high variability inherent in zero-tension lysimeter hydrology.

With that caveat, two effects are noteworthy. First, there were slightly more high-flow collection periods in the second year relative to the first. Second, the mean hydrologic flux collected did vary among treatments. Most significantly, in the hardwood stand, the total hydrologic flux collected in the high-N addition treatment amounted to only 50% and 66% of that collected in the other hardwood treatments in the first and second years respectively. These differences in hydrology may have affected the ion concentrations I measured. However, correcting for such effects would not be straightforward. In both stands there were significant relationships between the amount of solution collected and concentrations of sulfate, chloride, DOC and sodium.

Oa-leachate Chemistry

Reference Plots. Sulfate was the dominant anion of those studied in forest-floor leachate, followed by nitrate and chloride (table 2.1). Concentrations of each anion were higher in the pine stand than in the hardwood stand. In northeastern forest Spodosols sulfate often shows unchanged or slightly elevated (elevated particularly in coniferous stands) concentrations in Oa-leachate compared with throughfall (Mollitor and Raynal, 1982; David and Driscoll, 1984; Mitchell et al, 1992). In the present study, sulfate concentrations remained nearly constant in each stand in Oa-leachate despite large average changes in TF sulfate concentrations from the first to the second year.

Northeastern Spodosols similarly often show unchanged or increased H^+ concentrations in O horizon leachate relative to throughfall (Mollitor and Raynal, 1982; David and Driscoll, 1984). My data showed such a pattern. In the first year when TF H^+ inputs were high, volume-weighted H^+ concentrations in TF approximately equaled those in Oa solution. In the second year, when throughfall H^+ concentrations were lower, Oa-leachate concentrations were higher than TF concentrations in both stands.

Volume-weighted cation charge concentrations, averaged over the two years studied, were present in reference-plot Oa-leachate in the order $H^+ > Ca^{2+} > K^+ > Mg^{2+} > Na^+ > NH_4^+$ in the pine stand. In the hardwood stand potassium and calcium alternated in importance, but the average pattern appeared to be $H^+ > K^+ = Ca^{2+} > Mg^{2+} > Na^+ > NH_4^+$. Note that in both stands K concentrations declined in the second year while Ca and Mg concentrations were less variable and tended toward slight increases. The potassium decrease in the second year may be due primarily to a concentration-dilution effect, since the ratios in average K in the first year to the second year were similar to such a ratio for chloride. Though the average sample amount (hydrology) recovered per collection in the ZTL's was not on average higher in the second year, there was more rainfall (figure 1.2) and there were more collections (table 2.2).

Calcium and magnesium in forest-floor leachate appeared consistently elevated over concentrations in TF and appeared to maintain relatively constant average annual concentrations (table 2.1). Potassium, however, showed no such consistent relationship to throughfall levels and showed greater variability.

Nitrogen treatment effects. The effects of chronic N amendment at Harvard Forest on selected cations and anions in forest-floor leachate are shown in figures 2.2 through 2.9. Volume-weighted mean concentrations within each stand, litter year and N treatment are shown. Nitrate and ammonium concentrations (figures 2.2 and 2.3) show dramatic increases in N treatments relative to reference plots; 1993 and 1994 were the 6th and 7th years of NH_4NO_3 addition to these plots. In addition to the obvious patterns of increasing ammonium and nitrate with increasing N amendment, three broad patterns emerge in forest-floor leachate chemistry: (1) nitrate concentrations were consistently higher than ammonium concentrations; (2) total inorganic N concentrations were consistently higher in pine stand than in the hardwood stand; (3) in high-N treatments, nitrate and ammonium concentrations were both higher in year 1 than in year 2.

Volume-weighted calcium, potassium, magnesium and H^+ concentrations all increased significantly with N treatment in the red pine stand (figures 2.4 through 2.7). In the mixed hardwoods the patterns were varied and less clear. Hydrogen ion increased significantly in both years, the only cation to show a significant increase. In the first year Ca and Mg concentrations showed trends toward increases with N treatment, whereas K exhibited a decreasing trend with N treatment. In the second year in the hardwood stand, decreases in Ca and Mg with treatment were significant at the $p < 0.05$ level, whereas K concentrations appeared unaffected by treatment.

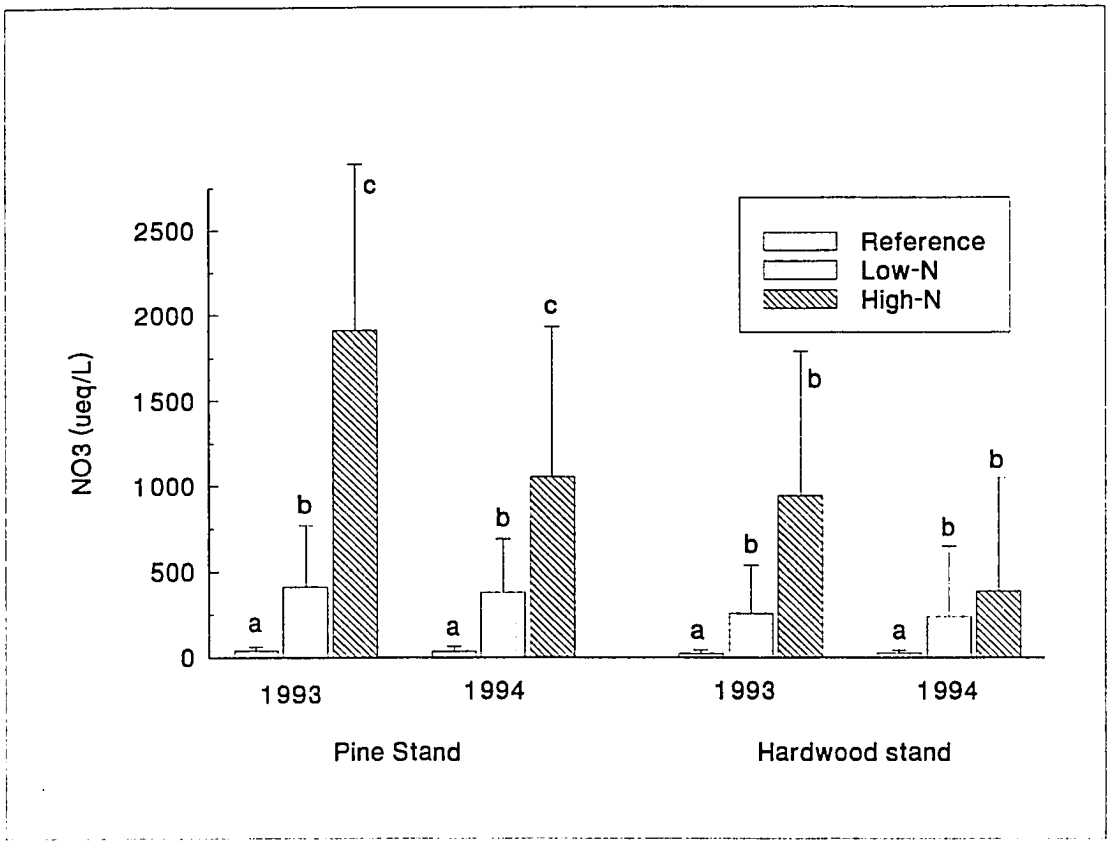

Figure 2.2. Nitrate concentrations in Oa-leachate by stand, year and N treatment. Data are volume-weighted and separated by litterfall year. Litter year 1 (1 October 1992 to 30 September 1993) is designated 1993; litter year 2 (1 October 1993 to 30 September 1994) is designated 1994. Error bars represent standard deviations within each sample set. For 1993, $n = 13$ in each bar shown; for 1994, $n = 20$ in each bar shown. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

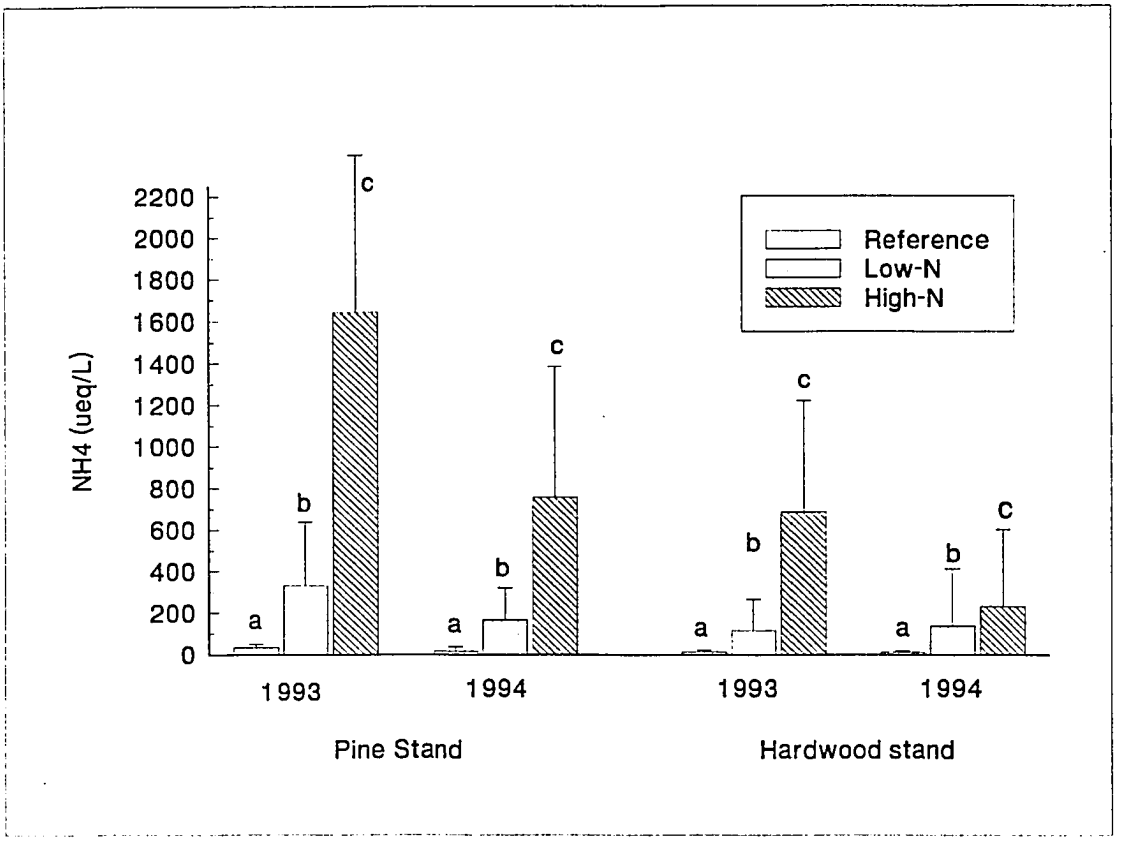

Figure 2.3. Ammonium concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

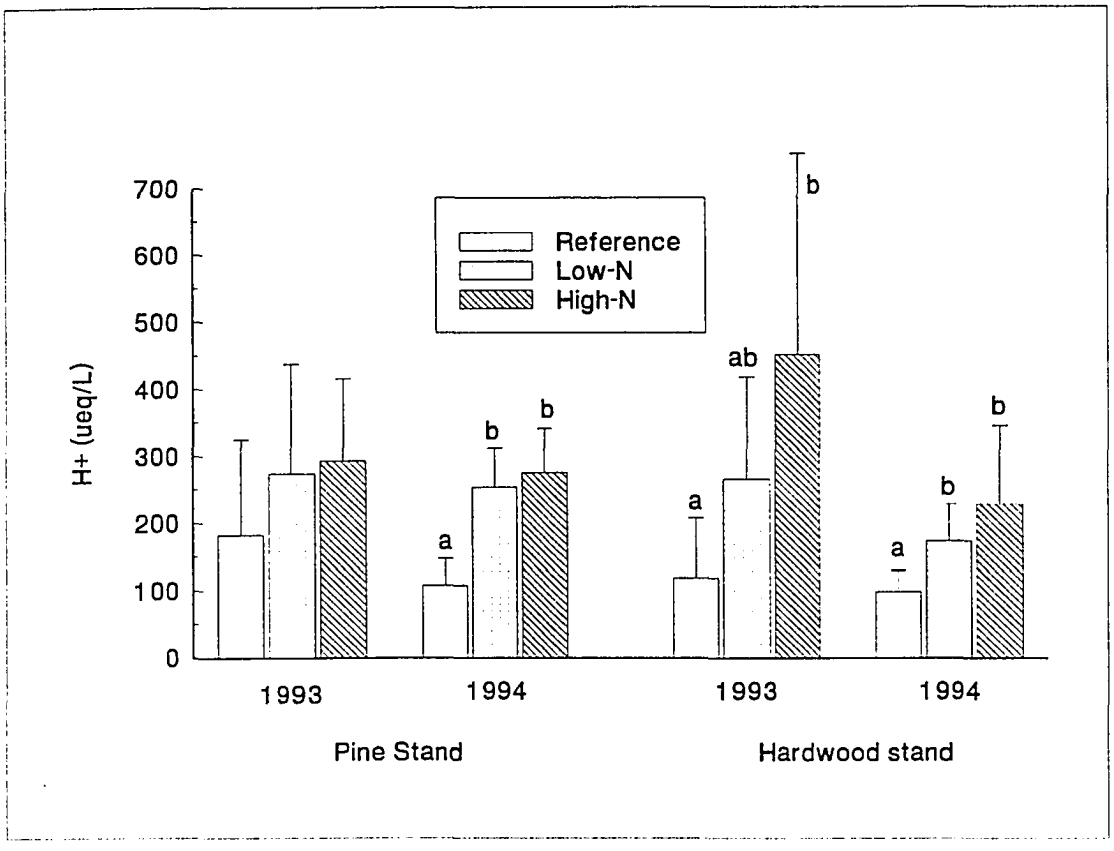

Figure 2.4. Hydrogen ion concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

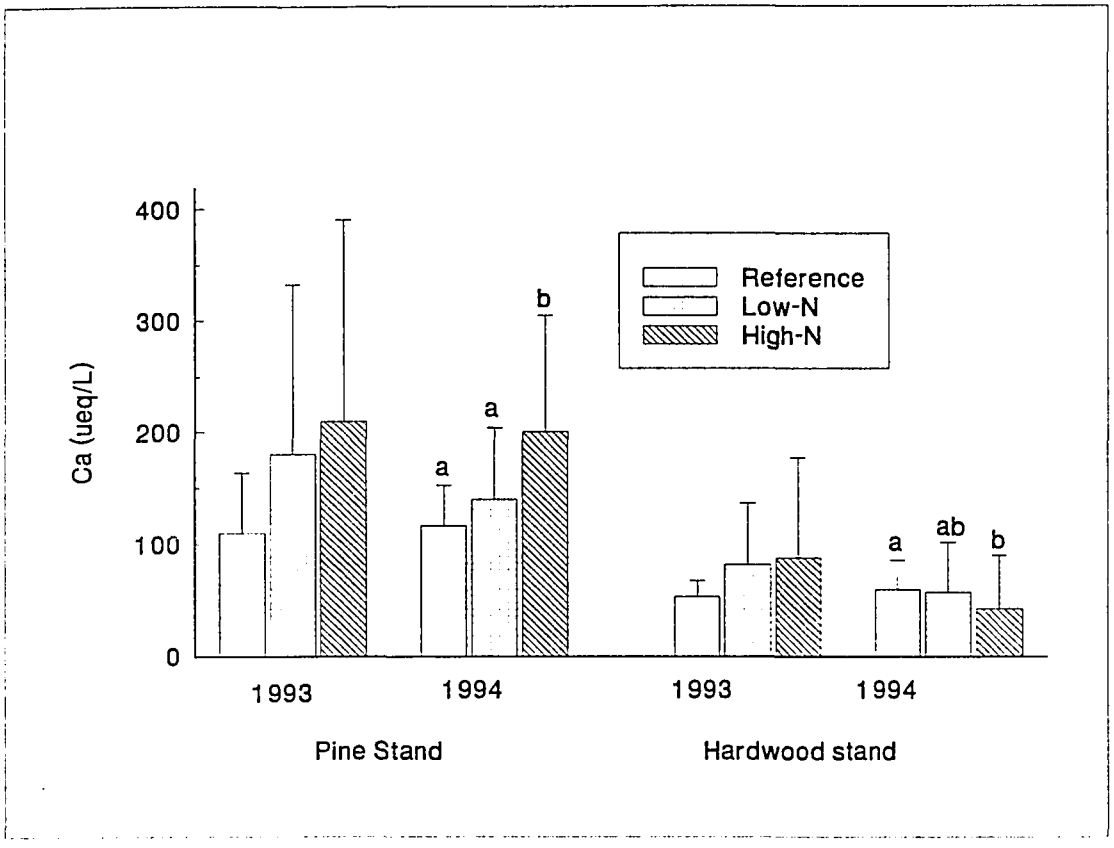

Figure 2.5. Calcium concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

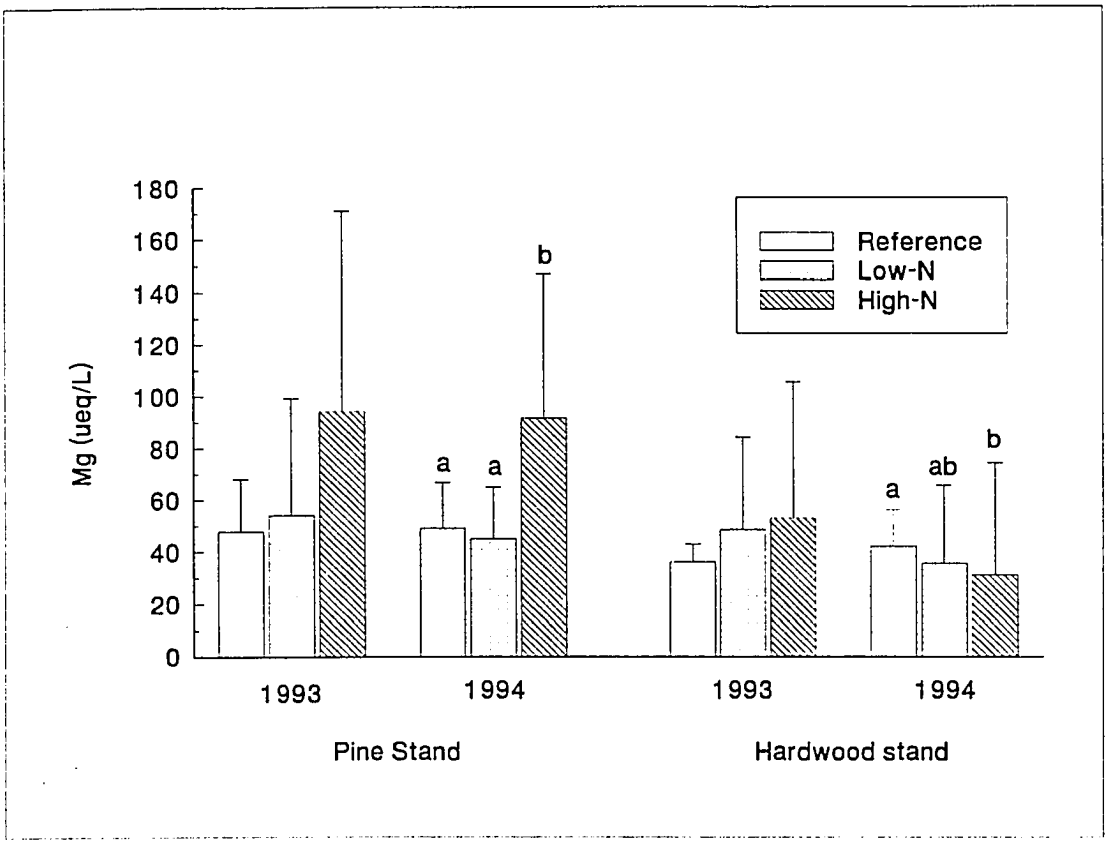

Figure 2.6. Magnesium concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

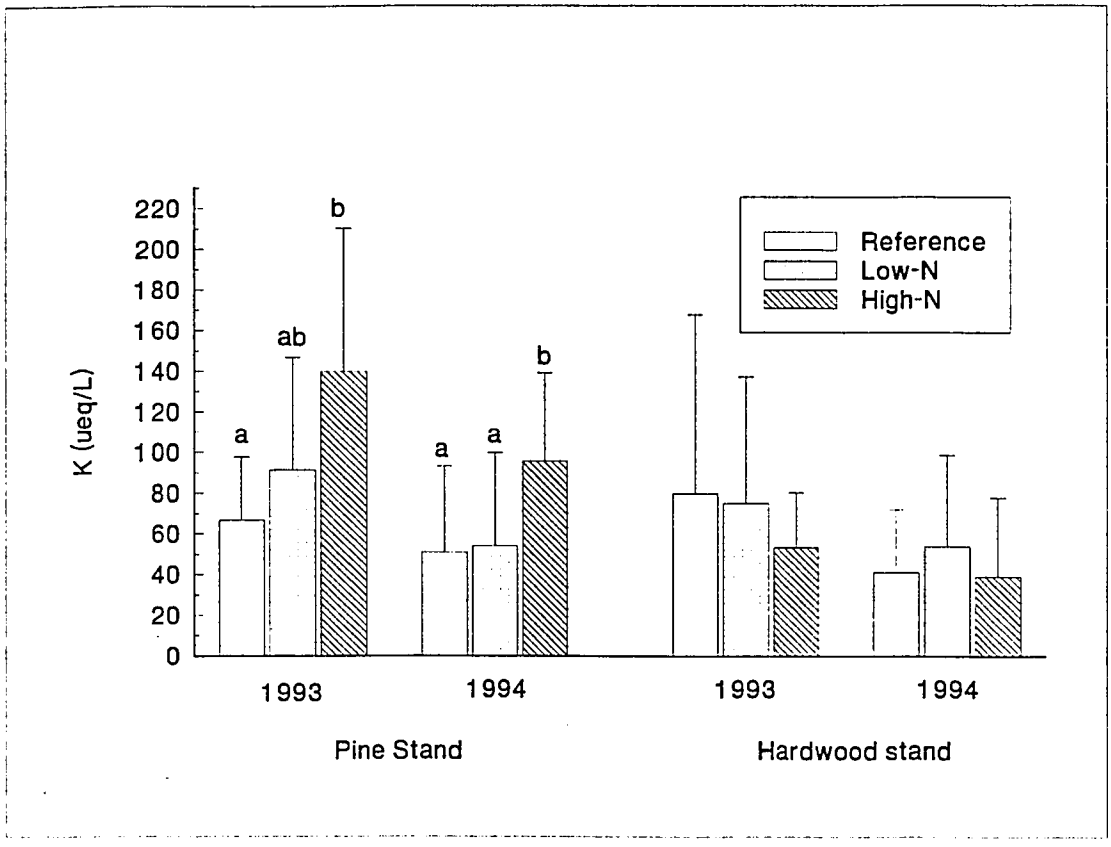

Figure 2.7. Potassium concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

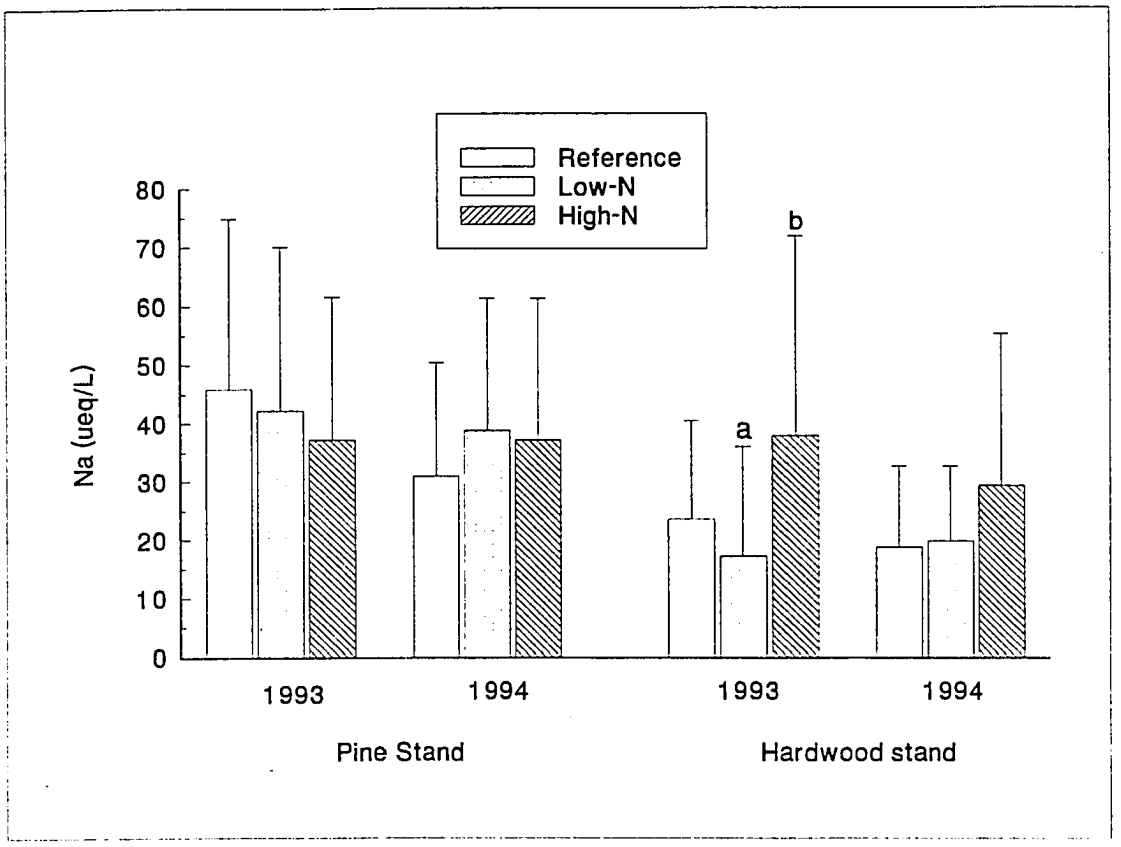

Figure 2.8. Sodium concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. Different letters indicate significant differences in means among N treatments within each stand and year ($p < 0.05$).

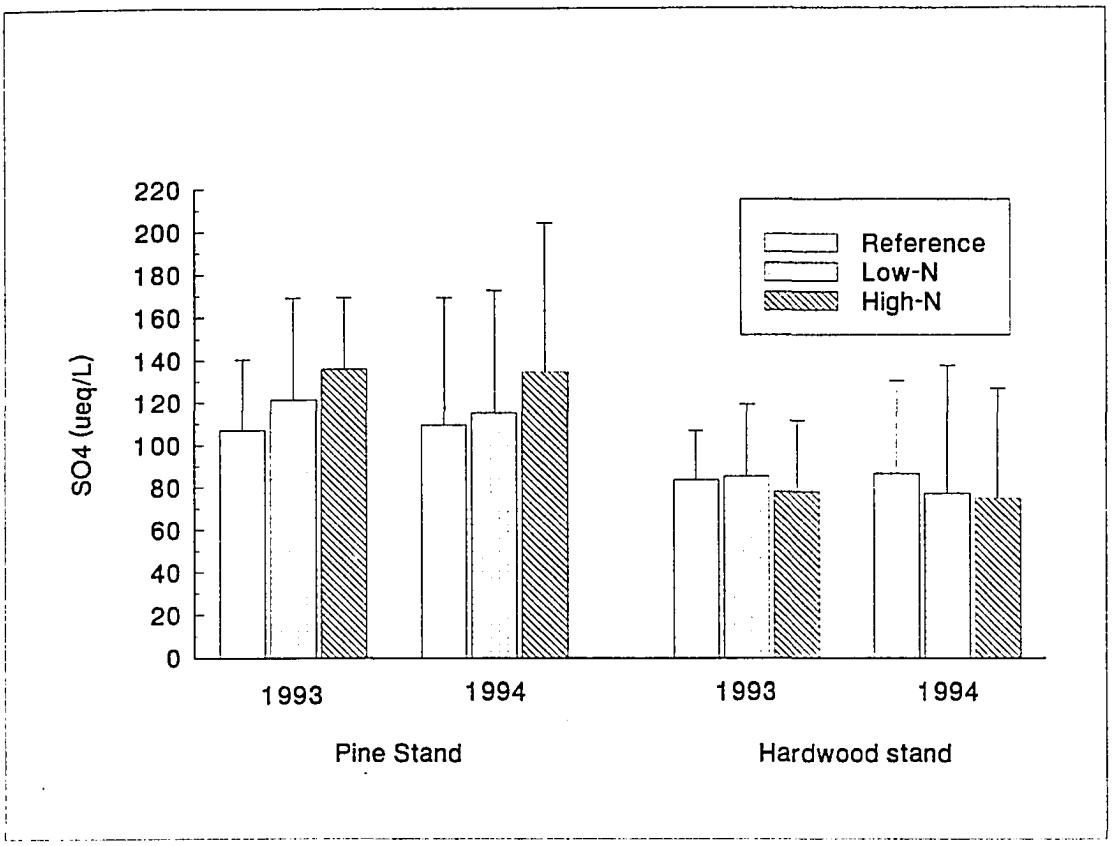

Figure 2.9. Sulfate concentrations in Oa leachate by stand, year and N treatment. Error bars and sample numbers are as in figure 2.2. No differences shown were significant at the confidence level $p < 0.05$.

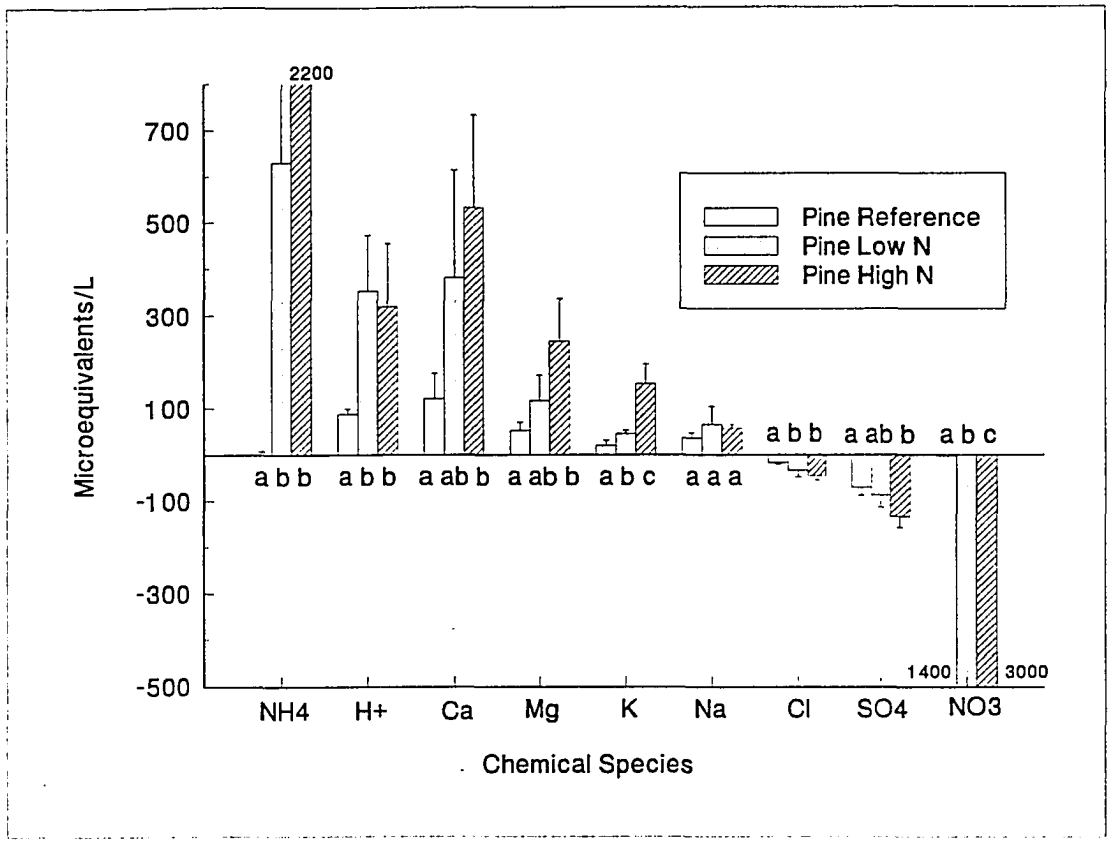

Figure 2.10. Pine stand Oa-leachate chemistry from a single collection set. Data shown are from an unbulked set of 30 separate ZTL samples collected 28 September 1994. Each bar represents a mean of 5 samples from each treatment. Error bars shown are standard deviations within the set of 5. Note that some nitrate and ammonium values extend beyond the drawn axes. Different letters indicate significant differences among N treatments ($p < 0.05$).

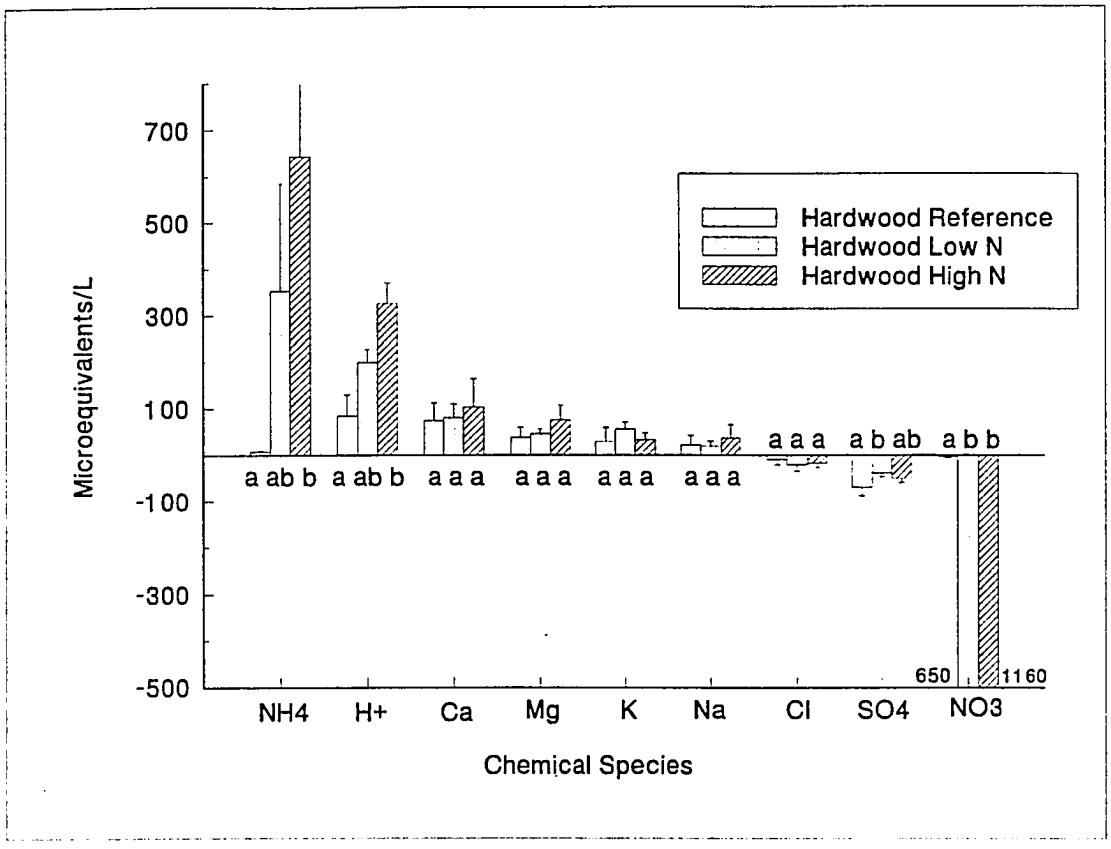

Figure 2.11. Hardwood stand Oa-leachate chemistry from a single collection set. Data shown are from an unbulked set of 30 separate ZTL samples collected 28 September 1994. Each bar represents a mean of 5 samples from each treatment. Error bars shown are standard deviations within the set of 5. Note that some nitrate and ammonium values extend beyond the drawn axes. Different letters indicate significant differences among N treatments ($p < 0.05$).

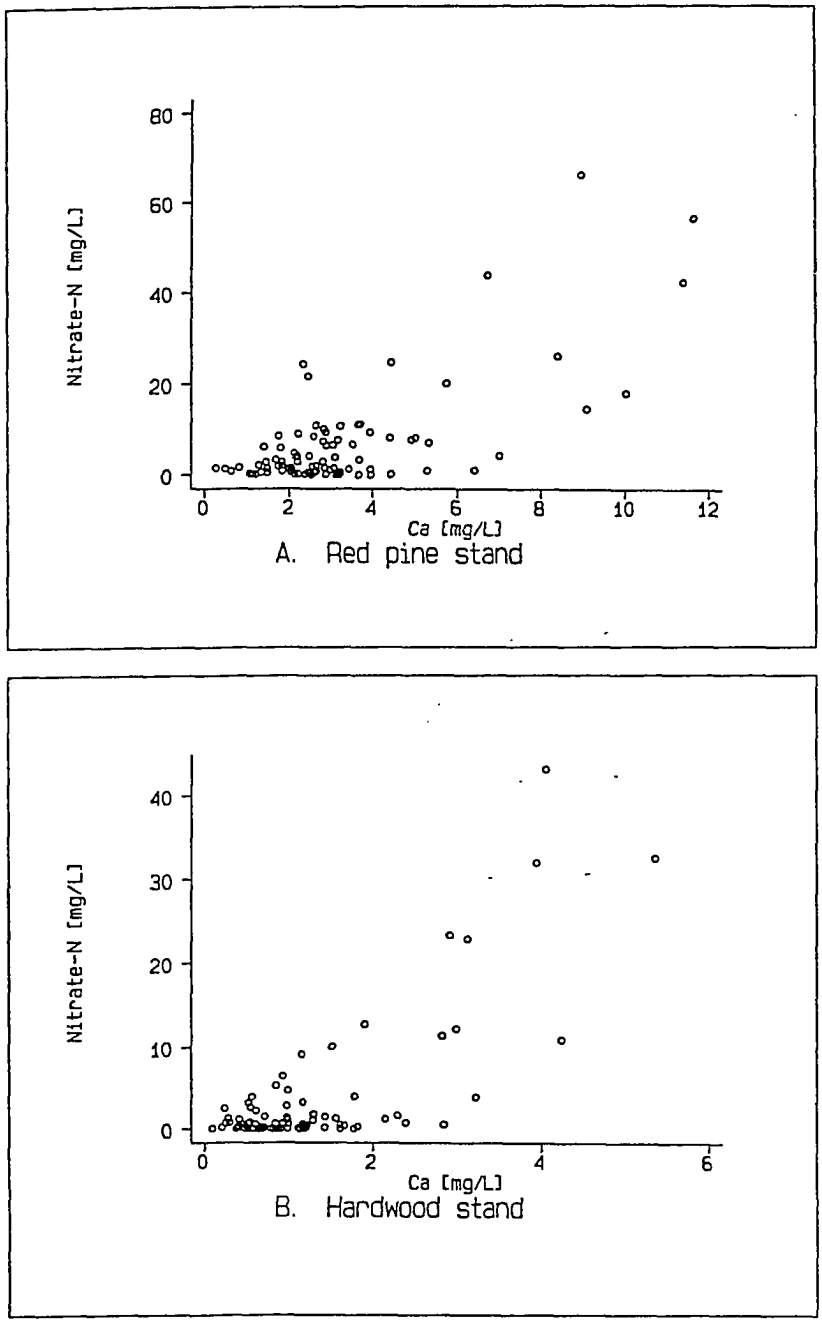

Figure 2.12. Nitrate versus calcium concentrations in Oa leachate. Data are reported in [mg L^{-1}] in this figure. Data are combined among plots within each stand (reference and nitrogen treatments), covering the entire two-year sampling period. (A). Red pine stand. (B). Hardwood stand.

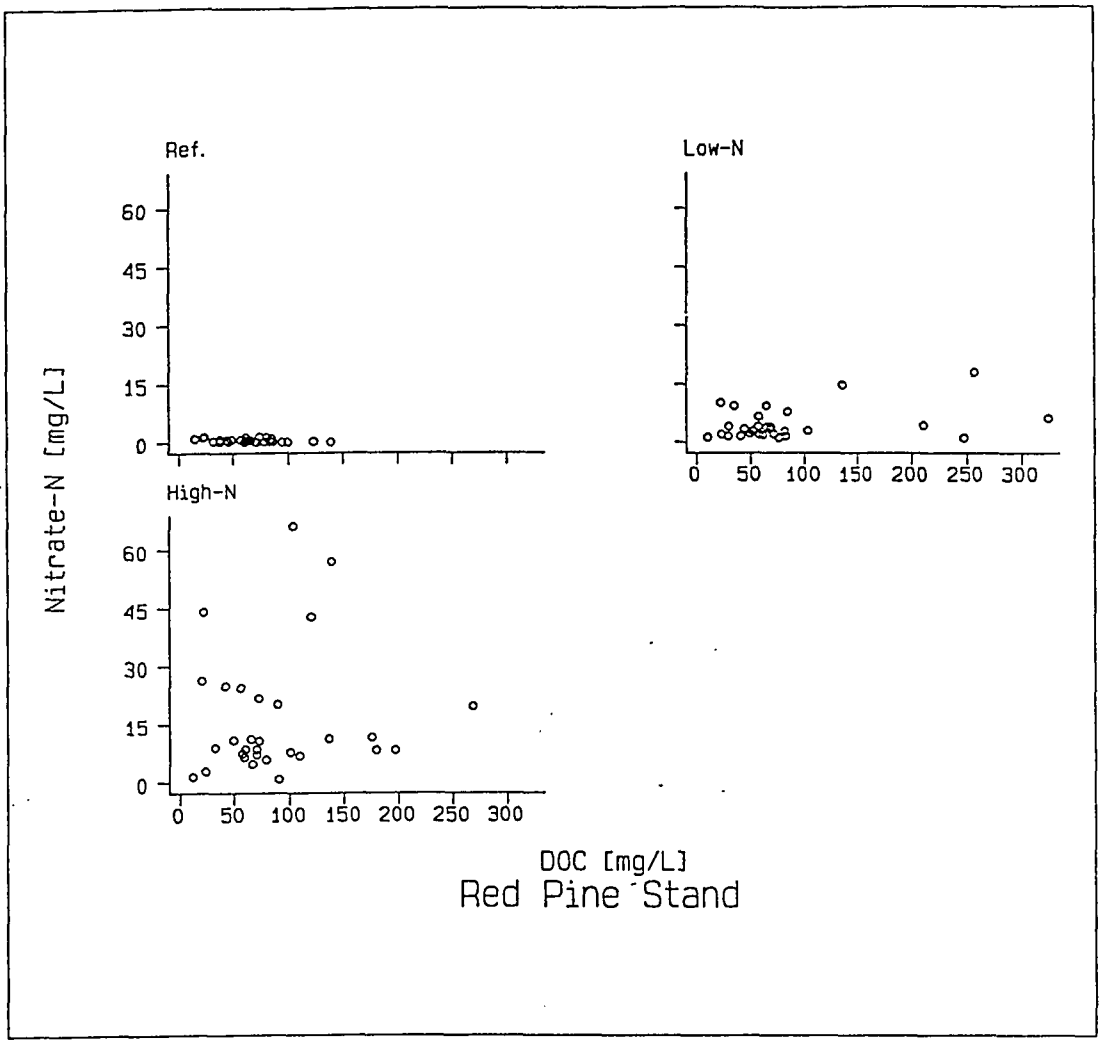

Figure 2.13. Pine stand nitrate-N versus DOC concentrations in Oa leachate. Nitrate-N data are reported in [mg N L^{-1}] and DOC data in [mg C L^{-1}]. Data are shown for red pine stand reference, low-N treatment and high-N treatment plots. Data cover the entire two-year sampling period.

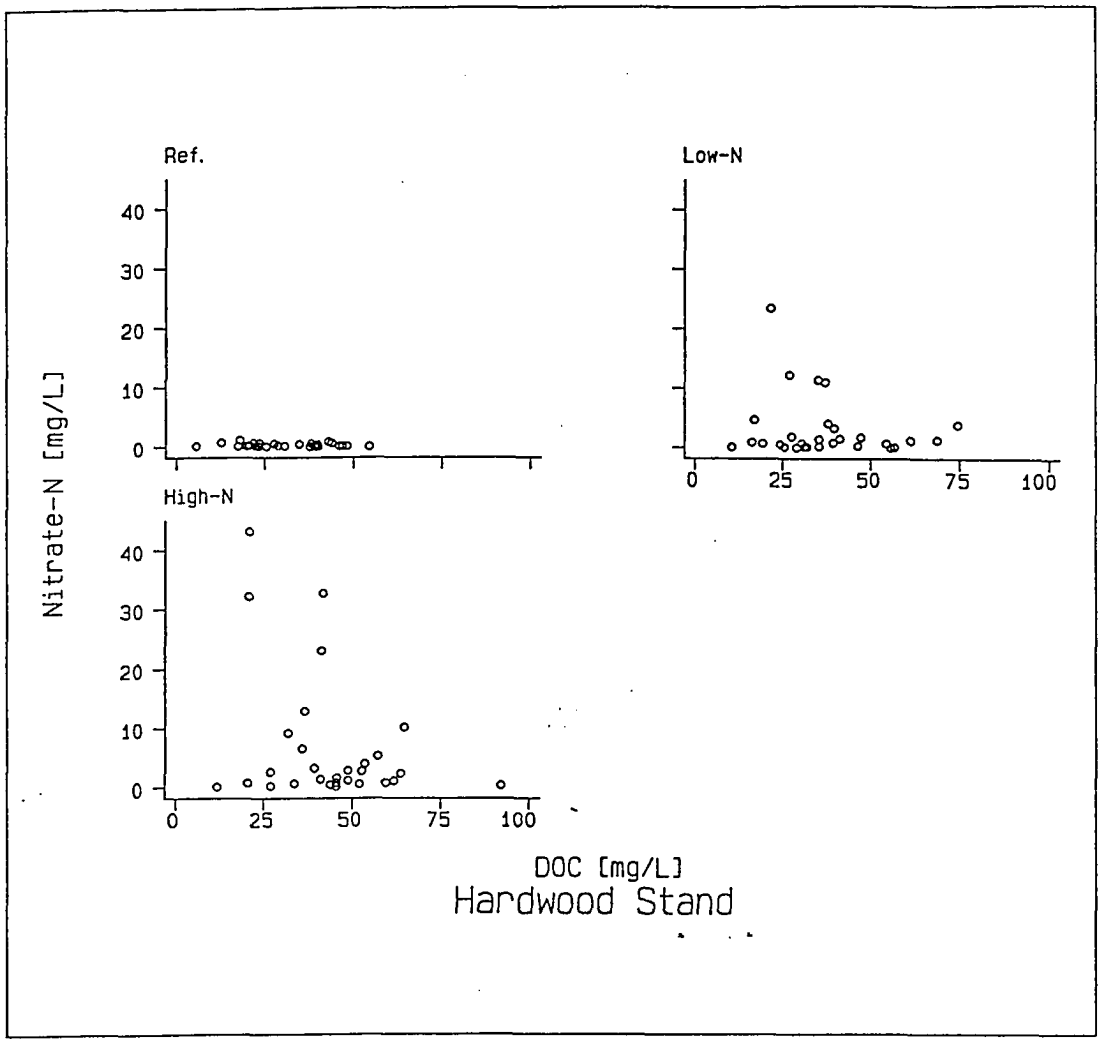

Figure 2.14. Hardwood stand nitrate-N versus DOC concentrations in Oa leachate. Nitrate-N data are reported in [mg N L^{-1}] and DOC data in [mg C L^{-1}]. Data are shown for red pine stand reference, low-N treatment and high-N treatment plots. Data cover the entire two-year sampling period.

Nitrate-N concentrations were positively correlated with calcium concentrations in Oa leachate in both stands (figure 2.12). The nitrate-calcium relationship in the pine stand, across reference and N treatment plots (figure 2.12 A), was highly significant with $p < 0.001$ and $r^2 = 0.51$. In the hardwood stand the relationship was also highly significant with $p < 0.001$ and $r^2 = 0.57$, however the calcium concentrations in solution were much lower (figure 2.12 B). Nitrate and DOC concentrations in the pine stand reference plot showed a negative correlation with a high degree of scatter ($p = 0.03$, $r^2 = 0.16$; figure 2.13). Nitrate and DOC concentrations were not significantly correlated in the hardwood reference plot or in the N-treated plots in either stand (figures 2.13 and 2.14).

Anion predominance (charge equivalence) in both stands and both high- and low-N treatments occurred in Oa leachate in the order $NO_3^- > SO_4^{2-} > Cl^-$. Cations in the red pine stand were present in the order $NH_4^+ > H^+ > Ca^{2+} > K^+ > Mg^{2-} > Na^+$, the same order as in reference plots but with ammonium moved from last to first in the hierarchy. In the hardwood stand the overall order was $NH_4^+ \geq H^+ > Ca^{2+} \geq K^+ > Mg^{2+} \geq Na^+$ in the high-N treatment, again similar to reference plots except with ammonium moved from last to first. In the low-N treatment, however, H^+ charge concentrations dominated over NH_4^+ (figures 2.4 and 2.3).

Unbulked collection sets. The unbulked ZTL collection sets provide confidence limits on chemical results from a single date, since five separate samples were collected and analyzed within each stand and treatment combination. The results from the single

unbulked collection retrieved on 28 September 1994, at the end of the two-year study, are shown in figures 2.10 and 2.11. Some patterns in the unbulked set mirror those in the two-year data; other patterns do not, highlighting the temporal variability in forest floor chemistry.

In the unbulked set shown here, the total, dissolved inorganic nitrogen component (nitrate plus ammonium) in the high-N treatments had a net negative charge of 800 ueq L^{-1} in the pine stand and nearly 600 ueq L^{-1} in the hardwood stand. These differences together with chloride and sulfate concentrations amounted to negative charges 3.1 times and 2.6 times the total cation charge in the reference plots on this date in the pine and hardwood stands, respectively. In the pine stand, offsetting this negative charge, Ca was the cation that increased to the highest charge equivalents, followed by H^+, Mg, and K; all of these elevated concentrations were significantly higher in the high-N treatment than in the reference plot.

Chemistry in the forest floor solution of the hardwood stand responded quite differently to the extreme concentrations of ammonium and nitrate and extreme charge imbalance in the total inorganic N component. Only H^+ increased significantly, and it increased more than threefold over reference concentrations.

Additional statistical tests. Results of other specific statistical tests on Oa-leachate chemistry (listed above in the Statistical Analysis methods section) are listed in table 2.3. There were significant concentration differences between hardwood and red pine reference plots in most species analyzed (column A); exceptions were H^+, K and

nitrate. There were not significant differences in most aspects of reference-plot Oa-leachate chemistry between the first and second years of the study (Column B). Exceptions were ammonium and sodium in the red pine reference, which were significantly lower in the second year.

When N treatments were included, there were many more evident differences between year 1 and year 2 of the study (table 2.3 column C). In the hardwood stand Ca was significantly lower in the second year. Potassium was significantly lower in both plots in the second year. Ammonium was significantly lower in both plots in the second year.

The answer to the question of whether I observed an analysis-of-variance interaction effect between stand type and N treatment was yes: significant interactions were discovered in all chemical species except hydrogen ion and ammonium (table 2.3 column D). This provides strong evidence that responses to chronically elevated nitrogen inputs can vary significantly between different forest ecosystem types in close proximity.

Table 2.3

Chemical Spp.	A	B Red Pine	B Hardwoods	C Red Pine	C Hardwoods	D
Ca^{2+}	$p < 0.001$	--	--	--	$p = 0.008$	$p = 0.002$
Mg^{2+}	$p = 0.025$	--	--	--	--	$p < 0.001$
K^{+}	--	--	$p = 0.055$	$p < 0.001$	$p = 0.004$	$p < 0.001$
Na^{+}	$p < 0.001$	$p = 0.049$	--	--	--	$p = 0.047$
SO_4^{2-}	$p = 0.013$	--	--	--	--	$p = 0.033$
NO_3^{-}	$p = 0.054$	--	--	--	$p = 0.068$	$p = 0.026$
NH_4^{+}	$p = 0.009$	$p < 0.001$	--	$p < 0.001$	$p = 0.033$	$p = 0.097$
H^{+}	--	--	--	--	$p = 0.067$	--

Table 2.3. Stand, year and N treatment differences in Oa-leachate chemistry. P-values resulting from analyses of variance are shown. Tests were performed on volume-weighted concentrations in ueq L^{-1}. P-values lower than 0.10 are listed, although only those below 0.05 are considered significant. To see whether differences were increases or decreases in concentration, see the data in figures 2.2 through 2.9. Columns represent test results for each chemical species for the following effects:

A. Difference between red pine reference and hardwood reference (two years grouped together).

B. Within each stand separately, a difference in chemistry between litterfall years 1 and 2 in reference plots.

C. Within each stand separately, a difference in chemistry between litterfall years 1 and 2 when reference and N treatment plots are included.

D. An interaction effect between stand and N treatment (two years grouped together).

Discussion

Soil Solution Acidification and Base Cation Leaching

Decomposition and leaching from foliar litter in the forest floor ordinarily release base cations because base cations are concentrated in decomposing litter more slowly than litter mass is lost (Staaf and Berg, 1982; Blair, 1988; Foster et al., 1989). Anions controlling the leaching of base cations from forest organic horizons can be bicarbonate, organic acid anions, sulfate or nitrate (Johnson et al., 1985; Morrison et al., 1992). In both stands at the Harvard Forest, sulfate was the dominant anion in throughfall and in the reference plots the dominant anion in Oa-leachate.

Sulfate concentrations were highly variable, but volume-weighted sulfate concentrations appeared to be tightly controlled in the hardwood stand in all treatments in both years. As noted above, sulfate remained close to its two-year mean concentration (in hardwood Oa-leachate) of 88 ueq L^{-1} even though sulfate in TF varied significantly ($p = 0.04$) from the first to the second year. In the pine stand, sulfate concentrations also remained nearly constant in Oa-leachate between the two years despite significant differences in concentrations of sulfate ($p = 0.02$) and other species in throughfall. These patterns may suggest an anion exchange mechanism at work in the forest floors of both stands. Anion exchange in the forest floor could also explain the trend toward increasing sulfate concentrations in Oa-leachate with increasing nitrate concentrations in the pine stand (figure 2.9).

Nitrogen amendment responses. Nitrate was the dominant anion in Oa-leachate in all four N-amended plots. Responses to chronic N amendment in both stands at Harvard Forest showed strong acid (nitric) acidification of Oa leachate with decreases in Oa-leachate pH. The fertilizer sprayed on the litter layer in the Chronic N treatment plots was a neutral salt. The net effect after forest-floor processes operated, however, was to increase inorganic N as an anion relative to inorganic N as a cation in Oa solution. The primary cause may be attributable to preferential retention of ammonium in the O horizons. Extractions (KCl) performed on these O horizons show a strong increase in extractable NH_4^+ with treatment in both stands, with minor or no increases in extractable NO_3^- (Magill et al., *in preparation*). Though both ammonium and nitrate are taken up in the forest floor through biotic processes (Aber et al., 1993), abiotic sorption of NH_4^+ in forest soils dominates significantly over sorption of NO_3^- (Johnson et al., 1986).

Chronic N amendments in the red pine stand have led to increased nitrification in the O horizon and to the presence of high nitrate concentrations in 60 cm deep tension lysimeters (Magill et al., *in preparation*). These symptoms of N saturation are similar to those at Turkey Lakes Watershed (TLW) in Ontario, an old-growth *Acer saccharum* (Sugar maple) forest exhibiting nitrification in and high concentrations of nitrate leaching from the forest floor (Mitchell et al., 1992). The nitrate leaching at TLW contributes to the leaching of base cations from the forest floor (Morrison et al., 1992).

Stand Differences

The greater nitrate leaching in the pine stand is not due to vegetation type *per se.* In the Adirondack Manipulation and Modeling Project (AMMP; Mitchell et al. 1994), a

plot-scale manipulation study similar in some respects to the Harvard Forest Chronic N study, nitrification and elevated nitrate leaching have occurred in three widely separated northern hardwood stands but not in a red pine stand.

In both stands at Harvard Forest, nitrate leaching from the forest floor is significant and nitrate concentrations in Oa leachate are correlated with Ca concentrations (figure 2.12). However, increased levels of nitrate leaching have led to increased leaching of base cations in N-amended plots more strongly and clearly in the pine stand than it has in the hardwood stand (figures 2.5 through 2.7; figure 2.12).

In the unbulked collection set shown in figures 2.10 and 2.11, H^+ was the only cation to increase significantly in the hardwood stand, offsetting the high net negative charge in inorganic N in solution. In the pine stand higher concentrations of base cations entered solution, mitigating the increase of solution H^+. Other processes could potentially have contributed to the dramatic H^+ concentration increase in the hardwood stand under N amendment. Some of these include increased oxidation of reduced minerals, increased generation of organic acids during decomposition, or greater accumulation of cations in the forest biomass over the seven years of N additions (Driscoll and Likens, 1982). The mixed hardwood stand is dominated by oaks (*Quercus* spp.; Aber et al., 1993), which are sometimes observed to posses relatively high biomass Ca concentrations (Johnson and Risser, 1974; Cole and Rapp, 1981). Upper mineral-soil solution under a mixed oak stand exhibited lower Ca fluxes than that under a pine stand in the same watershed, on presumably similar soils, in Wisconsin (Jepsen and Bockheim, 1983).

Oa leachate chemistry differences between years

As with the dissolved organic C and N concentrations discussed in Chapter I, I noted differences in the inorganic chemistry of Oa-leachate between the first and second years of the study (table 2.1). In the second year of sample collection relative to the first, calcium, potassium and nitrate concentrations decreased. It also appeared here (as in Chapter I) that differences between the first and second years may have been partly mediated through interactions with N availability or N leaching. In table 2.3, more differences between the two years were noted when N treatments were included (columns C) than when only reference plots were considered (columns B).

Disturbance effects. Disturbance to the forest floor has been hypothesized to cause increased nitrate and base cation leaching (Arthur and Fahey, 1993). When half of the forest floor that had developed under black spruce in Alaska was removed, Ca and Mg increased in forest-floor leachate without an attendant increase in nitrate (Van Cleve and Dyrness, 1983). In the treated plots in the present study, nitrogen fertilizer had been applied for five years prior to lysimeter installation, raising KCl-extractable NH_4^+ levels significantly in the treated O horizons relative to references. Ammonium (NH_4^+) concentrations in Oa-leachate were significantly higher in both stands the first year when treated plots were considered (table 2.3 column C). It seems plausible that disturbance due to ZTL installation may have stimulated mineralization of NH_4 in the first year, causing the interannual difference in ammonium leaching. The decrease in NH_4 in Oa-leachate the second year in the pine reference plot is especially notable. It may also have been plausible to expect, however, that disturbance to the Oa horizon causing

increased labile C availability (as hypothesized in Chapter I) should have increased microbial immobilization of NH_4 rather than mineralization.

Mitchell et al. (1994) installed tension lysimeters in mineral soil the same time of year that I installed the ZTL's (July and August), and considered the disturbance of lysimeter installation to cause elevated nitrate concentrations. The effect had diminished by the first spring following lysimeter installation. The bulk of my ZTL sample sets (11 of 13 the first year) were taken at least one winter and spring (9 months) after installation. Disturbance effects may have lasted longer here than in the Mitchell et al. (1994) study.

Another possibility to explain the interannual differences could be that increased rainfall in the second year resulted in diluted base cation inputs to the forest floor in TF as discussed above, affecting cation concentrations in forest-floor leachate. In sum, though some of the inorganic chemistry data may support the interpretations of disturbance made in Chapter I, the inorganic chemistry data do not in themselves provide strong evidence of disturbance.

Site Base Status

New England forest floors are ordinarily considered to have high buffer capacity, over a wide pH range, arising from cation exchange (Federer and Hornbeck, 1985; David et al. 1989). The greater Ca response to N treatment over K and Mg response in the pine stand is consistent with the contribution each ion ordinarily makes to saturation of the cation exchange complex (CEC) in O horizons in northeastern Spodosols (Dethier et al., 1988; Foster et al., 1989; David et al., 1990).

Leaching of base cations from the forest floor does not necessarily imply a loss of base cations from the ecosystem, because base cations can be taken up by roots in mineral soil and recycled to the forest floor in litterfall (Johnson et al., 1985). Over the time scale of forest aggradation, base cations can accumulate in forest biomass contributing to soil cation depletion and to acidification of forest soil (Driscoll and Likens, 1982). Whether the base status of forest stands in northeastern North America would be preserved under increased rates of nitrate leaching would depend on a number of factors. These include vegetation growth rates and accumulation of cations in biomass, removal of nutrient cation capital from forest sites during harvesting, soil parent material and mineral weathering rates, fluxes of anion leaching and rates of internal cation cycling in the ecosystems (Morrison et al., 1992; Currie et al., *in press*).

CHAPTER III

A PROCESS MODEL-BASED EXTRAPOLATION OF FOREST-FLOOR DECOMPOSITION DYNAMICS TO COVER A HETEROGENEOUS LANDSCAPE

Introduction to the Modeling Project

Because of the storage and transformations of carbon and nutrients in forest litter and humus layers, ecosystem ecologists have sought to understand controls on forest-floor mass and nutrient dynamics for decades (McFee and Stone, 1966; Gosz et al., 1976; Aber et al., 1978; Federer, 1984; Snyder and Harter, 1987). Understanding dynamics and distribution of mass of the forest floor (and thus C stores) requires quantifying material gains in litter fluxes and material losses through decomposition and leaching. Understanding controls on nutrient stores and nutrient transformations such as mineralization and immobilization requires additional complexity. Computer models of ecosystem dynamics or net ecosystem production make use of organic-matter decomposition submodels that typically describe two principal controls: climate, as represented by an index such as actual evapotranspiration (AET), and chemistry of fresh litter (Meentemeyer, 1978; Pastor and Post, 1986; Parton et al., 1987; Rastetter et al., 1991). Recent field studies have made it possible to incorporate more broadly-derived relationships into decomposition models and to test them more broadly as well (Berg et al., 1994; LIDET[1], *unpublished data*). In addition, an increasingly mechanistic

[1] LIDET: LTER (Long-Term Ecological Research) Intersite Decomposition Experiment Team.

understanding of litter mass and nutrient dynamics is developing as field investigators measure proximate carbon fractions in litter (Ryan et al., 1990) and conceptual models are developed that reference carbon fractions (Berg et al., 1984; White et al., 1988; Taylor and Parkinson, 1988; Aber et al., 1990; Means et al., 1992).

Across an actual landscape, the forest floor exhibits high levels of heterogeneity in structure and function. Topography, landform and soils, microclimatic variability, wind patterns and patch disturbances each contribute to variability in forest floor thickness, mass and nutrient cycles. Species distribution and stand age also exert important controls. The coupling of a process model to a Geographic Information System (GIS) through the use of data layers as model inputs and outputs (Aber et al., 1993) can directly address some spatial environmental heterogeneity. Also, some heterogeneity of ecological responses to global or regional change can be treated explicitly, affording more precise estimates of ecosystem responses at local scales. For example, a process-model coupled to a GIS could identify forest patches more likely to reach limits of nitrogen retention and to experience nitrogen saturation (*sensu* Agren and Bosatta, 1988; Aber et al., 1991). Watersheds more likely to export nitrate to surface and ground water (Kahl et al., 1993; Mitchell et al., 1994) could then be identified. In addition, process modeling across actual landscape heterogeneity could provide improved scaled-up estimates of ecosystem responses to change at regional or biome scales.

My objectives in this study were as follows: 1) To use field measurements of changes in proximate C fractions and N content over time to construct a process model of C fraction and N dynamics during decomposition and humification; 2) To model forest

floor dynamics during recovery from disturbance by including foliar, root and woody litter inputs over time; 3) To couple the decomposition process model to a production process model using GIS data layers as interfaces; and finally, 4) To apply the model across a heterogeneous landscape. During model development, I validated the basic equations through blind predictions of litter decomposition over a two-year period in widely disparate ecosystems. I then linked the forest-floor model, DocMod, to a spatially-explicit model of forest production, PnET-II (Aber and Federer, 1992; Aber et al., *submitted*), to model forest-floor mass and nitrogen capital across an area of 286,000 ha, the White Mountain National Forest (WMNF). The WMNF landscape has steep climatic gradients and well-documented elevational gradients in species distribution.

The White Mountains of New Hampshire

Vegetation

At elevations below approximately 760 m in White Mountain National Forest, the northern hardwood forest type predominates, comprising *Prunus pennsylvanica* or *Betula papyrifera* as pioneers, yielding to *Acer saccharum, Fagus grandifolia* and *Betula alleghaniensis* in later succession (Bormann and Likens 1979; Federer et al., 1990; Botkin, 1993). *Tsuga canadensis* is present at lower elevations, grading to *Picea rubens* above ca. 450 m (Reiners and Lang, 1979). *Pinus strobus* is also present at lower elevations in some locations with agricultural history (M.-L. Smith, *personal communication*). Spruce-fir forest occurs from ca. 760 m to ca. 1220 m with *Abies balsamea* predominating over *P. rubens*. at higher elevations, though *P. rubens* does extend higher into the subalpine fir zone. The latter zone begins above ca. 1220 m,

comprising largely *A. balsamea* with some *B. papyrifera* var. *cordifolia*. Above tree line (approximately 1450 m), low *krummholz* is present (Reiners and Lang, 1979), above which the vegetation community is arctic tundra.

Disturbance and land use history

Nearly all accessible New Hampshire forests were logged in the 19th or early 20th century for commercial timber or fuelwood, and much of the land was cleared and put into agriculture. The nadir of forest cover in NH was 48% in 1860. With abandonment of much agricultural land at the turn of the century, New Hampshire as a whole has reforested to a current level of 87% forest cover (Ober, 1992). At Hubbard Brook Experimental Forest (HBEF) in southeastern WMNF (elevations of 222 to 1015 m), selective cutting may have occurred prior to 1909, with subsequent heavy logging completed by 1917 (Bormann and Likens, 1979). Little logging has occurred in the subalpine fir zone of the White Mountains, but natural disturbances include avalanche, fir waves and hurricanes (Lang et al., 1981). Fir waves are a phenomenon in which a front of synchronous fir mortality moves through the forest with a period of approximately 60 years (Sprugel and Bormann, 1981). Hurricane tracks passed directly through WMNF in 1788 and 1815. A more recent hurricane track passed to the west in 1938 (Foster and Boose, 1992), causing substantial patch blowdowns in WMNF. Current land use in WMNF is 46% designated multiple use with timber management, 34% designated recreation without timber management, 14% wilderness and 6% other land use (Harper et al., 1990).

Climate

At HBEF at approximately 500 m elevation (weather station 1) long-term mean daily temperature is -8.8 C in January and 18.7 C in July. At the same point, average precipitation is 1327 $\pm$ 203 mm (sd) . It is distributed fairly uniformly throughout the year. Precipitation generally increases with elevation, though data throughout the region are sparse for sites above 600 m (Ollinger et al., 1993). Prevailing winds blow from the North or Northwest. Snow depths at HBEF reach 0.3 to 1 m on southern aspects and 1.5 m at high elevation (900 m) northern-aspect locations (Federer et al., 1990). In the subalpine fir zone in WMNF, annual wet deposition has been estimated as averaging 1460 to 1750 mm, with fog and rime ice deposition adding significantly to those figures. The number of months with mean temperature below 0° C is estimated as 7; the number with mean temperature above 10° C estimated as 4. Snowpacks last 7 months and accumulate 1 to 2 m (Fahey and Lang 1975; Reiners and Lang 1979).

Soils

Wisconsin glaciation in the White Mountains deposited variable till at lower and middle elevations. A greater amount of bouldery material is present as elevation increases from 1070 to 1370 m. Soils at HBEF in the northern hardwoods and lower spruce-fir zone are predominantly Haplorthods with a thick mor organic horizon (Gosz et al., 1976). Subalpine fir zone soils are chiefly lithic Cryorthods or Cryorhumods where there is well-drained mineral material, Borofolists (organic mats over rock) in rockier locations (which may be quite numerous), or saturated Histosols or frigid Fragiaquepts where drainage is poor (Reiners and Lang, 1979).

Background

Foliar litter is the most widely studied of forest litter types, with fine roots second, and decomposition paradigms are built largely on results of foliar and fine root decomposition studies. The distribution in size classes from fine to coarse to woody complicates the subject of root decomposition, together with the fact that different field methods for assessing fine root turnover can vary in their results by up to 50% (Burke and Raynal, 1994). Woody litter inputs (above and below ground) and decomposition may be the least well understood in the major litter classes. Woody litter is highly heterogeneous in space and time, is complicated by size classes, bark, surface area and fragmentation, and by the fact that much woody litter is standing or suspended out of contact with the forest floor. Plant reproductive parts and animal parts are often not considered in decomposition models due to the small quantities relative to foliar, root, wood and bark litter.

Decomposition comprises a complex web of processes, some of which begin even before litterfall. Soluble compounds leach from senescing tissue and fresh litter, while specialized microorganisms invade the tissues and attack the various classes of organic compounds. A high proportion of plant biomass is composed of recalcitrant organics such as lignins, which may be complexed in plant tissue with other compounds, for example hemicelluloses. The most labile and accessible compounds in a tissue are decomposed first, with the recalcitrant fraction of the initial material increasing in relative proportion in the remaining litter as time proceeds (Berg et al., 1982). All initial material is potentially decomposable by fungi (Zeikus, 1981). Limiting factors are climate,

metabolic energy requirements of decomposers relative to substrate lability (Zeikus, 1981) and in the case of fresh litter, potentially nutrient availability. As incomplete oxidation of litter material proceeds, secondary products play increasingly important roles in increasing the overall recalcitrance of litter. Eventually, depending strongly on climatic zone, some quantity of highly processed litter forms relatively stable humic substances and accumulates in the forest floor and mineral soil organic matter. There are competing theories concerning the pathways and mechanisms of humus formation, though all involve the chemical complexation of partially oxidized material into resistant polymers (Stevenson, 1982).

The negative exponential function (e^{-kt}, where k is an empirical rate constant; Olson, 1963) to describe mass remaining over time captures the essential feature of a decreasing rate of mass loss very well for the first few years of foliar and fine root decomposition. It fails to account for the eventual slowing of decomposition in advanced stages, however. Conceptual models that do have this ability, while providing a mechanistic explanation, include those that calculate decomposition rate as a function of a litter-quality index that changes through time (Berg et al., 1984). This is the essence of the *lignocellulose index, LCI* (Melillo et al., 1989), defined as lignin / (lignin + cellulose).

As partially decomposed organic material in forest soils increases in recalcitrance, it also increases in nitrogen content. Microorganisms take up available N to produce enzymes and amino sugars, compounds which eventually comprise a significant portion of humus (Stevenson, 1982). The processes of microbial immobilization of N,

mineralization of litter carbon, and complexation of N-rich compounds into resistant polymers all contribute to a narrowing C:N ratio in organic matter through time.

The present paper continues a long effort to model forest-floor mass and nutrient dynamics (Aber et al., 1978; Aber and Melillo, 1982). The model presented here, DocMod, derives from a series of field studies and analyses of litter decomposition dynamics conducted in temperate forested regions over the past 12 years (Aber & Melillo, 1982; Melillo et al., 1982; McClaugherty et al., 1985; Melillo et al., 1989; Aber et al., 1990).

Methods

Model description

Mass Dynamics. DocMod manages short-term decomposition by placing fresh litter mass into four pools: Ligno-cellulose, unprotected cellulose, and extractable material for foliar and fine root litter, and for woody litter a separate woody pool. Foliar and root mass enter each pool based on laboratory analysis (proximate carbon fractionation) performed on samples of particular litter types. The three fractions are defined as extractable, acid-soluble ("holocellulose") and acid-insoluble ("lignin") material (Ryan et al., 1990). All of the acid-insoluble material, together with an equivalent amount of acid-soluble material, enters the ligno-cellulose (LC) pool. This represents lignins and the celluloses bound with lignin in the plant tissue. The remainder of the acid-soluble material in initial litter is placed in the unprotected cellulose (C) pool, while extractable material enters the extractable (E) pool.

Material in each litter pool is subject to exponential decay. The decay constants in the LC, C and E pools are calculated on a monthly timestep from the total litter LCI, which changes as decomposition proceeds. The decay constants k in each pool are calculated from regressions of k as functions of LCI in each proximate C class, from first- and second-year mass loss data (table 3.1; Aber et al., 1990). Data derives from buried-bag incubations conducted at Blackhawk Island in Wisconsin, the Harvard Forest in Massachusetts, and Hubbard Brook in New Hampshire. Since C and E material disappear more rapidly than LC material (higher k parameters), this means C and E mass loss rates control decomposition in the early stages, whereas LC exerts more control in the later stages (Berg and Staaf, 1980; McClaugherty, 1983).

Table 3.1

$\Delta LC(t) = LC(t-1)\gamma(AET)(1-e^{-k_{LC}(t)})$	$k_{LC}(t) = 0.0011 + 0.053 \cdot LCI(t)$
$\Delta C(t) = C(t-1)\gamma(AET)(1-e^{-k_C(t)})$	$k_C(t) = 0.0476[1 - LCI(t)]$
$\Delta E(t) = E(t-1)\gamma(AET)(1-e^{-k_E(t)})$	$k_E(t) = 0.115[1 - 1.5LCI(t)]$
$\Delta H(t) = H(t-1)\gamma(AET)(1-e^{-k_H})$	$k_H = 0.00116/month$ (hardwoods, pines)
	$k_H = 0.000625/month$ (spruce-fir)
	$k_H = 0.000893/month$ (mixed, above 450m)
$\Delta W(t) = W(t-1)(1-e^{-k_W})$	$k_W = 0.067/month$
Lignocellulose index (LCI):	$LCI(t) = \frac{lignin}{(lignin+holocellulose)}$
Microbial production:	$P_M(t) = \alpha(\Delta LC(t)\beta_{LC} + \Delta C(t)\beta_C + \Delta E(t)\beta_E)$
N limitation factor α =	$\begin{cases} 1 \text{ if } \frac{N_{available}}{\Delta N_M(t)_{required}} \geq 1 \\ \frac{N_{available}}{\Delta N_M(t)_{required}} \text{ otherwise} \end{cases}$
$\Delta N_M(t)required = P_M(t) \cdot n_M$	
n_M = N content of microbial biomass	$n_M = (7\%)$
Microbial production-to-respiration ratio:	$\beta_i = \frac{e_i}{1-e_i}$
e_i = microbial efficiency on substrate i	$\beta_{LC} = 0; \beta_C = 0.3; \beta_E = 0.4$
Microbial biomass proximate C fractions:	$M_{LC} = 50\%; M_C = 10\%; M_E = 40\%$

Table 3.1 Basic litter mass-loss equations used in DocMod. LC = lignocellulose pool; C = holocellulose pool; E = extractables pool; H = humus, W = woody litter. Regressions for k values vs. LCI derive from Aber et al. (1990). $\gamma(AET)$ derives from Berg et al. (1993) (figure 3.2), where AET denotes actual evapotranspiration in [mm].

On a monthly time step, based on the weight loss in each class and on microbial efficiency while decomposing each class of substrate, living microbes incorporate material from the C and E pools. These fluxes are designated $P_{M(C)}$ and $P_{M(E)}$ for microbial productivity on each substrate (figure 3.1). This mechanism embodies a labile C limitation on microbial growth (Lynch, 1982; Zak et al., 1990). Microorganisms have a production-to-respiration ratio of 0.4 on extractable (E) material. This corresponds to the lowest microbial efficiency found by Ladd et al. (1992) for soil microbes metabolizing glucose. I chose a lower production-to-respiration ratio (0.3) for microbial metabolism of holocellulose (C) material because the degradation of holocellulose requires enzyme systems in addition to those needed for glucose metabolism (Ljungdahl and Eriksson, 1985). Though microbial enzyme systems can decompose LC material, in DocMod the microbial efficiency on this material is zero (Tate, 1987; Paul and Clark, 1989).

Microbial biomass turns over completely each month. Dead microbial biomass is redistributed to the litter LC, C and E pools according to the amounts of LC, C and E material present in microbial biomass, modeled as 50%, 10% and 40% of microbial mass respectively. These values were hypothesized because measurements of proximate C fractions of forest-floor microbial biomass were not found. Sensitivity analysis of changes to microbial litter quality showed negligible changes to total mass remaining (LC + C + E + H + M, where H = humus mass and M = microbial mass) after one year of decomposition.

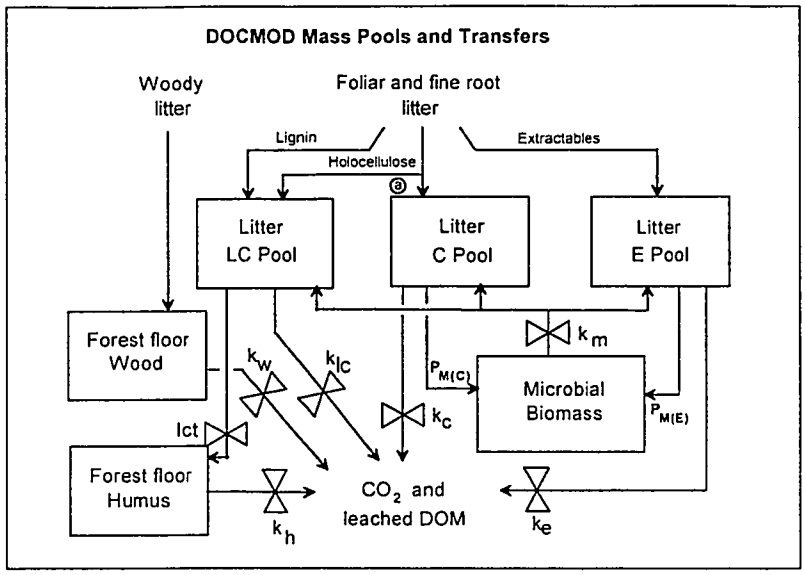

Figure 3.1. DocMod mass pools and transfers. (a). Amount of holocellulose entering ligno-cellulose pool is equivalent to the amount of lignin, making the ratio (by mass) L:C = 1:1 in ligno-cellulose pool (see text). Remaining holocellulose enters "cellulose" (C) pool.

Actual evapotranspiration (AET) has proven convenient as a surrogate for modeling climatic influence on decomposition, because (a) it combines temperature and moisture information, and (b) monthly estimates of AET in various ecosystems are readily available. DocMod models climatic effects through an AET effect based on the data of Berg et al. (1993). Berg et al. reported the effect of AET on first-year mass loss of Scots pine needle litter in 39 sites with climates ranging from subarctic to subtropical and Mediterranean. The authors split the resulting decomposition data into two groups; those near the European west coast or exposed to an Atlantic climate, versus those in Central Europe and North America. Data from the latter group, which I feel best represents North America, are reproduced in figure 3.2 along with the regression used in DocMod. Although Berg et al. supplied a linear regression of first-year mass loss *vs*

AET, I use a logarithmic regression. The logarithmic fit would be linear in AET *vs* the *k* parameter, rather than AET *vs* fractional mass loss. My curve fit for the Berg et al. data, shown in figure 3.2 is given by equation (1) where AET is annual total evapotranspiration in [mm]:

$$\text{Fractional mass loss} = 0.000693(\text{AET}) - 0.126 \qquad (1)$$

My r^2 value for this curve fit is essentially equivalent to that of the linear fit (0.72), and the logarithmic regression has the benefit of never producing negative mass-loss values at low values of AET.

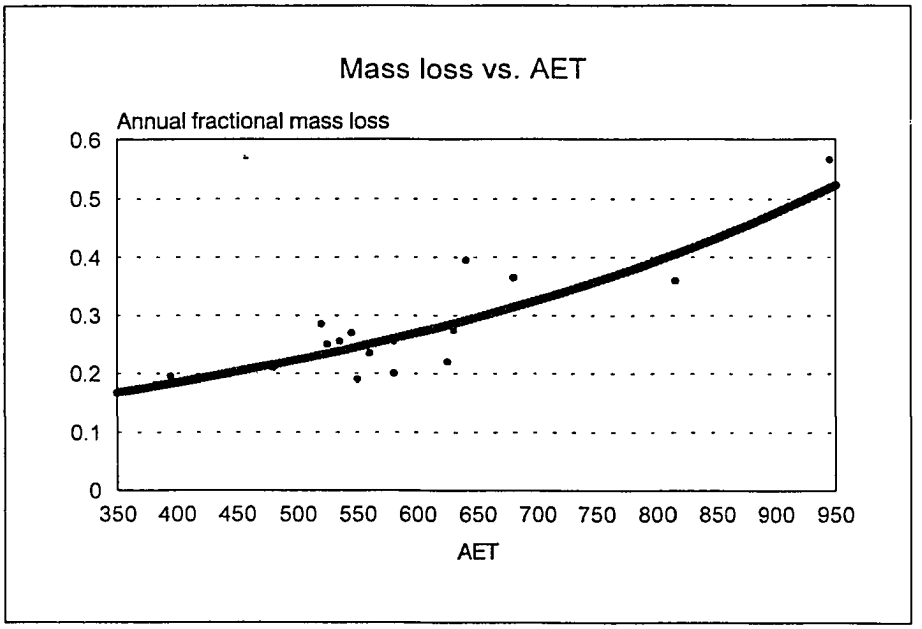

Figure 3.2. AET effect on mass loss for all mass compartments in DocMod. Annual fractional mass loss is plotted against actual evapotranspiration (AET) in [mm]. Data shown are from Berg et al. (1993); regression fit is my own ($r^2 = 0.72$).

DocMod models decomposition of above- and belowground woody litter separately from foliage and fine roots. Only fine woody debris (FWD) is included, defined as branches, twigs boles and woody roots initially 5 cm in diameter or smaller (Mattson et al., 1987). Controlling factors in woody litter decomposition appear to include species, fungal colonization, position on or above the forest floor; and in clear-cut patches, aspect (Gosz et al., 1973; Mattson et al., 1987). Though smaller material offers increased surface area to decomposers (Tate, 1987), size class within the FWD fraction is not necessarily found to relate to k (Abbot and Crossley, 1982; Barber and Van Lear, 1984). Species differences may partly result from differences in litter quality, since litter-quality differences in wood are apparent (Ryan et al., 1990), and woody-material k has been weakly related to lignin content (Alban and Pastor, 1993). However studies reporting both woody litter quality and observed decomposition rates are rare. Species differences may be partially mediated by other factors such as the manner of bark fragmentation or rates of drying. Data in the literature are insufficient at present to establish the extent to which a litter-quality index could predict rates of wood decomposition. Out of parsimony, therefore, decomposition of woody material in DocMod is independent of litter quality.

Another difference in woody litter as distinct from foliar or fine root litter is in the effects of temperature and moisture on decomposition; in some cases data exist that appear contradictory (Abbot and Crossley, 1982; Mattson et al., 1987). In any event, there is no preponderance of evidence that a combined temperature-moisture term such as AET correlates positively with rates of wood decomposition. For example, Coweeta,

North Carolina has higher temperatures and greater moisture on average than central Minnesota. Yet Mattson et al. (1987) found a mass-loss rate at Coweeta for coarse woody debris (>5 cm diameter) corresponding to a *k* value of 0.077, whereas Alban and Pastor (1993), studying boles decomposing in central Minnesota, found a nearly equivalent coarse woody debris *k* value of 0.076. (Time periods covered in the two studies were 6 years or greater.) Decomposition of FWD in DocMod, therefore, was independent of AET. I parameterized woody *k* at 0.080, the average mineralization rate (mass loss corrected for fragmentation) observed over all sizes of FWD by Mattson et al. (1987) for a six-year period.

DocMod contains a humus pool in which highly processed material undergoes very slow decomposition. Each month, a quantity of material equal to 1/3 the mass lost from the LC pool (represented by 'lct' in figure 3.1) is transferred to humus. The value of the transfer to humus corresponds, for litter of average chemical composition, to an ultimate transformation of approximately 20% of initial litter mass to humus (Aber et al., 1990). Using the LC pool as the source means that the lignin:cellulose ratio of well-decayed litter is approximately 1:1 (Berg, 1986). Well-decayed wood is not passed to humus; it continues to decay in the woody litter pool at the same rate. An exponential decay rate with a single *k* value has been used to describe bolewood decomposition in the field throughout a chronosequence spanning 64 years (Foster and Lang, 1982).

Rates of decay of humus were calibrated to two values, one for northern hardwood forest cover and another for spruce-fir forest cover. In addition, for modeling forest-floor response to clear-cutting, 20% of humus mass was considered to be lost at the time of the

clearcut. This estimate is based on measurements of severe forest-floor disturbance or presence of bare soil after logging operations (Stone, 1973). For the hardwoods calibration, total forest-floor mass in year 57 after clear-cutting at an elevation of 645 m was constrained to be close to the value measured for Watershed 6 at HBEF by Covington (1981). This resulted in a humus k value of 0.014 yr^{-1}. At this rate humus mass would have a half-life $t_{1/2}$ of 50 yr, where $t_{1/2} = 0.693/k$. This value appears realistic to me for two reasons. First is the presence, in soil organic matter (SOM), of exceedingly old material, ^{14}C-dated to have mean residence times of 1000 yr and longer. These great ages for SOM are typically reported for SOM in mineral soil horizons (Stevenson, 1982), where complexation with mineral particles of various texture greatly affects turnover rates of some SOM fractions (Christensen, 1992; Amato and Ladd, 1992). Second is the fact that water leaching from forest-soil organic horizons carries significant quantities of dissolved organic matter (DOM), much of it soluble humic substances (Qualls et al., 1991). A model that predicted mineralization of C from humus accurately but that left out the leaching component would seriously overestimate humus mass in the forest floor. I believe the seemingly short half-life of 50 yr for forest-floor humus is consistent with the inclusion of a leaching mechanism as well as presently possible.

The rate of humus decay in spruce-fir forest was calibrated to humus mass measurements reported by Gosz et al. (1976). I constrained humus mass 52 years following clear-cutting at 795 m elevation at HBEF to total approximately 5500 g m^{-2}. This required a humus k value of 0.0075 yr^{-1}. In coniferous forest below 450 m I considered the dominant vegetation to be pine. Lacking data on rates of pine

litter-derived humus, I chose to assign the value I had obtained through calibration for mixed hardwoods at similar elevation. I believed this to be the most economical assumption to make. For 'mixed' hardwood-coniferous forest above 450 m elevation I averaged the two *k* values obtained separately for hardwoods and spruce-fir forest.

DocMod Nitrogen Dynamics. Nitrogen in plant litter initially enters one of two pools; one associated with the ligno-cellulose C fraction or one associated with the extractable C fraction. Material entering the ligno-cellulose pool has N content equal to that of fresh litter; the remainder of the nitrogen in fresh litter enters the extractable pool (Aber et al., 1984). Exogenous available N, together with any N mineralized during short-term decay, enters an Available N pool (figure 3.3). Microbial growth, controlled primarily by litter mass loss and microbial efficiencies on the three substrates (LC, C and E material), draws N from the Available N pool. Microbial growth is limited by the N available. I assume no transfer of N to the forest floor from mineral soil. Unless initial litter N is very low and/or exogenous available N is very low, however, microbial growth is limited by labile carbon. Microbial turnover transfers N to the E and C pools with microbial E and unshielded-C carbon fractions, in direct proportion to the transfer of carbon to the E and C pools and based on microbial biomass percent N (7%; Smith et al., 1986; Ladd et al., 1992). Observations of litter-chemistry changes during decomposition in Wisconsin (Aber et al., 1984) showed that N increased in the acid-soluble material as decomposition proceeded (though no N was present in this litter chemistry class initially). Microbial N not associated with extractable or acid-soluble material enters the available

N pool. The LC pool immobilizes N from or mineralizes N to the Available N pool through a separate empirical relationship described below.

All N transfers but two are calculated as mass transfer multiplied by the N content of the source pool. The two exceptions are immobilization of N by the LC pool and concentration of N in humus. Immobilization of N in the LC pool is determined by initial concentration of N in the LC pool at the start of each annual period. Low N concentration results in immobilization by this pool, while high N results in release. The relation describing this effect, shown in figure 3.4, was derived from buried-bag foliar-litter decomposition studies conducted in Wisconsin (Aber et al., 1984; McClaugherty et al., 1985). During model development, with litters of varying C fractions this function produced patterns of N immobilization more closely in agreement with observed patterns, than did a function representing microbial N uptake and synthesis of N-rich LC material. (Microbial N uptake and LC-N synthesis produced a pattern of decreasing N immobilization with increasing LCI, contrary to the findings of Aber and Melillo [1982].) The empirical N dynamics of the litter lignocellulose pool in DocMod are presumed to model biotic and/or abiotic mechanisms of N retention in this pool (Stevenson, 1982; Johnson, 1992). Since humus derives from material in the LC pool, the LC pool and its N retention in effect model the formation of 'prehumic' substances as lignin-rich derivatives (Melillo et al., 1982).

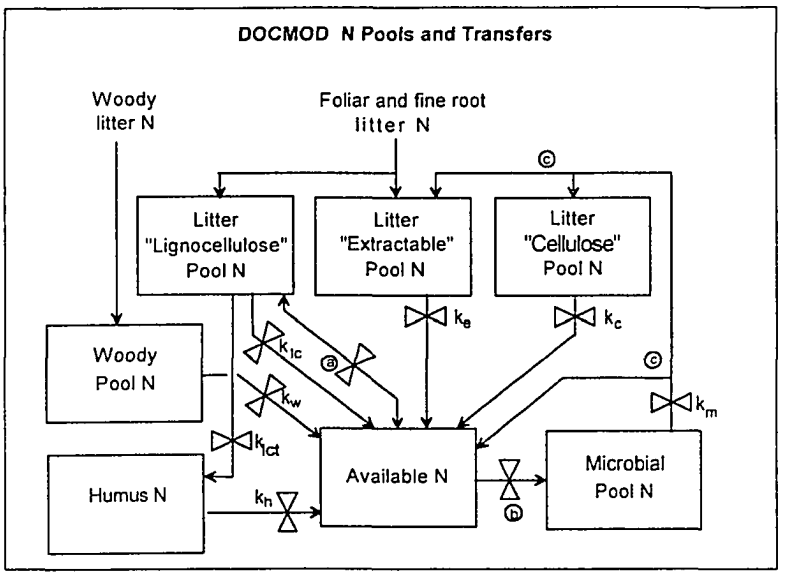

Figure 3.3. DocMod nitrogen pools and transfers. 'Available N' is a quantity tracked for purposes of N limitation to microbial growth (secondary to labile C limitation) and to ligno-cellulose pool N immobilization (see text).

Notes:

a. Immobilization of N into ligno-cellulose pool is effected by an empirical relation presumed to represent biotic and abiotic N incorporation into ligno-cellulosic material.

b. Microbial N uptake depends on microbial biomass production and N content of microbial tissue.

c. Km denotes microbial turnover, modeled as complete turnover each timestep (each month). N in microbial litter is passed to the appropriate pool, with N associated with the ligno-cellulose pool passed to Available N (see text).

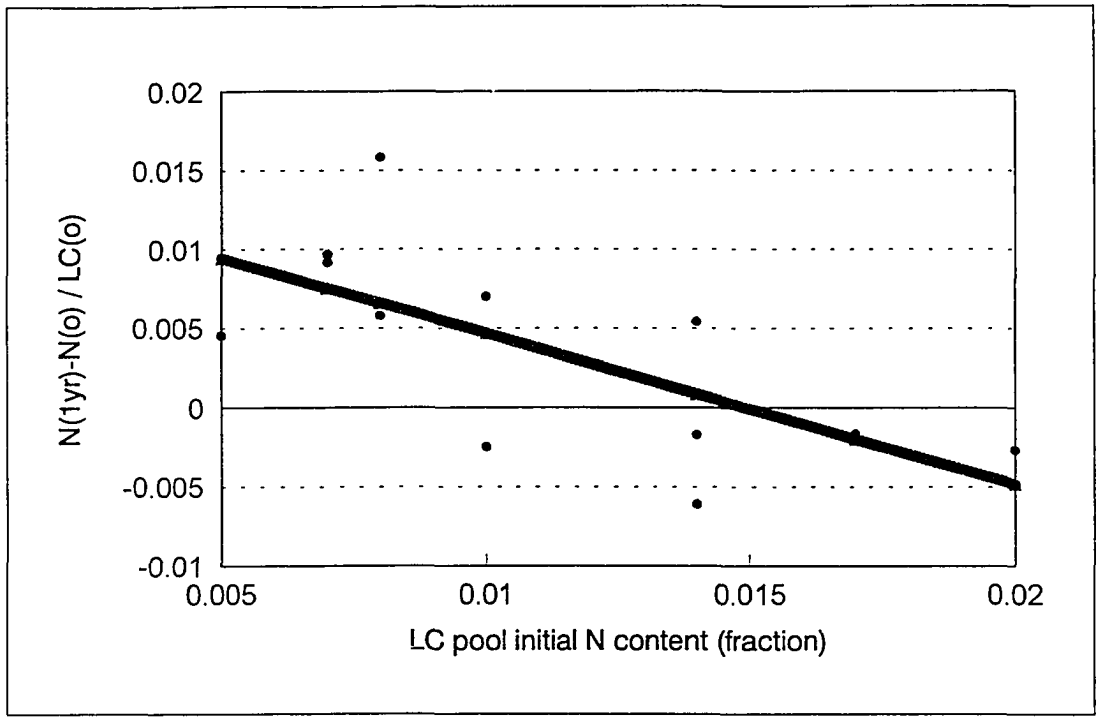

Figure 3.4. DocMod LC pool nitrogen immobilization algorithm. The line shown represents DocMod calculation of annual N immobilization in the ligno-cellulose pool per unit ligno-cellulose mass, versus ligno-cellulose pool initial N concentration. Positive y-axis values represent N immobilization; negative values mineralization. Data are from a decomposition study of six foliar litters in forest-floor litter bags in Wisconsin over one and two-year periods (Aber et al., 1984). For regression shown, $r^2 = 0.45$.

As mass is lost from the humus pool, N is lost from the humus pool as well, but at a somewhat slower rate. This allows humus to concentrate N over time, eventually reaching a steady-state C:N ratio narrower than that of the litter LC pool. The quantitative rate of N concentration in humus was chosen in concert with the parameterization of the N dynamics of the woody litter pool to produce well-decomposed material in both pools at steady-state C:N ratios of 25:1. This C:N ratio represents something of a compromise in that well-decayed wood is often observed to have higher C:N ratios (McFee and Stone, 1966; Lang et al., 1981; Alban and Pastor, 1993), and

humus to have lower C:N ratios (Stevenson, 1982). One ratio was used for material in the most advanced stages of decay in both pools, however. In the field it is probably not possible to distinguish material in the most advanced stages of decay and humification in the Oa horizon by its original source, foliar *vs.* fine root *vs.* wood. The N present in woody litter enters the woody litter N pool in DocMod. There it concentrates without release (Alban and Pastor, 1993) until the C:N ratio of the entire pool reaches 25:1, at which level the C:N ratio is maintained through woody pool N mineralization.

Model tests against parameterization datasets

During model development I tested its performance in various climatic regimes and with various litter types to ensure that the modeled N dynamics could work reasonably well across a wide range of climates and litter qualities. Modeled foliar litter mass and N content are compared with field data supplied by Aber et al. (1984) in figures 3.5 (A) and (B). The curves shown represent *Tsuga canadensis* (hemlock) foliage decomposing in Wisconsin over a two-year period beginning with fresh litter.

Litter chemistry of five foliar litters is shown in figure 3.6 (A), while their modeled and field-observed N content after 24 months of decomposition are shown in figure 3.6 (B). Three of these litters were studied in Wisconsin and three in Coweeta, North Carolina. Blackberry and mountain laurel litter were chosen for illustration because of their highly different litter qualities. Blackberry foliar litter had very high N content with high E and very low L content, whereas mountain laurel had high E with relatively high L and very low N. DocMod reproduced the 24-month N content acceptably in both cases. In figure 3.6, model results are shown in two scenarios of

exogenous N availability, chosen as 0.1 and 0.7 g N m^{-2} yr^{-1} respectively. Exogenous N availability in the field studies is not known, but a value of 0.5 g N m^{-2} yr^{-1} is approximately equal to half of a representative growing-season flux of nitrate-N plus ammonium-N in throughfall (Neary and Gizyn, 1994). The remainder I allow for plant uptake since it is not included in DocMod. For my model application in WMNF, I also approximated exogenous N availability as 0.5 g N m^{-2} yr^{-1}.

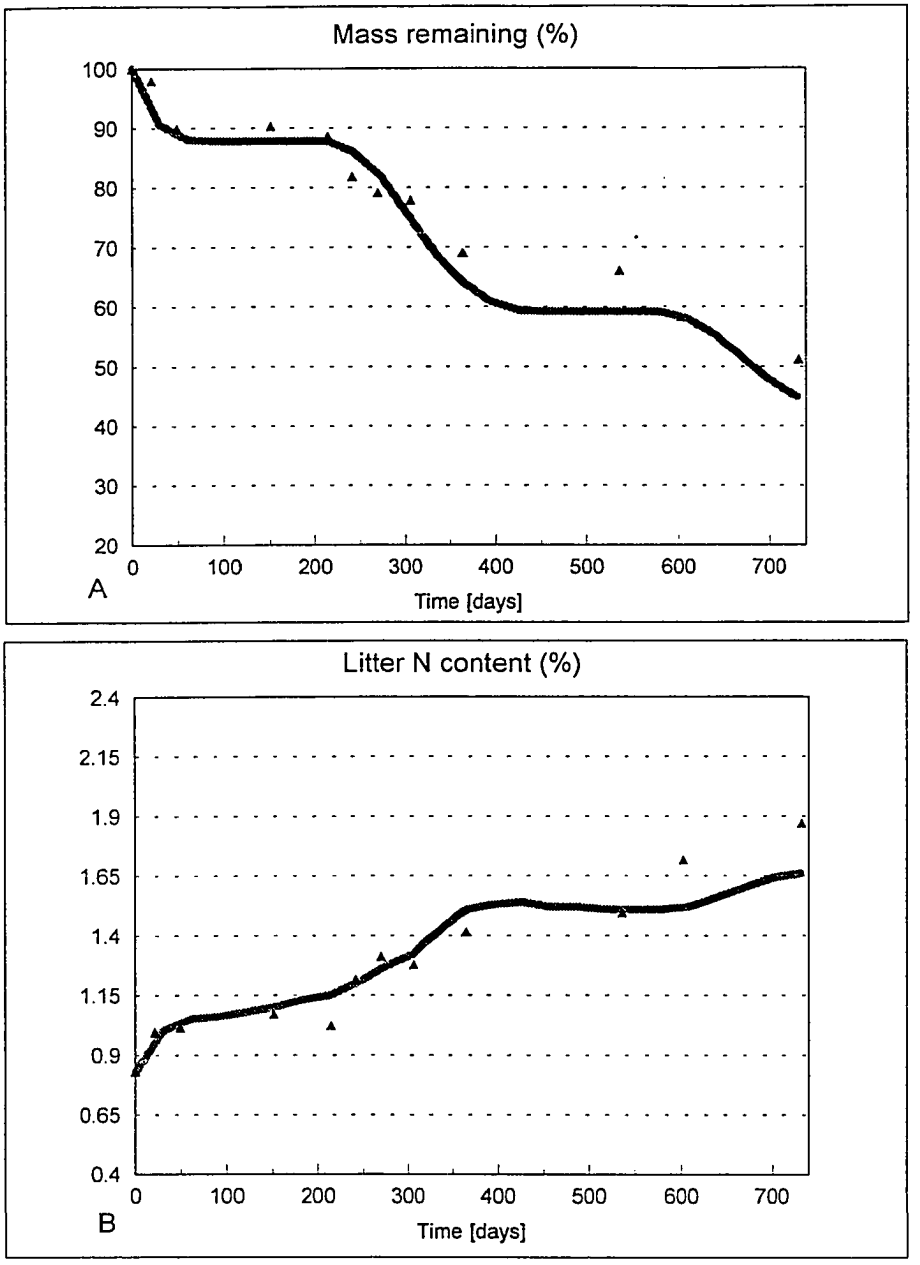

Figure 3.5. DocMod fresh foliar litter mass and N dynamics over two years. DocMod results are shown alongside field data for *Tsuga canadensis* (hemlock) foliage decomposing in Wisconsin (Aber et al., 1984). DocMod results are represented by the shaded curves. Filled triangles represent field data. (A) Litter mass remaining, (B) Litter N content.

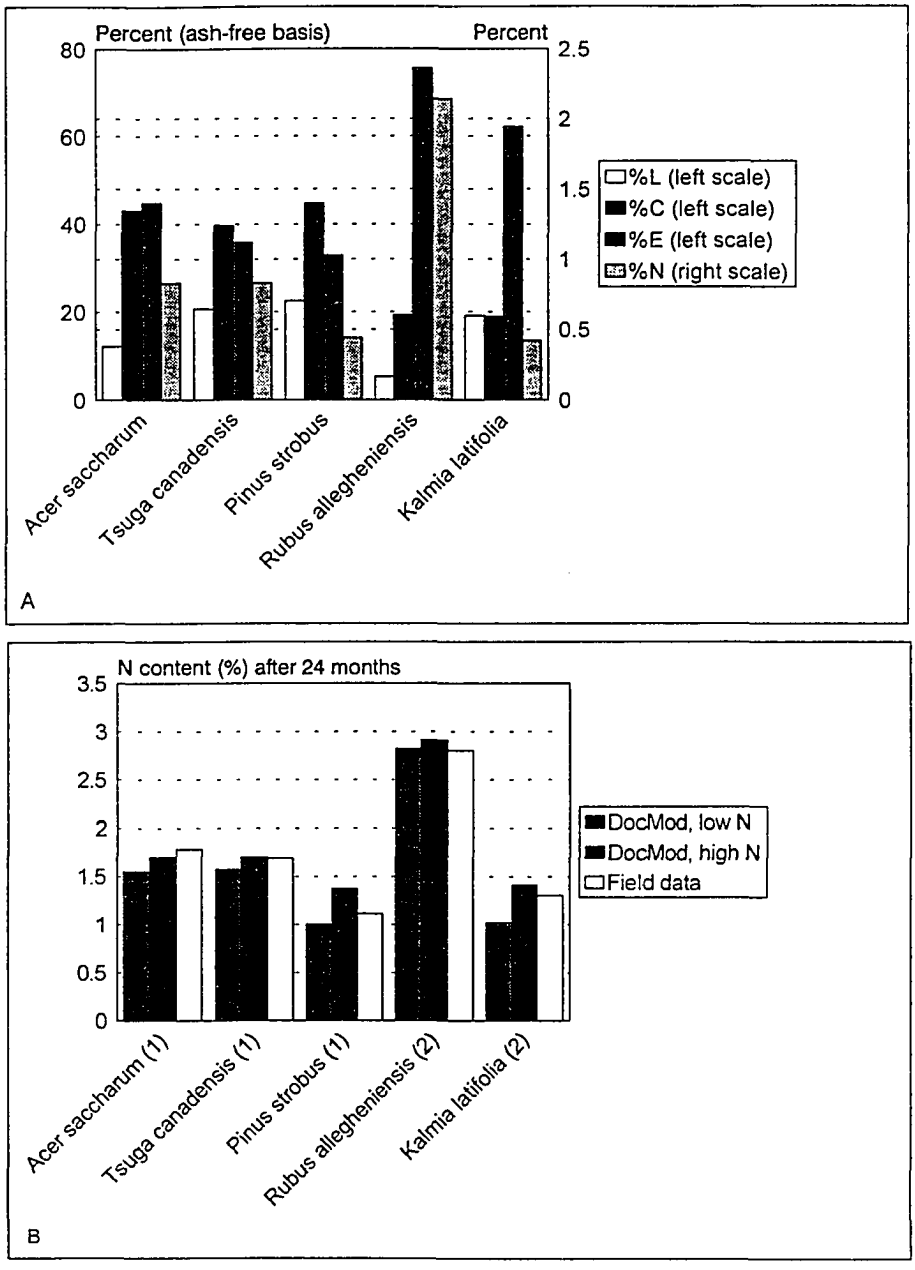

Figure 3.6. DocMod N dynamics in five litters used during model development. (A) Initial litter quality of foliar litter from five forest species. (B) DocMod results for litter N content after 24 months of decomposition, compared with field data.

1. Aber et al., 1984 (Blackhawk Island, Wisconsin.)
2. White et al., 1988. (Coweeta, North Carolina.)

Annual litter inputs and climate driver

Preceding sections have described the mechanisms of mass losses, transfers and N transfers among pools in the forest floor. Here I describe the use of the ecosystem model PnET version II (Aber et al., *submitted*) to supply average annual climate and annual litter inputs to the forest floor. PnET includes a model of monthly mean temperatures and monthly mean levels of precipitation, based on regressions over latitude, longitude and elevation for the New England and New York region (Ollinger et al., 1993). As described above, DocMod uses actual evapotranspiration (AET) in calculating the effect of temperature and moisture on rates of decomposition. AET is a central parameter in the PnET model and is calculated internally as a value consistent with biomass production (Aber et al., 1992). PnET-II was run in each GIS cell (see below for discussion of GIS application) to produce AET and steady-state production of foliage, fine roots and wood. PnET-II was run for 30 years at each pixel, which preliminary testing showed to provide steady-state production in each component. Steady-state was used in this work to refer to a forest stand that had reached maturity to the extent that production and litterfall in each tissue component would fluctuate naturally (in the absence of major disturbance) about some mean equivalent value, that mean being the steady-state value (Bormann and Likens, 1979).

DocMod models the forest floor at each point as aggrading, recovering from some major disturbance, such as clear-cutting or a fir wave. DocMod used two sets of functions to calculate litter inputs to the forest floor, each year, from steady-state values calculated by PnET. The first functions represent changing annual forest-floor inputs of

each litter type, through time, growing from zero immediately following disturbance, to steady-state values as the forest matures. The curve denoting foliar litter input following disturbance follows Bormann and Likens (1979), shown in figure 3.7. Bormann and Likens (1979) considered the dip in foliar production after year 5 to be due to nutrient limitation. Reasoning that similar limitations might apply to root production, I used the same curve to approximate fine root litter inputs (relative to steady-state) during aggradation.

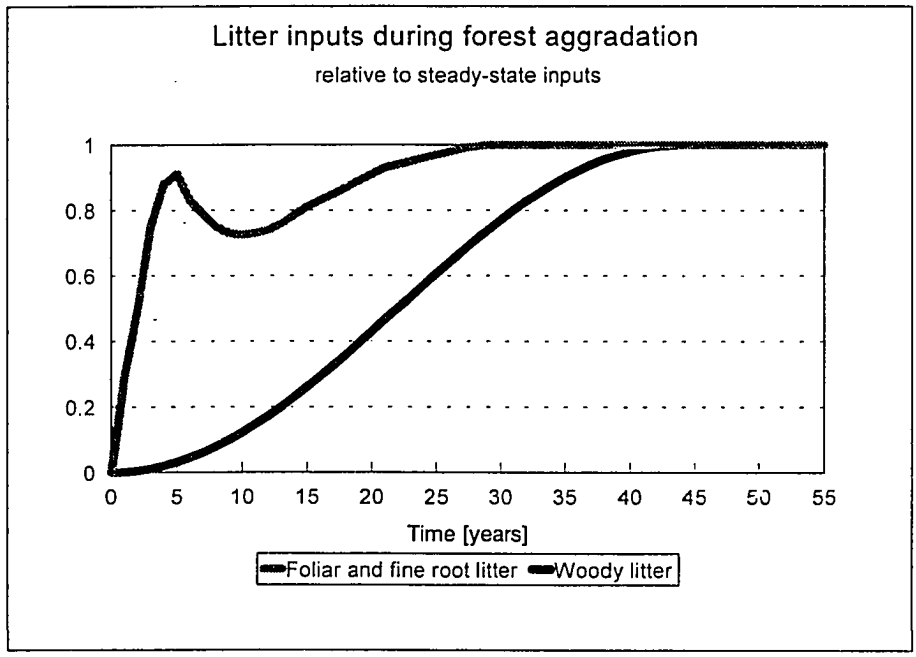

Figure 3.7. DocMod litter inputs during forest aggradation. Litter inputs are represented as they are calculated in DocMod, as fractions of steady-state (mature forest) litter inputs. Foliar litter curve is reproduced from Bormann and Likens (1979). Woody litter curve is derived in the text.

Woody litter input as a function of steady-state total woody litter is also shown in figure 3.7. I developed this curve through the following reasoning. There are two

sources of woody litter input during aggradation; entire dead trees created by forest self-thinning, and branch and woody root inputs from surviving trees. JABOWA simulations for Northern Hardwood forests at HBEF have simulated total dead wood inputs from tree death as increasing slowly from zero, reaching half maximum in approximately 25 years and peaking in approximately 60 years (Bormann and Likens, 1979). I reasoned that during aggradation following clear-cutting, woody litterfall from living trees would add increasingly to fine woody litter produced by tree mortality, reaching a maximum at approximately the time of maximum production during aggradation, and remaining at that level thereafter. I thus chose the time to reach steady-state in woody litter production as 45 years. In the first 45 years, the fraction of total steady-state woody litter in year t, $fw_{SS}(t)$, as a function of steady-state total woody litter W_{SS} and the year that peak (steady-state) woody litter is reached, T_{SS}, was modeled as a logistic-like function given by equation 2 where *cos* is calculated in radians:

$$fw_{SS}(t) = 0.5W_{SS}(1 - \cos(t\pi/T_{SS})) \qquad (2)$$

The second set of functions DocMod uses to calculate forest-floor litter inputs represent the fraction of *total* litter production that is *forest-floor* litter input. Since DocMod predictions of forest floor mass and N content are compared (below) with measured values, the model must capture the quantity measured in field studies as 'forest floor mass'. For foliage, DocMod models all litter as input to the forest floor. For fine roots, 48% of litter is input to the forest floor; the rest is considered to be enter mineral soil (McClaugherty et al., 1982). For woody litter, I formulated DocMod to model the

forest-floor input and decomposition of fine woody debris (FWD), defined as initially 5 cm or less in diameter, above or below ground (but excluding mineral-soil inputs of woody roots). This size material would be more homogeneous than larger material, would be more likely to be incorporated into the forest floor beyond the point of separation in the field, and would still be included in mass measurements that specifically avoided stumps or fallen boles.

A variable in DocMod, f_{FWD}, quantifies my estimate of the fraction of total wood production that occurs as FWD and that is likely to be measured in forest-floor mass measurements. I estimate that the fraction of total woody-litter production that meets these criteria increases with elevation in WMNF. At lower elevations, I expect a greater percentage of woody production to occur in large size-class boles, limbs and stumps. At higher elevations, I expect a greater fraction of wood production to occur in boles, branches and woody roots less than 5 cm diameter. After reviewing the literature on woody litter distribution in Eastern forests I estimated that f_{FWD} equals approximately 20% at low elevations in the White Mountains and 36% in the highest-elevation spruce-fir forests (Harris et al., 1973; Rolfe et al., 1978; Whittaker et al., 1979; Lambert et al., 1980; Mattson et al., 1987; Fahey et al., 1988). The function embodying these estimates is given by equation 3 (where E is elevation in meters):

$$f_{FWD} = \exp[(0.0008 \cdot E) - 2] \quad (3)$$

Model validation

The LIDET study. I have had the recent opportunity to test DocMod predictions in a true validation test. As part of the Long-Term Ecological Research (LTER) Intersite Decomposition Experiment Team (LIDET) project, DocMod and three other models participated in making standardized, blind predictions of mass loss and nitrogen dynamics (Moorhead et al., *unpublished data.*) As part of the standardization, three of the models were altered to use the same function to represent temperature and moisture effects, the 'abiotic' factor from the CENTURY model (Parton et al ., 1987); CENTURY was the fourth model. The abiotic factor was based on calculation of soil temperature through a relation derived expressly for grassland sites (Parton, 1978), plus calculation of potential evapotranspiration (PET) and actual evapotranspiration (AET).

Four substantially different ecosystems and two litter types representing extremes in litter quality were used in the blind predictions. The ecosystems comprised a tropical forest, an arctic tundra site, a warm desert and a humid temperate forest. The two litters used in the blind predictions were *Triticum aestivum* (wheat), with very high lignin content with low N, and *Drypetes glauca* (a tropical broadleaf), with low lignin and very high N content. After decomposing in the field for two years, mass remaining varied from 8% to 87%. DocMod blind predictions agreed with mass-remaining values with an average absolute deviation of 10% from observations. This validates the basic equations used in the model, across a range of climates and litter qualities. After the blind intercomparison, to model temperature and moisture effects I used my own AET effect derived from the extensive Berg et al. (1993) data from forests throughout Central Europe

and North America. This improved agreement with LIDET observations further, over the already satisfactory standardized comparisons with the field data.

Forest-floor mass and N capital. I compared modelled values of forest-floor mass and N capital with published field measurements made in WMNF. I sought sites at which multiple forest-floor mass measurements had been taken so that average and standard-error values were available. This is consistent with my use of the model in predicting forest-floor mass as subject only to major controlling factors and in relatively large patches (10 ha) in landscape-scale applications.

Two sets of sites with good average values were available in the literature. The first of these comprised two sets of mid-elevation mixed hardwood forest floors, a set of 14 measured by Covington (1981) and a similar set of 13 measured by Federer (1984). In both cases, even-aged stands of similar elevation (420-700 m) but varying age were located in southern WMNF. The total forest-floor (O horizon) mass was measured at each site and results presented as a chronosequence as a means of estimating forest-floor mass dynamics at a hypothetical single, average site through time. Watershed 6 at HBEF, aged 57 years at the time of the Covington study, at 600-690 m elevation had a forest-floor mass value that was representative of the chronosequence. This age, 57 years, also serves to mark the transition from an aggrading forest floor to one approaching steady-state mass (Gosz et al., 1973; Covington, 1981) and thus provides an opportune point for comparison. For the model run described in table 3.2, actual HBEF temperature and precipitation were not used, though the data are available. Instead, the regional climate regressions DocMod used to estimate these parameters across the WMNF were

used (Ollinger et al., 1993), with the latitude, longitude, elevation and aspect of HBEF watershed 6. This way, the model run serves as a demonstration of the coupled climate, production and decomposition models. The second set of sites used for comparison were measurements of forest floor mass in 13 high-elevation *Abies balsamea* stands atop Mt. Moosilauke in eastern WMNF (Lang et al., 1981).

Table 3.2

Parameters	Hubbard Brook, NH	Mt. Moosilauke, NH
Elevation:	645 m	1235 m
Forest type:	Northern hardwoods	*Abies balsamea*
Latitude, longitude:	43° 56' N, 71° 41' W	44° 01' N, 71° 48' W
Historical treatment:	Clearcut	Unlogged
Model results		
Steady-state foliar production:[2]	3.3 Mg ha^{-1} yr^{-1}	2.7 Mg ha^{-1} yr^{-1}
Steady-state total fine root production:[2]	3.0 Mg ha^{-1} yr^{-1}	2.4 Mg ha^{-1} yr^{-1}
Steady-state total wood production:[2]	7.9 Mg ha^{-1} yr^{-1}	3.4 Mg ha^{-1} yr^{-1}
Average AET:[2]	558 mm	495 mm
Forest floor mass:	73 Mg ha^{-1} at age 57	97 Mg ha^{-1} at steady-state
Total forest floor N capital:	1.2 Mg ha^{-1} at age 60	2.0 Mg ha^{-1} at steady-state
Field measurements for comparison		
Forest floor mass:	70 ± 10 Mg ha^{-1} at age 57[3]	95 ± 13 Mg ha^{-1} at maturity[4]; range 81 to 106 Mg ha^{-1}.
Total forest floor N capital:	1.3 Mg ha^{-1} at age 60[5]	2.3 Mg ha^{-1} at maturity[4]

Table 3.2. DocMod forest floor mass and N capital comparisons with field measurements. DocMod input parameters and forest floor results are compared with field data from two studies. Notes and references:

1. FWD = fine woody debris (<5 cm diam.); see text.

2. Production and AET (actual evapotranspiration) calculated by the PnET-II model (Aber et al,. *submitted*), linked to DocMod for the present study.

3. (Covington, 1981), HBEF Watershed 6.

4. (Lang et al., 1981).

5. (Bormann and Likens, 1979).

GIS Application of DocMod

Actual land use - land cover (LULC) data, interpreted from Landsat Thematic Mapper (TM) imagery, was obtained from the GRANIT project (Complex Systems Research Center, University of New Hampshire) for the portion of White Mountain National Forest in the state of New Hampshire (I do not consider the small part of WMNF that extends into Maine). The LULC data were in NH State Plane format, contained within the rectangle extending from 71.0° to 72.0° W and 43.75° to 44.65° N. Resolution was 30 m *x* 30 m, with pixels classified as hardwood, coniferous, or mixed forest, and several nonforest categories. Nonforested pixels, approximately 5% of the area, contained wetland, agricultural, exposed bedrock, open, water, urban and alpine tundra land-cover categories. Interpretations among forest types had been checked against reference data to approximately 80% accuracy (D. Justice, *personal communication*). The LULC image was converted from the Arc/Info Geographic Information System (GIS) Grid format into Idrisi format and transferred to a desktop PC. State Plane coordinates were converted to planar latitude and longitude using the CORPSCON program (US National Geodetic Survey). All subsequent GIS analysis was performed in IDRISI (Clark University Geography Department). Resampling to the planar latitute and longitude system was accomplished in IDRISI, with a simultaneous coarsening of scale from 30 m *x* 30 m pixels to 316 m *x* 316 m (10 ha) pixels. A digital elevation model (DEM) for the region was obtained in USGS DEM format at the scale of 1:250,000 (approximately 800 m *x* 800 m), converted to IDRISI format, aligned with the LULC image and resampled using bilinear interpolation to 316 m *x* 316 m scale.

The PnET model version II (Aber et al., *submitted*) was used to calculate, in each of the 32,000 10-ha forested cells, values of annual AET and of steady-state forest litter in three components (foliar, fine root and fine woody) as described above. PnET was linked to DocMod not directly, but via IDRISI images; PnET produced output images that DocMod read as input images. This served two purposes: First, PnET and DocMod acted as independent modules that could each easily be matched with other counterpart models for the purposes of intercomparisons. Second, the intermediate images (AET, and litter production in each component) were saved and analyzed.

PnET version II had been parameterized for stands of mixed northern hardwood forest, for pine stands (*Pinus strobus* and *P. resinosa*) and for spruce-fir stands. Pixels with the LULC cover type 'hardwoods' at all elevations (67.5% of the forested land) modeled in PnET as mixed hardwoods, and in DocMod litter was estimated as comprising 33% *Fagus grandifolia* litter, 39% *Acer saccharum*, 23% *Betula lutea*, and 5% *Picea rubens* (Bormann and Likens, 1979). The cover type 'coniferous forest' at 450 m elevation and higher (17.8% of the forested land) was modeled as spruce-fir in PnET and as 85% *Abies balsamea* and 15% *Picea rubens* litter in DocMod (Reiners and Lang, 1979). Coniferous forest pixels below 450 m elevation (2.7% of the forested land) were modeled as pines in PnET and *Pinus strobus* for DocMod litter quality parameters. 'Mixed forest' pixels at elevations below 450 m (2.5% of total forest) were considered mixed hardwoods, hemlock phase. These were modeled in PnET as mixed hardwoods, and in DocMod litter was estimated as comprising 35% *Acer rubrum*, 25% *Picea rubens*, 20% *Tsuga canadensis*, 10% *Betula lutea*, 5% *Fagus grandifolia* and 5% *Abies*

balsamea (Hornbeck and Leak, 1990). Finally, the LULC cover type 'mixed forest' at elevations 450 m and higher (9.5% of forested land) was considered 50% mixed hardwood forest and 50% spruce-fir.

Results

Ecosystem-level dynamics

The dynamics of the recovery of forest-floor mass following removal of vegetation and during forest regrowth in DocMod are shown in figure 3.8. The forest-floor mass curve agrees very well with curves drawn by Covington (1981) and Federer (1984) based on field studies of chronosequences of the forest floor under mixed hardwoods at 400-700 m elevation in the White Mountains. Gosz et al. (1976) suggested that such a forest floor should virtually reach steady-state by year 60, also in agreement with the curve in figure 3.8. From Covington's (1981) chronosequence data, it was unclear whether the nadir of forest-floor mass *ca.* year 15 was sharp or smooth. DocMod predicts that it should be smooth.

I know of no chronosequence with which to compare the dynamics in forest-floor N capital. DocMod predicts that N capital drops rapidly with mass loss and to the same extent, but recovers more slowly. This is probably due to the increasing importance of woody litter contributions to forest floor mass as the forest ages; woody litter is much lower in N content than foliar and fine root litter. Recovery of N capital in northern hardwood forest as estimated by DocMod requires approximately 90 years.

Landscape-scale patterns

Litter production. Steady-state foliar and fine root litter showed a band of maximum values in the elevational range approximately 550 to 800 m. The transition from lower production at lower elevations to higher production at 600 m was not associated with species transitions; nearly all pixels were northern hardwood forest. Lower production at lower elevation in the model is probably due to lower precipitation levels and to higher summer temperatures reaching above the photosynthetic optimum (Aber et al., *submitted*). The decline in foliar and fine root production as elevation increased in the zone surrounding 800 m, however, was primarily due to a shift from northern hardwood to spruce-fir forest. Another noticeable decline in foliar and fine root litter production occurred in the spruce-fir zone above 1100 m elevation, due to lower temperatures and shorter growing season. These litterfall patterns agree in general with measurements made by Reiners and Lang (1987) along two elevational transects (from 670 m upward) on Mt. Moosilauke and Mt. Jackson. In that study, however, the decline in foliar coniferous litterfall began at somewhat higher elevation, 1295 m.

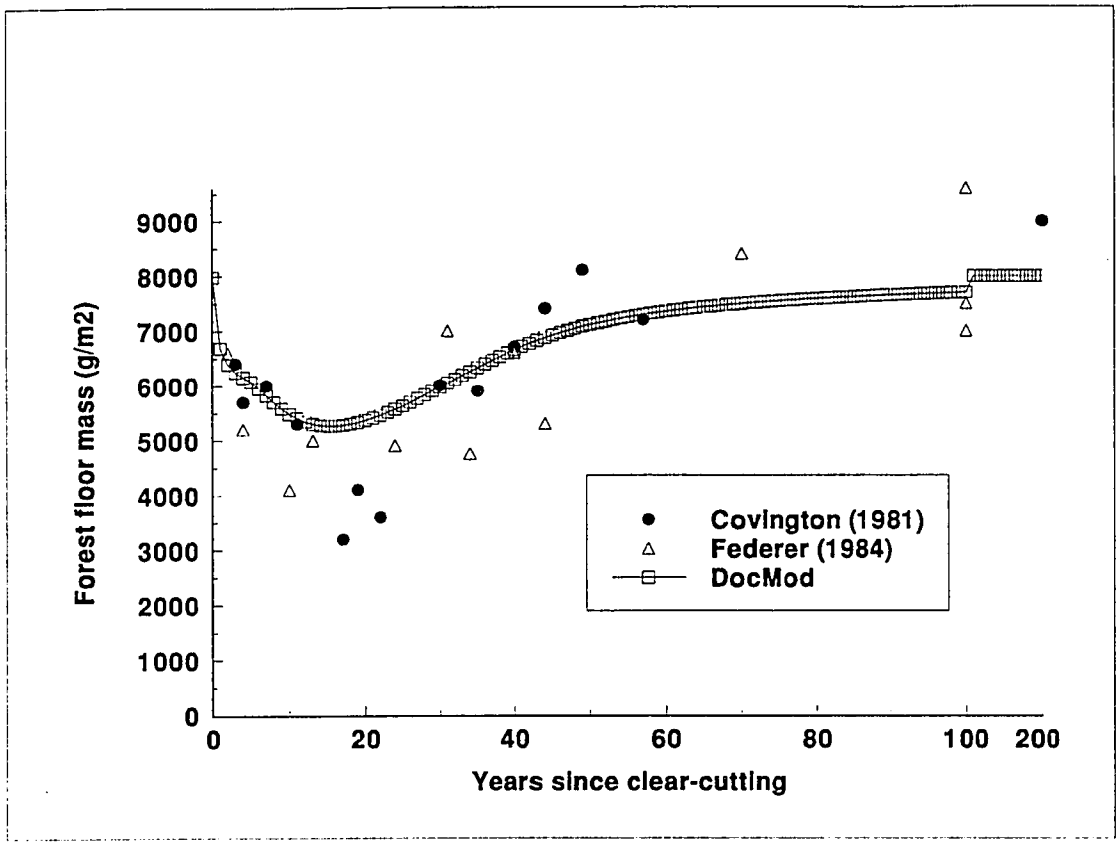

Figure 3.8. DocMod simulation of forest-floor mass recovering from clear-cutting. The simulation shown represents a northern hardwood forest in WMNF at 645 m elevation. Chronosequence forest-floor mass data reported by Covington (1981) and Federer (1984) are shown for comparison.

Forest floor mass. Steady-state forest-floor mass values in 10-ha patches as estimated by DocMod for the White Mountain National Forest are depicted in figure 3.9. The edge of the shaded area represents the borders of WMNF except for the eastern edge, which is the border of the state of New Hampshire. Forest-floor mass is plotted against elevation for each LULC cover type in figure 3.10; statistics by cover type are listed in table 3.3. A general trend of increasing forest-floor mass with elevation (apart from

mountain peaks) is evident in both the landscape image and the graphs. DocMod models the forest floor under northern hardwoods stands as increasing smoothly, peaking at approximately 950 m elevation and decreasing with elevation thereafter (figure 3.10). Coniferous stands show an abrupt increase in forest-floor mass at 450 m elevation, associated with the transition from pine to spruce-fir. A large factor in this abrupt transition is the higher humus decay constant I used for the lower-elevation pine stands. The extent to which such abrupt transitions occur in the landscape is unknown; a similarly abrupt transition in forest-floor mass between hardwoods and spruce-fir was however measured by Gosz et al. (1976).

The spruce-fir forest floor results shows higher variability at given elevations, probably due to differences in temperature, rainfall and production. Spruce-fir steady-state forest floor mass remains well above hardwood forest-floor mass throughout the spruce-fir range. An abrupt decrease in forest-floor mass occurs in the subalpine fir forest, in DocMod simulations, at approximately 1250 to 1300 m elevation, which corresponds to the elevation at which Reiners and Lang (1979) measured a decline in coniferous litterfall.

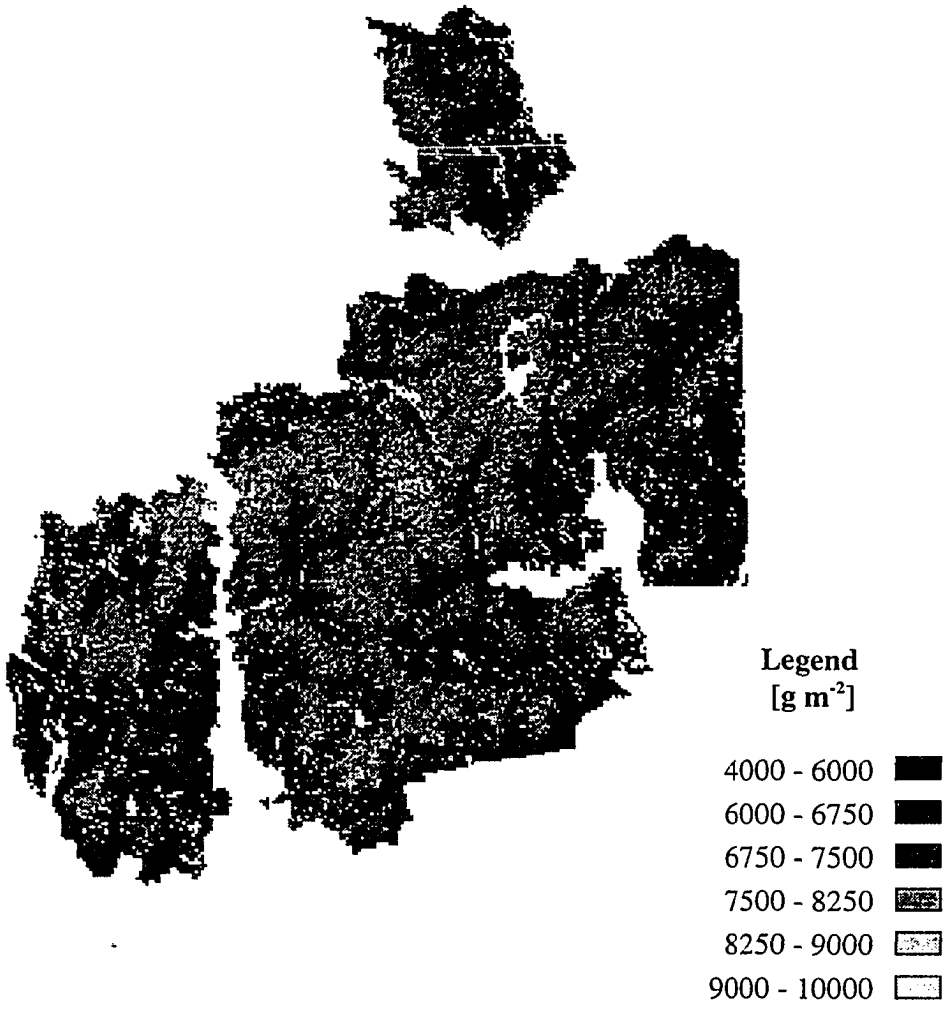

Figure 3.9. DocMod image of steady-state forest-floor mass in the WMNF. The image shown covers the White Mountain National Forest from west longitude 72.0 to 71.0°, north latitude 43.8 to 44.6°. Each shaded pixel represents a patch 10 ha in size. White pixels are outside WMNF or represent non-forested land cover, for example the top of Mt. Washington where the vegetation cover is alpine tundra.

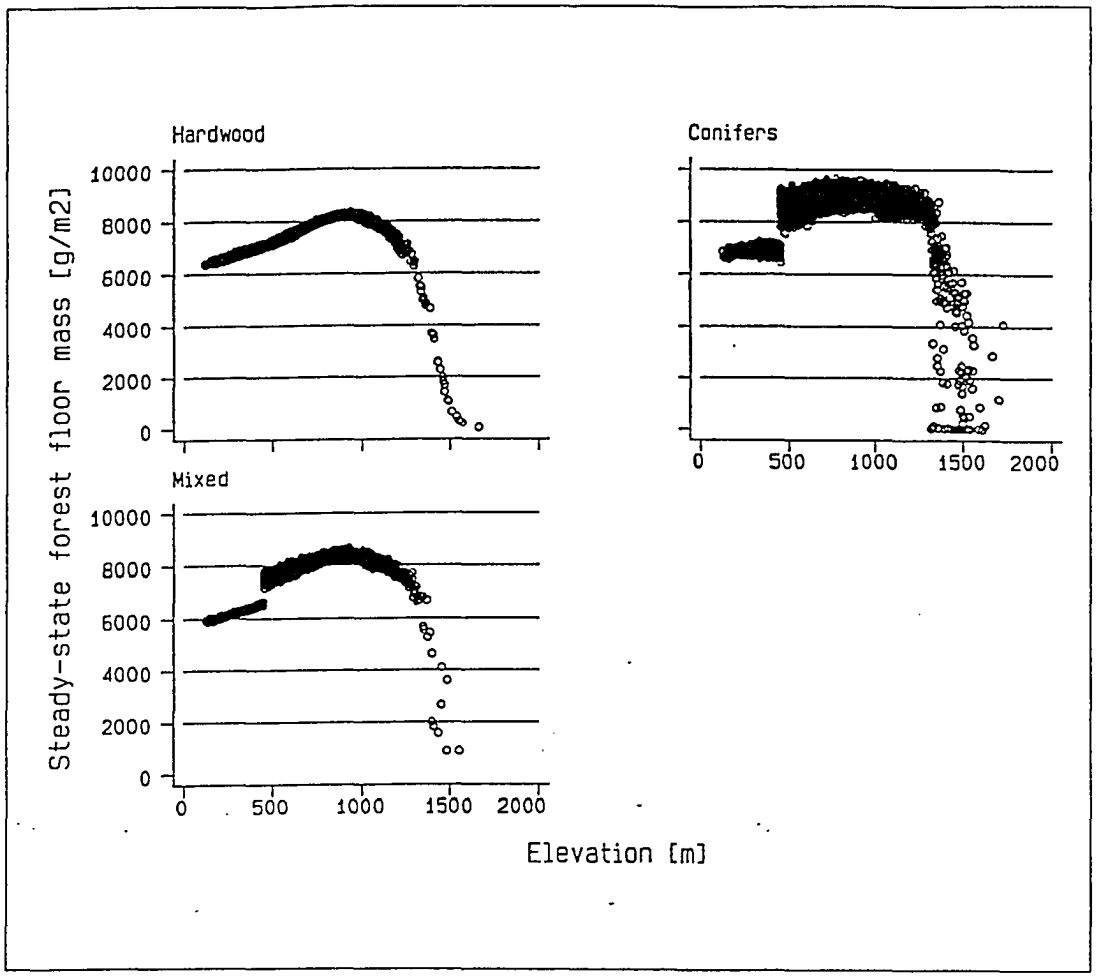

Figure 3.10. DocMod forest-floor mass versus elevation in the WMNF. Steady-state forest-floor mass in [g m^{-2}] is plotted against elevation in [m] for the three forested land-cover types in the White Mountain National Forest: Northern hardwoods, conifers, and mixed pixels.

Table 3.3

Cover Type	Mean [g m^{-2}]	Standard Deviation
Northern hardwoods	7,420	520
Spruce-fir	8,730	920
Pine	6,900	120
Mixed hardwood-hemlock	6,310	190
Mixed hardwood spruce-fir	8,050	460

Table 3.3. Modeled steady-state forest-floor mass by cover type in the WMNF. Statistics within each forested land cover class are listed.

Discussion

DocMod is chiefly a mechanistic model, though many of the functions that make up the model were formulated empirically. Underlying the use of each empirical function there is an hypothesis concerning the mechanism at work. Thus acid-insoluble material is modeled as decomposing more slowly than acid-soluble, the hypothesis being that lignins in the acid-insoluble fraction are less suitable as a microbial substrate (Paul and Clark, 1989). The model constitutes an interconnected set of such hypotheses, some of which are well accepted and others more speculative. For example, decaying wood in the model does not increase in recalcitrance as it ages, as foliar and root litter do. Wood is also not passed to humus. In reality some woody material probably does become humified, although what fraction of humus derives from wood is an open question.

Model mechanisms

Some hypotheses in DocMod concern mechanisms of N immobilization by decaying litter. Laboratory and field studies have demonstrated that microbial uptake is

important, even necessary, for stabilization of N in surface soils (He et al., 1988; Zak et al., 1990). If a model is to capture mechanisms of N retention in soils, microbial uptake must then be included. This allows the possibility of modeling controls on microbial activity as a means of modeling N cycle processes. I have done so here by including different microbial efficiencies on each carbon fraction in decomposing litter pools, thus placing a labile C limitation on microbial growth and N uptake. Microbial growth in DocMod can also be limited by N (table 3.1) when initial litter is low in N content. (Nitrogen limitation occurs more readily if N is low relative to available labile C). But microbial uptake and synthesis of N-rich compounds may not be the only mechanism of litter N immobilization (Johnson, 1992); as described above, to account for patterns observed in the field I found it necessary to allow the lignocellulose pool to incorporate N independent of microbial growth.

A mechanism absent from DocMod is any direct effect of N availability on rates of mass loss during decomposition. This is in agreement with the analysis of Wisconsin decomposition data performed by McClaugherty et al. (1985). However, studies on short- and long-term decomposition of other litter types have found N content to impact decay rates (Berg, 1986). A goal in the present paper was to construct a synthesis of the primary processes controlling forest-floor mass and N dynamics across the forested landscape. Certainly, factors additional to the ones I included could have been used. But another aim of ours was to capture essential mechanisms with relative simplicity, using no more functions than needed. Further along these lines, I adopted the 'lumped parameter' approach often used to reduce complexity (Rastetter et al., 1992; Aber and

Federer, 1992). DocMod was run independently in each 10 ha-sized cell across the landscape, averaging over environmental variability, species composition and organism and ecosystem functions within each cell. Reiners and Lang (1987) concluded that it was possible to find general trends in litterfall distribution in the White Mountains only at large spatial scales and with low levels of resolution. That is the approach I adopted here. The grid cell size was chosen at a scale appropriate for the primary controls on forest-floor mass in the model: changing elevation (meaning temperature and precipitation gradients) and changing species presence. The modeling of 32,000 such cells in the White Mountain National Forest (WMNF) provides a large statistical sample of forest stands in WMNF, and the use of a GIS provides a spatially explicit context.

GIS Environment

The coupling of a process model to spatially-explicit data layers in a GIS provides important links between ecosystem and landscape ecology. I was able to predict stand-scale causes of landscape heterogeneity, for example differences in forest-floor mass under different vegetation types. With the lumped-parameter approach, I was even able to show organism-level causes of landscape heterogeneity; for example an increase in forest-floor mass with elevation due partly to increased production of woody litter in small size classes. I was able to describe controls on forest floor mass in a combinatorial, nonlinear way as a set of superimposed gradients across the landscape. Using spatially-explicit data layers and comparing model results with field measurements allowed me to formulate mechanisms that, when combined, give rise to observed landscape patterns. Or alternatively, to predict landscape patterns from hypothesized

mechanisms. My results for forest-floor N and mass dynamics here should be viewed as referencing reality to the greatest extent presently possible, since this work made use of actual land use - land cover data, actual elevation and a model of actual climate in the region.

The use of GIS images as a means of transferring data between two linked, process-based models worked well in this case but there are limitations to its general application. The method was feasible because the models could be linked by passing a small number of data planes. Estimates of steady-state production in each tissue type at each grid cell location were produced by PnET and read by DocMod. The fact that both models used steady-state quantities as a point of reference made the link unambiguous. The fact that there were no feedbacks from forest-floor processes, such as N mineralization, to forest production made the link straightforward.

Dynamics in Forest Floor Mass

Immediately following a major disturbance to a forest stand such as clear-cutting, decomposition outpaces forest litter inputs and the forest floor loses mass. There are two apparent reasons why forest-floor mass recovers in the time frame shown in figure 3.8 (60-80 years). First, approximately 20% of average foliar litter enters forest-floor humus, and forest-floor aggradation continues at least until the humus mass pool reaches steady-state. Second, wood decomposes slowly and woody litter inputs become more important after year 10 to 20 (Covington, quoted by Bormann and Likens, 1979). DocMod simulations showed both of these to be important mechanisms. Foliar and fine root litter inputs arrested the loss of forest floor mass in the first 20 years, but woody litter

inputs contributed significantly to subsequent forest-floor aggradation. DocMod woody litter inputs reached steady-state in year 45, and the forest-floor mass nearly reached its asymptotic level within 25 years afterward.

Forest-floor mass dynamics are intimately tied to several factors apart from controls on decomposition: the time that has passed since disturbance, the species present and their rates of growth at a location, and tree growth forms at that location. On a longer time scale, disturbance regime is critical. An unmanaged stand of northern hardwood forest in the White Mountains may be subject to hurricane blowdown stochastically, with a mean return time of centuries and with great variability in the interval between events. The subalpine balsam fir forests, in contrast, are often subject to fir-wave mortality with a return time of 60 years. In field observations in the subalpine fir zone, the forest floor mass did not appear to change significantly with different points in the fir-wave cycle (G. E. Lang et al., *personal observation,* quoted by Lambert *et al.*, 1980). A contributing factor may be that because of slower growth at high elevations and the rapid return time of fir waves, mortality produces bole litter in much smaller size classes compared with lower-elevation hardwood forests (Lambert et al., 1980). This may make woody litter more evenly distributed in space and time in the subalpine fir zone. The massive forest floor, undergoing apparently insignificant changes under natural disturbance, prompted Sprugel and Bormann (1981) to suggest that these forests may represent ecosystems in equilibrium with their environment. (Such a concept of steady-state is a landscape-scale, patch-averaging concept, different from the mature-forest steady-state concept used in PnET and DocMod).

The time needed to reach steady-state in mass in any forest-floor component, once inputs have stabilized, is inversely related to the exponential decay constant *k* in that component. In DocMod, the lowest *k* value corresponds to humus. In reality, some humic material remains in the soil even longer, and thus a *k* representing mineralization to CO_2 would be even lower. Significant fluxes of carbon and nitrogen leach, in organic form, from the forest floor to the mineral soil. My future plans for DocMod include parameterizing the model to include forest-floor leaching fluxes explicitly, hence the name DocMod (DOC for dissolved organic carbon). Leaching fluxes from the forest floor have been found to equal 5 to 24% of leaf litter C flux and 15 to 37% of leaf litter N flux (McDowell and Likens, 1988; Qualls et al., 1991; Vance and David, 1991). Much of this material comprises humic substances that sorb in the mineral soil (Qualls and Haines, 1991). Thus, although 60-90 years may be a reasonable time frame for the forest-floor mass and N capital to reach steady-state, this leaves open questions concerning mineral soil organic matter. Much remains to be learned concerning the contributions of foliar, root and woody litter to humus, turnover rates in humus, the leaching of dissolved organic matter from humus and illuviation to mineral soil horizons.

Limitations and Future Work

Some facets of this work were limited by the amount and nature of field data available. One of the functions of synthesis work like the modeling presented here is to identify areas where data are needed and where relationships need to be better understood. One gap in current knowledge that proved significant here concerns the distribution of woody litter in space, time and by size class. Accurate modeling of woody

litter decomposition and nutrient dynamics will probably require separating woody litter into several categories, including size classes and a category denoting whether the material is on or above the ground. Dead boles in the White Mountains can remain standing for as long as 40 years (Sprugel, 1984), undergoing significant decay before contributing to forest floor pools (Harmon, 1982). Placement of wood is an important consideration for nutrient dynamics as well; Lang et al. (1981) measured a C:N ratio of 150:1 for well-decayed wood on the surface of the forest floor, and a C:N ratio of 56:1 for buried wood.

Standards should be developed and recognized for the measurement of litter components in the field. In quantifying litter, investigators sometimes exclude stumps, large woody roots, boles and woody litter above a certain diameter that varies among studies (Covington, 1981; Mattson et al., 1987). Others do include boles in measurements of forest-floor mass and nutrient content (Lambert et al., 1980). Still other studies do not mention either including or excluding woody litter, leaving it open to question (Gosz et al., 1976.) Apart from the problem of standards, quantities of woody litter distributed by size class, by tree age, stand age or by vegetation type are largely unknown. In the present paper I generated hypotheses concerning inputs of total woody litter through time as a forest stand aggrades, fraction of total woody litter that is in FWD size classes, and the change of this fraction with elevation. In doing so I needed to make a number of estimations and assumptions in interpreting published measurements of woody biomass pools and woody litter. The lumped-parameter approach was helpful because I knew I was making estimates averaged across 10 ha patches of forest. Other

approaches, such as an individual-based modeling approach, would have both the capacity and the need to make much more explicit formulations of woody litter distribution.

I see many other areas where better data and better understanding of processes could contribute to improvement of decomposition models. I included no litter quality effect on woody litter decomposition because data were sparse. Tate (1987) suggests that the species of woody litter should not determine its rate of decomposition, but Mattson et al. (1987) found species to be the most significant factor correlating with decay rates of fine woody debris. As another example, nearly all decomposition models use actual or potential evapotranspiration (AET or PET) as a surrogate for temperature and moisture effects when modeling climatic controls on decomposition. As noted above, I found AET to be inadequate for describing climatic effects on woody litter decomposition. A more process-based approach to foliar and root litter decomposition would also be possible if more data were available concerning the direct effects of temperature and moisture on decomposition. Microclimatic effects related to aspect and slope should also be evaluated. Any microclimatic difference related to aspect in WMNF has not been quantified and is not present in the climatic relations used in PnET and DocMod (Ollinger et al., 1993).

The current work makes an incremental step toward the modeling of actual carbon and nutrient cycles in a spatially-explicit manner. By its nature the model application presented here generates dozens of testable hypotheses. Forest-floor mass along any transect in figure 3.9 could be considered a testable hypothesis. If I have accurately

modeled the most important controlling processes at the landscape scale, then transect patterns in the aggregate would prove true, even though individual transects may be inaccurate. Once the first-order effects were accepted, second- and third-order effects could be incorporated. It may be the case that for forest floor mass, there is a first-order effect at the 10-100 ha scale that is not included here such as slope, or aspect effect on foliar litter decomposition, or soil water-holding capacity through its effects on moisture regime. If so, that will be borne out by testing predictions of this model and others like it against field data. I believe the paradigm of litter-quality and climate controlling decomposition rates (Meentemeyer, 1978) stands to be broadened and to yield to increasingly mechanistic understanding of processes as more data become available. Improvements can continue to be made incrementally as more data layers become available and as our understanding and modeling of processes continues to improve.

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APPENDIX

APPENDIX. Sample Chemistry Data

ST: Sample type. P = precipitation; TF = throughfall; Oa = Oa-leachate
Sta.: Stand. 1 = red pine stand; 2 = hardwood stand
Tmt.: Treatment. 1 = reference plot; 2 = low-N addition plot; 3 = high-N addition plot
Amt.: Sample amount collected, reported as hydrologic flux in [cm]

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	10/17	92	1	1	0.18	.	2.51	0.33	0.56	27.03	1.04	3.94	3.72	4.96	13.68	5.37
TF	10/17	92	1	3	0.16	.	3.03	0.55	0.66	29.15	1.15	4.16	3.57	6.09	12.46	5.06
TF	10/17	92	1	2	0.19	.	2.66	0.39	0.43	26.57	1.10	3.82	3.97	6.20	5.39	5.22
TF	10/17	92	2	1	0.19	.	1.69	0.29	0.32	18.94	0.59	3.31	2.08	5.53	3.02	3.29
TF	10/17	92	2	2	0.18	.	1.68	0.16	0.51	40.08	1.34	3.50	3.00	10.30	13.75	4.02
TF	10/17	92	2	3	0.20	.	2.32	0.14	0.40	30.92	1.23	3.60	2.85	9.79	2.85	3.99
P	10/25	92	0	0	1.23	3.65	0.64	0.65	0.00	1.34	0.02	0.55	0.13	0.33	2.50	1.33
TF	10/25	92	1	1	1.07	3.70	0.70	0.27	0.31	9.05	0.42	1.23	1.66	2.05	1.83	3.19
TF	10/25	92	1	3	0.95	3.78	0.83	0.38	0.18	9.05	0.32	1.22	1.25	1.94	1.40	2.86
TF	10/25	92	1	2	1.07	3.74	0.88	0.31	0.17	9.86	0.45	1.28	2.08	1.97	1.36	3.41
TF	10/25	92	2	1	0.85	3.86	0.65	0.44	0.09	4.09	0.14	0.93	0.53	1.51	1.02	2.05
TF	10/25	92	2	2	0.95	3.89	0.71	0.36	0.07	6.21	0.27	0.91	0.80	3.24	1.28	2.70
TF	10/25	92	2	3	0.91	3.95	0.73	0.43	0.05	4.49	0.20	0.87	0.54	2.01	0.71	2.27
Oa	10/25	92	1	1	0.08	3.02	0.13	0.57	1.05	83.41	1.10	7.23	4.51	2.71	26.87	3.83
Oa	10/25	92	1	3	0.16	3.52	11.20	11.55	4.06	135.38	0.77	4.09	3.80	4.63	2.55	4.12
Oa	10/25	92	1	2	0.17	3.33	3.44	2.86	1.63	67.26	0.60	3.62	3.77	2.23	18.25	4.37
Oa	10/25	92	2	1	0.18	3.90	0.09	0.09	0.46	23.33	0.38	3.09	0.89	2.20	2.22	2.40
Oa	10/25	92	2	2	0.14	3.58	0.26	0.10	0.78	35.25	0.55	3.63	1.51	2.07	4.77	2.87
Oa	10/25	92	2	3	0.15	3.49	1.09	0.72	1.52	61.69	0.32	3.64	1.06	0.84	2.59	2.27
P	11/13	92	0	0	3.03	4.60	0.08	0.08	0.00	0.00	0.02	0.37	0.09	0.18	0.62	0.32
TF	11/13	92	1	1	2.34	4.22	0.16	0.06	0.13	8.44	0.22	1.37	0.97	0.98	1.08	1.50

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	11/13	92	1	3	2.20	4.27	0.24	0.09	0.20	9.26	0.20	1.18	0.84	1.04	1.08	1.33
TF	11/13	92	1	2	2.01	4.20	0.23	0.06	0.07	9.92	0.27	1.31	1.14	1.15	1.26	1.65
TF	11/13	92	2	1	1.97	4.73	0.09	0.04	0.03	1.79	0.08	0.96	0.29	0.48	0.85	0.56
TF	11/13	92	2	2	2.34	4.63	0.14	0.06	0.09	3.10	0.13	1.10	0.41	0.89	0.99	0.75
TF	11/13	92	2	3	2.10	4.88	0.08	0.04	0.15	19.11	0.35	1.08	0.51	1.54	1.11	0.59
Oa	11/13	92	1	1	0.40	3.75	0.00	0.06	1.07	60.08	0.70	2.41	2.61	1.73	1.95	2.83
Oa	11/13	92	1	3	0.57	3.60	5.89	6.69	1.39	78.40	0.41	1.87	1.88	2.66	1.61	2.76
Oa	11/13	92	1	2	0.54	3.64	2.92	1.70	1.07	50.92	0.42	2.18	2.26	1.77	1.49	2.62
Oa	11/13	92	2	1	0.78	3.96	0.00	0.19	0.46	25.56	0.34	1.64	0.73	1.70	1.26	1.48
Oa	11/13	92	2	2	0.85	3.98	0.00	0.08	0.67	28.99	0.45	1.60	0.98	1.84	1.51	1.15
Oa	11/13	92	2	3	0.66	3.69	0.17	0.36	1.20	45.61	0.20	2.02	0.73	0.61	1.52	1.14
P	4/23	93	0	0	1.17	4.01	0.48	0.23	0.10	0.97	0.06	1.13	0.13	0.32	1.12	0.84
TF	4/23	93	1	1	0.91	3.87	0.61	0.15	0.49	12.01	0.25	2.41	0.81	0.98	2.87	1.46
TF	4/23	93	1	3	0.80	3.82	1.08	0.21	0.29	14.62	0.29	2.60	0.89	1.23	2.93	1.54
TF	4/23	93	1	2	0.69	3.90	0.76	0.17	0.33	15.03	0.28	3.29	1.01	1.20	3.88	1.71
TF	4/23	93	2	1	0.90	4.05	0.20	0.13	0.69	4.09	0.11	1.70	0.34	0.64	1.91	0.87
TF	4/23	93	2	2	0.87	3.89	1.17	0.29	0.29	6.93	0.23	2.55	0.60	1.08	2.53	1.08
TF	4/23	93	2	3	0.89	4.02	0.72	0.21	0.11	4.97	0.15	2.09	0.34	0.78	1.88	0.90
Oa	5/31	93	1	1	0.26	3.97	0.52	0.25	0.90	44.48	0.50	2.46	1.56	2.75	2.39	1.76
Oa	5/31	93	1	3	0.24	3.60	10.86	8.72	1.57	49.36	0.74	2.70	2.74	5.32	2.54	2.48
Oa	5/31	93	1	2	0.37	3.69	3.39	1.99	1.47	43.41	0.34	2.62	1.76	3.55	2.49	2.09
Oa	5/31	93	2	1	1.06	4.36	0.09	0.14	0.62	45.97	0.41	1.53	0.87	3.31	1.12	1.28
Oa	5/31	93	2	2	0.19	4.24	0.70	0.35	1.17	30.38	0.38	3.09	0.91	2.89	2.32	1.82
Oa	5/31	93	2	3	0.12	4.17	2.82	1.81	1.53	48.75	0.27	6.20	1.05	4.22	3.45	1.82
P	6/16	93	0	0	0.20	3.71	1.51	0.72	0.41	7.54	0.25	1.60	0.95	0.98	2.59	2.06
TF	6/16	93	1	1	0.03	.	2.82	1.40	2.37	49.09	0.18	1.26	0.49	1.53	1.86	0.98
TF	6/16	93	1	3	0.04	.	2.91	1.62	1.50	37.79	0.20	1.40	0.54	1.36	1.91	1.12
TF	6/16	93	1	2	0.06	.	2.29	0.99	1.35	30.97	0.24	1.39	0.60	2.48	2.24	1.42

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	6/16	93	2	1	0.10	.	2.67	1.21	1.57	58.31	0.59	1.87	1.56	3.88	2.67	2.65
TF	6/16	93	2	2	0.06	.	4.57	1.85	2.19	58.11	0.76	1.95	1.68	5.52	3.31	2.43
TF	6/16	93	2	3	0.06	.	5.68	4.03	5.61	102.91	0.97	3.03	1.60	7.97	3.60	4.78
P	6/23	93	0	0	0.45	.	0.59	0.23	0.17	2.99	0.05	2.93	0.18	0.75	2.05	1.09
TF	6/23	93	1	1	0.56	.	2.02	0.33	1.10	48.43	0.87	3.18	2.83	9.97	3.62	4.69
TF	6/23	93	1	3	0.60	.	2.99	0.89	1.11	41.48	0.88	2.16	2.78	8.38	2.07	4.39
TF	6/23	93	1	2	0.46	.	2.41	0.49	0.99	47.11	0.84	2.65	2.93	10.60	3.05	4.77
TF	6/23	93	2	1	0.77	.	0.97	0.18	0.39	33.12	0.47	1.83	1.42	3.93	1.14	2.48
TF	6/23	93	2	2	0.58	.	2.03	0.31	0.86	35.38	0.92	1.91	2.14	7.69	1.48	3.49
TF	6/23	93	2	3	0.74	.	1.50	0.35	0.72	27.46	0.81	1.71	1.58	7.56	1.26	3.37
Oa	6/23	93	1	1	0.11	.	0.52	1.30	1.38	82.74	0.94	3.09	3.23	4.51	4.35	3.31
Oa	6/23	93	1	3	0.06	.	66.40	56.52	.	103.54	3.06	6.09	9.02	12.70	6.09	4.02
Oa	6/23	93	1	2	0.08	.	4.39	4.58	6.84	210.76	1.31	3.19	7.10	9.85	4.27	5.35
Oa	6/23	93	2	1	0.20	.	0.06	0.07	0.82	54.57	0.82	2.81	1.86	3.83	2.54	1.98
Oa	6/23	93	2	2	0.35	.	3.92	1.96	1.96	74.57	1.29	2.78	3.29	6.96	2.78	2.82
Oa	7/10	93	1	1	5.10	4.59	0.74	0.13	0.90	24.73	0.50	1.29	1.51	4.92	1.67	1.95
Oa	7/10	93	1	1	0.75	5.13	0.43	0.34	0.69	19.49	0.22	2.89	0.91	2.76	2.50	1.50
Oa	7/10	93	1	1	0.73	4.60	0.57	0.21	0.85	26.21	0.32	3.00	1.07	4.12	2.77	1.77
Oa	7/10	93	1	1	4.23	4.13	0.48	0.09	0.68	24.52	0.29	1.26	1.08	2.07	1.53	1.65
Oa	7/10	93	1	1	4.46	4.52	0.61	1.81	1.58	41.72	0.19	1.44	0.58	4.32	1.72	1.91
Oa	7/10	93	1	3	5.23	3.89	28.67	23.47	3.87	37.69	0.93	1.51	2.89	8.62	1.92	2.15
Oa	7/10	93	1	3	5.28	3.78	16.67	15.26	2.81	39.77	0.33	1.37	1.03	4.82	1.64	2.43
Oa	7/10	93	1	3	2.96	4.08	6.06	6.03	1.84	27.71	0.13	1.57	0.52	3.29	2.04	1.82
Oa	7/10	93	1	3	5.29	3.93	41.68	36.62	3.92	33.03	1.24	1.06	4.10	7.58	1.78	1.85
Oa	7/10	93	1	3	4.29	3.57	55.32	49.00	9.90	42.68	0.94	1.67	3.57	7.03	2.16	2.93
Oa	7/10	93	1	2	4.70	4.12	2.20	1.49	0.93	26.79	0.20	1.26	0.96	3.28	1.62	1.97
Oa	7/10	93	1	2	5.20	4.20	6.25	5.40	0.75	27.27	0.34	1.24	1.10	4.39	2.06	1.74
Oa	7/10	93	1	2	2.54	4.34	6.18	5.63	1.19	22.75	0.18	1.11	0.92	3.95	1.39	1.63

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	7/10	93	1	2	4.98	4.40	2.70	3.46	1.45	39.42	0.18	1.18	1.89	8.16	1.42	1.99
Oa	7/10	93	1	2	2.34	4.26	5.55	5.70	0.99	31.46	0.16	1.39	0.73	4.57	1.68	1.69
Oa	7/10	93	2	1	0.79	5.74	0.28	0.09	0.45	17.86	0.29	3.25	0.72	2.46	2.37	1.10
Oa	7/10	93	2	1	5.28	4.49	0.35	0.15	0.46	22.28	0.42	1.04	1.19	2.13	1.02	1.33
Oa	7/10	93	2	1	4.62	4.78	0.37	0.20	0.53	16.08	0.36	1.07	0.83	2.62	1.05	1.30
Oa	7/10	93	2	1	5.25	5.16	0.48	0.25	0.72	24.85	0.49	1.09	1.40	4.27	1.30	1.44
Oa	7/10	93	2	1	5.19	4.39	0.38	0.16	0.59	20.68	0.33	1.08	0.80	2.87	1.37	1.50
Oa	7/10	93	2	2	4.36	5.02	1.32	1.30	0.93	17.02	0.31	1.13	0.91	2.58	1.23	1.40
Oa	7/10	93	2	2	5.19	4.96	1.48	1.17	0.97	17.09	0.14	1.01	0.44	5.39	1.18	1.41
Oa	7/10	93	2	2	5.24	4.36	1.50	1.07	0.97	16.68	0.20	1.09	0.51	2.32	1.13	1.48
Oa	7/10	93	2	2	2.59	4.55	1.47	1.23	0.98	14.11	0.14	1.21	0.42	1.76	1.02	1.21
Oa	7/10	93	2	2	5.33	4.89	1.73	1.92	1.17	15.92	0.26	1.33	0.76	2.12	1.75	1.36
Oa	7/10	93	2	3	5.22	5.28	8.02	8.16	0.74	13.86	0.25	1.35	0.71	2.26	1.06	1.36
Oa	7/10	93	2	3	1.04	5.38	5.92	6.25	1.34	20.53	0.06	2.29	0.35	3.13	1.89	1.25
Oa	7/10	93	2	3	0.62	3.97	11.88	8.18	1.93	16.59	0.37	3.27	0.75	2.28	3.33	1.00
Oa	7/10	93	2	3	4.28	4.01	6.05	5.29	1.40	25.63	0.15	1.07	0.37	1.63	1.08	1.38
Oa	7/10	93	2	3	0.52	4.17	65.40	59.68	6.27	21.96	1.32	3.53	2.74	6.98	3.51	1.53
P	7/21	93	0	0	1.54	4.61	0.20	0.13	0.08	1.02	0.02	0.81	0.05	0.33	0.94	0.67
TF	7/21	93	1	1	1.25	4.06	1.00	0.34	1.00	33.31	0.45	1.21	1.28	2.80	1.63	1.44
TF	7/21	93	1	3	1.12	3.99	1.44	0.85	1.33	45.47	0.60	1.34	1.84	3.89	1.69	1.65
TF	7/21	93	1	2	0.88	3.87	1.74	0.71	1.34	49.21	0.64	1.54	2.35	4.01	2.33	2.15
TF	7/21	93	2	1	0.95	4.43	0.43	0.30	0.76	25.58	0.35	1.47	0.95	2.51	1.58	1.12
TF	7/21	93	2	2	0.96	4.32	0.73	0.47	1.10	44.21	0.49	1.53	1.09	4.94	2.46	1.35
TF	7/21	93	2	3	1.21	4.57	0.56	0.28	1.21	35.44	0.45	1.55	0.85	4.37	2.36	1.17
Oa	7/21	93	1	1	0.69	4.05	0.57	0.55	0.93	43.71	0.46	1.57	1.41	4.24	2.01	1.43
Oa	7/21	93	1	3	0.58	3.70	21.66	20.44	1.32	72.41	0.71	1.92	2.53	7.58	2.66	1.98
Oa	7/21	93	1	2	1.14	3.79	2.90	3.36	1.41	80.54	0.36	1.95	1.90	4.07	2.50	1.53
Oa	7/21	93	2	1	2.33	4.05	0.12	0.05	0.60	30.66	0.39	1.09	0.95	2.45	1.28	1.03

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	7/21	93	2	2	0.55	3.96	1.32	0.63	1.73	68.73	0.59	1.44	1.64	7.56	1.97	1.69
Oa	7/21	93	2	3	0.31	3.82	5.29	5.67	1.66	57.24	0.32	1.40	0.92	2.79	1.45	1.22
P	7/28	93	0	0	1.51	3.78	0.57	0.36	0.03	1.30	0.03	0.76	0.13	0.21	1.02	1.53
TF	7/28	93	1	1	1.47	3.83	0.71	0.19	0.68	20.65	0.34	1.14	1.10	2.05	1.58	1.95
TF	7/28	93	1	3	1.56	3.99	1.16	0.69	0.89	26.20	0.39	1.30	1.34	2.86	1.53	1.98
TF	7/28	93	1	2	1.44	3.78	1.02	0.39	1.03	40.48	0.49	1.34	2.04	2.81	1.86	2.34
TF	7/28	93	2	1	1.35	4.05	0.54	0.12	0.33	10.48	0.20	1.24	0.74	1.76	1.33	1.70
TF	7/28	93	2	2	1.25	4.18	1.64	0.65	0.61	15.53	0.33	1.47	0.85	3.57	1.52	1.85
TF	7/28	93	2	3	1.56	4.11	2.00	1.17	0.75	13.47	0.33	0.99	0.68	3.11	1.33	1.79
Oa	7/28	93	1	1	0.56	3.99	0.49	0.45	1.33	60.68	0.77	1.78	2.56	3.33	1.80	2.03
Oa	7/28	93	1	3	0.50	3.75	7.15	6.21	.	70.23	1.76	1.65	5.41	7.44	2.27	2.52
Oa	7/28	93	1	2	1.11	3.50	14.73	8.96	6.23	135.25	1.77	2.49	9.17	5.81	2.06	2.36
Oa	7/28	93	2	1	2.04	4.07	0.22	0.04	0.47	28.86	0.54	1.26	1.29	2.17	1.31	1.76
Oa	7/28	93	2	2	2.26	3.64	11.01	4.33	2.42	37.00	1.67	1.00	4.32	7.88	1.65	1.84
Oa	7/28	93	2	3	0.70	3.59	23.00	18.06	6.57	41.33	1.18	1.42	3.19	4.31	1.21	1.67
TF	8/4	93	1	1	.	3.74	0.99	0.23	0.22	8.98	0.21	0.49	0.86	0.89	1.37	2.01
TF	8/4	93	1	3	.	3.70	1.13	0.35	0.31	10.06	0.22	0.48	0.93	1.17	1.36	2.11
TF	8/4	93	1	2	.	3.65	0.97	0.28	0.27	9.35	0.20	0.45	0.86	0.87	1.26	1.96
TF	8/4	93	2	1	.	3.72	0.97	0.24	0.25	8.70	0.20	0.58	0.87	1.19	1.09	1.89
TF	8/4	93	2	2	.	3.62	1.05	0.24	0.24	5.59	0.19	0.47	0.63	1.27	1.14	1.89
TF	8/4	93	2	3	.	3.65	1.03	0.37	0.14	4.85	0.16	0.40	0.44	1.20	1.28	1.86
Oa	8/4	93	1	1	2.88	3.67	0.67	0.50	0.85	48.26	0.56	1.06	2.11	2.01	2.09	2.02
Oa	8/4	93	1	3	3.94	3.43	24.33	22.12	0.00	55.89	0.72	1.04	2.41	3.67	2.95	2.14
Oa	8/4	93	1	2	3.75	3.55	4.12	3.37	2.05	55.94	0.44	0.89	2.26	2.21	1.30	2.17
Oa	8/4	93	2	1	3.96	3.68	0.58	0.08	0.77	23.65	0.52	0.77	1.23	0.97	1.12	1.89
Oa	8/4	93	2	2	5.23	3.55	1.80	0.58	1.10	27.50	0.46	0.87	1.38	1.44	1.37	1.72
Oa	8/4	93	2	3	3.04	3.35	6.47	5.30	2.90	35.98	0.35	0.87	1.00	1.57	1.21	1.72
Oa	8/16	93	1	1	0.42	3.29	0.55	0.29	2.15	65.90	0.79	1.34	3.30	2.15	3.97	2.28

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	8/16	93	1	3	0.57	3.55	0.86	0.11	17.69	90.57	0.59	1.04	2.73	2.92	4.95	3.03
Oa	8/16	93	1	2	1.23	3.29	1.11	0.20	5.46	75.22	0.60	1.15	3.05	1.90	1.97	2.56
Oa	8/16	93	2	1	1.39	3.51	1.10	0.28	0.01	18.18	0.54	0.70	1.37	1.51	1.71	2.03
Oa	8/16	93	2	2	1.53	3.35	0.68	0.07	0.94	19.12	0.39	0.86	1.25	1.57	2.29	2.06
Oa	8/16	93	2	3	0.65	3.11	0.61	0.06	2.96	33.90	0.17	1.05	0.54	0.89	3.42	1.99
P	8/17	93	0	0	0.60	3.38	0.86	0.32	0.00	2.40	0.03	0.52	0.11	0.13	2.35	1.26
TF	8/17	93	1	1	0.37	3.43	0.74	0.51	0.36	31.72	0.31	0.90	1.21	1.67	1.26	2.22
TF	8/17	93	1	3	0.39	3.46	1.14	0.19	0.81	30.08	0.33	0.81	1.38	2.46	1.26	2.24
TF	8/17	93	1	2	0.31	3.52	1.09	0.30	0.87	35.03	0.41	1.71	1.92	2.00	1.66	2.61
TF	8/17	93	2	1	0.45	3.68	0.60	0.15	0.48	26.44	0.31	0.85	1.28	2.30	1.11	1.89
TF	8/17	93	2	2	0.40	3.98	0.76	0.16	0.33	23.28	0.38	0.91	1.08	4.54	1.30	2.07
TF	8/17	93	2	3	0.45	3.87	1.19	0.52	0.83	85.69	0.66	0.78	1.29	6.16	1.00	2.23
TF	8/23	93	1	1	.	3.94	0.23	0.08	0.22	12.75	0.13	0.59	0.50	0.95	0.82	1.22
TF	8/23	93	1	3	.	3.88	0.51	0.09	0.32	15.59	0.17	0.51	0.77	1.68	0.88	1.51
TF	8/23	93	1	2	.	3.65	0.48	0.14	0.53	22.06	0.23	0.70	1.23	1.55	1.04	1.98
TF	8/23	93	2	1	.	4.06	0.20	0.05	0.19	9.31	0.18	0.49	0.72	1.24	0.73	1.16
TF	8/23	93	2	2	.	4.03	0.32	0.07	0.15	6.52	0.16	0.48	0.52	2.13	0.77	1.34
TF	8/23	93	2	3	.	4.40	0.13	0.06	0.11	6.72	0.15	0.76	0.35	2.12	0.85	1.17
Oa	8/23	93	1	1	0.75	3.51	0.08	0.93	3.13	137.80	0.82	1.84	3.75	2.48	1.44	1.34
Oa	8/23	93	1	3	0.72	3.43	8.24	9.55	8.17	196.32	0.96	1.55	4.50	2.26	1.26	2.19
Oa	8/23	93	1	2	1.29	3.30	1.07	1.91	6.87	246.79	1.01	2.18	6.48	1.72	1.35	1.62
Oa	8/23	93	2	1	1.22	3.69	0.04	0.25	1.05	37.86	0.50	0.96	1.20	0.58	0.83	1.23
Oa	8/23	93	2	2	1.84	3.46	0.07	0.22	1.76	56.55	0.33	0.69	1.06	1.49	1.58	1.12
Oa	8/23	93	2	3	1.20	3.31	0.32	0.92	3.45	92.17	0.24	1.27	0.75	1.41	1.81	0.94
TF	9/9	93	1	1	.	3.59	0.92	0.24	0.54	21.39	0.45	0.78	1.95	2.33	1.46	3.01
TF	9/9	93	1	3	.	3.57	1.68	0.47	0.78	25.29	0.52	1.00	2.14	3.83	1.60	2.91
TF	9/9	93	1	2	.	3.58	1.50	0.42	0.59	22.36	0.55	0.97	2.13	3.17	1.71	2.94
TF	9/9	93	2	1	.	3.92	0.04	0.11	0.17	15.87	0.28	1.52	1.15	2.74	1.56	2.14

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	9/9	93	2	2	.	3.86	0.50	0.07	0.24	14.21	0.36	0.81	1.22	3.42	1.19	2.38
TF	9/9	93	2	3	.	3.90	0.64	0.08	0.46	43.56	0.46	1.00	0.98	5.23	1.20	2.20
Oa	9/9	93	1	1	0.84	3.52	1.22	0.41	1.78	79.88	1.09	1.42	4.03	4.49	2.54	3.22
Oa	9/9	93	1	3	0.85	3.52	56.92	47.44	16.22	138.65	3.26	2.15	11.70	14.00	3.26	4.09
Oa	9/9	93	1	2	1.27	3.50	18.14	17.28	8.81	256.25	1.81	2.29	10.10	8.61	3.72	4.12
Oa	9/9	93	2	1	2.98	4.57	0.06	0.10	2.14	54.50	0.54	1.26	1.69	11.90	2.77	2.11
Oa	9/9	93	2	2	2.06	3.36	11.45	7.20	3.70	34.83	1.05	0.93	2.90	6.83	1.64	2.79
Oa	9/9	93	2	3	0.72	3.09	10.09	7.91	4.86	64.48	0.58	1.00	1.60	3.16	2.05	3.00
P	9/10	93	0	0	0.58	4.02	0.26	0.27	0.06	0.63	0.01	0.43	0.06	0.17	0.72	0.95
TF	9/10	93	1	1	0.37	3.54	0.79	0.17	0.40	21.09	0.32	0.88	1.53	1.63	1.80	2.58
TF	9/10	93	1	3	0.46	3.53	1.43	0.46	0.58	23.53	0.38	0.88	1.57	2.64	1.91	2.54
TF	9/10	93	1	2	0.35	3.54	0.99	0.32	0.47	17.83	0.27	0.83	1.12	1.82	1.56	2.26
TF	9/10	93	2	1	0.40	3.76	0.32	0.13	0.38	18.47	0.33	0.90	1.39	1.98	1.68	1.79
TF	9/10	93	2	2	0.33	3.83	0.88	0.21	0.33	13.96	0.26	0.68	0.93	3.22	1.21	2.01
TF	9/10	93	2	3	0.41	3.89	0.54	0.07	0.31	16.88	0.28	0.93	0.71	3.56	1.30	1.93
Oa	9/10	93	1	1	0.03	.	0.22	0.53	2.87	122.08	0.21	1.09	1.20	0.62	1.58	0.70
Oa	9/10	93	1	3	0.05	.	19.49	25.98	12.01	268.12	.	.	.	.	2.30	2.33
Oa	9/10	93	1	2	0.02	.	6.26	7.30	13.34	323.90	0.21	1.42	1.48	0.71	1.74	0.77
Oa	9/10	93	2	1	0.07	.	0.11	0.57	1.64	39.65	0.29	1.25	0.67	3.74	4.67	1.12
Oa	9/10	93	2	2	0.14	.	0.34	0.15	1.21	46.31	0.55	1.26	1.90	2.31	2.08	1.85
Oa	9/10	93	2	3	0.04	.	3.95	1.97	1.99	53.54	0.18	1.41	0.64	0.79	2.10	0.87
Oa	9/27	93	1	1	1.55	3.67	0.04	0.14	2.04	98.87	0.79	1.51	3.29	0.73	1.47	1.59
Oa	9/27	93	1	3	1.74	3.32	42.64	30.74	5.73	120.09	2.88	1.29	11.45	5.70	1.82	2.37
Oa	9/27	93	1	2	1.34	3.38	7.84	3.09	3.50	83.59	0.95	1.59	5.01	1.59	1.16	1.51
Oa	9/27	93	2	1	4.29	3.84	0.02	0.34	1.36	40.09	0.41	0.85	0.90	2.08	0.97	1.37
Oa	9/27	93	2	2	4.66	3.44	4.05	0.72	1.54	37.78	0.63	0.70	1.87	1.53	0.99	1.02
Oa	9/27	93	2	3	2.02	3.08	32.70	17.65	3.61	41.70	1.93	1.25	5.43	2.10	1.29	1.00
P	9/28	93	0	0	0.48	.	0.16	0.13	0.05	0.02	0.03	0.70	0.07	0.23	1.23	0.59

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	9/28	93	1	1	0.29	4.35	0.12	0.10	0.34	19.34	0.15	0.75	0.66	1.61	1.58	0.87
TF	9/28	93	1	3	0.32	4.36	2.57	2.37	0.57	16.05	0.16	0.67	0.48	1.77	1.60	0.74
TF	9/28	93	1	2	0.23	.	1.14	1.08	0.76	29.05	0.26	1.15	1.31	2.13	2.10	1.38
TF	9/28	93	2	1	0.28	4.67	0.12	0.10	0.18	7.70	0.10	0.77	0.38	1.37	1.38	0.63
TF	9/28	93	2	2	0.23	4.65	1.08	0.91	0.37	9.21	0.11	0.91	0.31	2.10	1.48	0.71
TF	9/28	93	2	3	0.30	4.89	0.65	0.58	0.40	8.02	0.09	0.84	0.21	1.97	1.35	0.67
TF	10/5	93	1	1	.	4.03	1.08	0.06	0.30	18.68	0.33	1.05	1.21	3.62	1.97	1.85
TF	10/5	93	1	3	.	3.90	1.69	0.59	0.31	15.57	0.30	1.14	1.08	2.78	1.77	1.62
TF	10/5	93	1	2	.	3.86	1.33	0.25	0.33	13.39	0.28	0.88	0.93	2.22	1.62	1.57
TF	10/5	93	2	1	.	4.04	0.98	0.07	0.22	10.10	0.22	0.81	0.83	2.73	1.24	1.39
TF	10/5	93	2	2	.	4.27	1.31	0.06	0.29	15.63	.	.	.	.	1.59	1.54
TF	10/5	93	2	3	.	4.32	1.15	0.25	0.38	14.26	.	.	.	.	1.32	1.43
Oa	10/5	93	1	1	0.03	.	0.16	0.44	1.75	85.65	.	.	.	.	3.12	0.77
Oa	10/5	93	1	3	0.26	3.62	11.47	14.31	6.96	175.72	.	.	.	.	2.12	2.41
Oa	10/5	93	1	2	0.16	3.42	3.07	0.55	4.06	102.57	.	.	.	.	1.88	2.09
Oa	10/5	93	2	1	0.20	3.98	0.40	0.13	1.35	34.89	0.46	1.30	1.29	3.74	2.04	1.50
Oa	10/5	93	2	2	0.58	3.45	0.69	0.09	1.57	54.41	0.32	1.04	1.07	0.60	2.01	1.59
Oa	10/5	93	2	3	0.05	.	2.28	0.81	2.38	63.54	0.17	1.58	0.69	0.41	1.57	0.80
TF	10/14	93	1	1	.	4.30	0.84	0.08	0.52	15.01	0.30	0.97	1.11	2.40	1.80	1.40
TF	10/14	93	1	3	.	4.07	1.47	0.29	0.73	14.21	0.33	1.07	1.45	2.10	1.90	1.51
TF	10/14	93	1	2	.	4.17	0.92	0.12	0.46	12.43	0.24	0.90	0.88	2.09	1.55	1.23
TF	10/14	93	2	1	.	4.44	0.42	0.12	0.36	14.03	0.26	0.76	0.77	2.26	1.37	0.97
TF	10/14	93	2	2	.	4.44	0.75	0.11	0.44	16.65	0.23	0.80	0.61	3.63	1.59	1.04
TF	10/14	93	2	3	.	4.45	0.61	0.19	0.26	15.35	0.19	0.70	0.43	2.43	1.36	0.84
Oa	10/14	93	1	1	0.54	3.69	0.18	0.11	1.62	77.50	0.74	1.41	2.96	2.28	3.09	2.09
Oa	10/14	93	1	3	1.04	3.52	8.53	6.71	0.59	70.01	0.60	0.86	2.68	2.00	2.00	1.79
Oa	10/14	93	1	2	1.70	3.60	1.88	1.37	1.90	57.11	0.33	1.17	1.82	0.98	1.78	1.71
Oa	10/14	93	2	1	1.52	3.90	0.08	0.04	0.49	22.53	0.29	0.87	0.64	1.57	1.62	1.25

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	10/14	93	2	2	2.70	3.70	0.25	0.07	0.79	31.36	0.17	0.93	0.48	0.95	1.75	0.99
Oa	10/14	93	2	3	1.76	3.61	0.80	1.07	2.01	45.52	0.12	0.96	0.38	0.42	1.59	1.11
Oa	10/27	93	1	1	0.16	3.79	0.06	0.40	2.01	93.90	0.90	2.15	4.04	0.98	3.55	2.70
Oa	10/27	93	1	3	0.43	3.46	8.19	9.85	6.39	179.80	1.06	1.59	5.09	2.51	2.64	3.20
Oa	10/27	93	1	2	0.78	3.50	1.56	0.53	2.79	81.71	0.50	1.59	3.15	0.60	1.62	2.47
Oa	10/27	93	2	1	0.19	3.76	0.06	0.15	1.29	39.02	0.48	1.42	1.19	2.58	4.03	1.29
Oa	10/27	93	2	2	0.68	3.51	0.05	0.09	1.26	55.53	0.28	1.30	0.92	1.38	2.89	1.73
Oa	10/27	93	2	3	0.51	3.46	0.76	0.99	1.83	59.45	0.16	1.51	0.59	0.60	3.17	1.65
TF	11/4	93	1	1	.	4.22	0.22	0.05	0.08	7.12	0.12	0.75	0.42	0.79	1.00	0.96
TF	11/4	93	1	3	.	4.10	0.51	0.06	0.21	10.48	0.13	0.78	0.50	1.17	1.11	1.05
TF	11/4	93	1	2	.	4.09	0.38	0.06	0.20	9.20	0.15	0.80	0.66	1.00	1.15	1.17
TF	11/4	93	2	1	.	4.31	0.25	0.06	0.09	5.27	0.11	0.68	0.40	1.18	0.90	0.79
TF	11/4	93	2	2	.	4.28	0.52	0.08	0.12	6.10	0.16	0.80	0.43	2.00	1.19	0.95
TF	11/4	93	2	3	.	4.38	0.25	0.08	0.02	5.32	0.07	0.62	0.20	1.34	0.86	0.75
Oa	11/4	93	1	1	0.53	3.73	0.07	0.11	1.83	71.52	0.73	3.46	3.22	1.05	3.31	2.22
Oa	11/4	93	1	3	0.68	3.48	7.70	6.25	6.15	100.51	0.74	3.45	3.26	3.64	3.50	2.24
Oa	11/4	93	1	2	0.76	3.57	1.88	0.41	2.49	60.67	0.45	3.45	2.63	1.05	3.45	2.08
Oa	11/4	93	2	1	0.47	3.90	0.06	0.09	1.41	39.34	0.55	2.81	1.28	2.03	2.61	1.58
Oa	11/4	93	2	2	0.70	3.78	0.08	0.11	0.87	31.11	0.23	2.23	0.77	0.88	2.93	1.34
Oa	11/4	93	2	3	0.66	3.66	0.42	0.71	1.69	43.95	0.14	3.08	0.48	0.92	3.10	1.29
Oa	11/30	93	1	1	2.06	3.75	0.19	0.13	1.22	45.59	0.58	1.16	2.45	0.91	3.10	1.92
Oa	11/30	93	1	3	2.48	3.47	4.80	4.25	2.88	66.28	0.53	1.30	2.19	2.82	3.36	2.08
Oa	11/30	93	1	2	2.72	3.48	1.57	0.46	1.64	40.04	0.37	1.23	2.12	0.70	3.29	2.10
Oa	11/30	93	2	1	2.80	3.91	0.12	0.11	0.65	20.14	0.26	1.37	0.58	1.77	2.07	0.94
Oa	11/30	93	2	2	3.54	3.66	0.13	0.09	0.77	25.46	0.17	1.02	0.54	1.40	2.54	1.15
Oa	11/30	93	2	3	2.88	3.61	0.26	0.35	1.00	27.01	0.09	1.11	0.29	0.80	2.12	1.07
Oa	4/14	94	1	1	.	4.14	0.87	0.08	0.28	14.18	0.24	1.18	0.71	0.55	1.18	1.05
Oa	4/14	94	1	3	.	4.18	1.46	1.00	0.29	12.20	0.12	1.02	0.35	1.48	1.42	1.10

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	4/14	94	1	2	.	4.12	1.31	0.23	0.31	9.69	0.17	1.17	0.57	0.94	1.56	0.97
Oa	4/14	94	2	1	.	4.92	0.08	0.05	0.05	5.67	0.06	0.73	0.18	0.59	0.79	0.40
Oa	4/14	94	2	2	.	4.63	0.08	0.04	0.15	10.67	0.04	0.72	0.18	0.81	0.92	0.50
Oa	4/14	94	2	3	.	4.44	0.11	0.28	0.32	12.17	0.07	1.06	0.17	0.54	1.24	0.89
Oa	5/4	94	1	1	0.87	3.93	1.40	0.36	0.50	23.35	0.61	1.31	2.07	1.98	1.44	2.82
Oa	5/4	94	1	3	0.26	3.90	2.83	1.86	0.67	23.83	0.52	1.59	1.52	4.03	1.63	3.07
Oa	5/4	94	1	2	0.28	3.74	2.04	0.92	0.59	22.89	0.40	1.86	1.91	1.88	2.05	3.27
Oa	5/4	94	2	1	2.19	4.21	0.77	0.22	0.32	13.04	0.44	0.80	1.00	1.62	1.26	1.61
Oa	5/4	94	2	2	0.85	3.97	0.92	0.14	0.35	16.26	0.28	0.95	0.62	1.56	1.19	1.59
Oa	5/4	94	2	3	1.16	4.15	0.77	1.15	0.82	20.63	0.13	0.99	0.34	1.61	1.04	1.55
TF	5/6	94	1	1	0.22	4.17	1.10	0.25	0.52	15.25	0.17	1.52	0.90	0.82	1.73	1.11
TF	5/6	94	1	3	0.17	4.08	2.17	0.96	0.87	21.08	0.26	2.10	1.31	1.77	2.55	1.40
TF	5/6	94	1	2	0.17	4.19	1.38	0.47	0.78	18.75	0.21	2.37	1.23	1.36	2.85	1.27
TF	5/6	94	2	1	0.25	4.58	0.50	0.13	0.39	8.49	0.10	1.29	0.60	0.84	1.40	0.68
TF	5/6	94	2	2	0.23	4.31	1.20	0.37	0.53	10.71	0.18	1.38	0.84	1.16	1.60	0.82
TF	5/6	94	2	3	0.28	4.42	1.18	0.66	0.57	9.49	0.14	1.53	0.53	1.11	1.68	0.70
TF	5/11	94	1	1	.	4.30	0.28	0.07	0.07	6.03	0.07	0.87	0.29	0.35	0.98	0.97
TF	5/11	94	1	3	.	4.26	0.42	0.13	0.26	8.56	0.09	0.77	0.37	0.66	0.82	1.04
TF	5/11	94	1	2	.	4.20	0.38	0.09	0.12	10.92	0.11	0.87	0.58	0.53	1.06	1.26
TF	5/11	94	2	1	.	4.49	0.26	0.12	0.07	6.39	0.09	0.76	0.39	0.64	0.70	0.81
TF	5/11	94	2	2	.	4.35	0.40	0.14	0.07	3.18	0.06	0.71	0.21	0.62	0.81	0.86
TF	5/11	94	2	3	.	4.46	0.35	0.19	0.08	2.41	0.05	0.62	0.16	0.58	0.64	0.81
Oa	5/11	94	1	1	0.88	4.10	0.11	0.07	0.83	37.66	0.35	1.20	1.28	1.11	0.85	1.49
Oa	5/11	94	1	3	0.19	.	26.21	5.08	0.83	19.87	3.40	3.20	8.48	7.45	2.16	1.56
Oa	5/11	94	1	2	0.32	3.69	4.15	0.17	0.81	29.57	0.67	2.15	2.56	1.62	0.99	1.81
Oa	5/11	94	2	1	1.22	4.30	0.15	0.04	0.35	17.59	0.28	0.91	0.55	0.93	0.84	0.93
Oa	5/11	94	2	2	0.43	3.85	4.73	0.20	0.58	16.89	0.67	1.50	1.06	2.43	1.05	1.08
Oa	5/11	94	2	3	0.58	3.14	32.13	5.82	0.00	20.78	2.12	3.64	4.03	7.23	1.37	0.91

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	5/27	94	1	1	0.28	4.10	0.26	0.06	0.73	31.54	0.32	1.18	1.14	1.38	1.22	1.65
Oa	5/27	94	1	3	0.11	.	9.00	4.89	0.72	32.38	0.76	1.95	2.29	3.83	2.09	1.86
Oa	5/27	94	1	2	0.07	.	1.64	0.46	0.81	28.74	0.20	1.70	0.90	0.99	1.01	1.21
Oa	5/27	94	2	1	0.72	4.31	0.20	0.05	0.54	20.83	0.34	0.91	0.78	1.21	0.99	1.21
Oa	5/27	94	2	2	0.32	3.53	0.56	0.11	0.70	24.16	0.31	1.15	0.68	2.09	8.95	1.31
Oa	5/27	94	2	3	0.15	.	2.59	2.30	0.91	26.90	0.11	1.95	0.33	1.68	2.55	1.13
Oa	6/6	94	1	1	0.93	4.13	1.31	0.07	0.43	21.65	0.45	0.85	1.56	2.55	1.39	1.69
Oa	6/6	94	1	3	0.70	3.49	44.04	31.33	0.77	22.39	2.21	1.03	6.80	5.41	1.64	1.70
Oa	6/6	94	1	2	0.54	3.61	10.17	4.85	1.05	21.92	0.68	1.12	2.92	2.77	1.58	1.80
Oa	6/6	94	2	1	1.41	4.67	0.62	0.16	0.56	21.96	0.43	0.76	0.99	3.66	0.93	1.39
Oa	6/6	94	2	2	1.28	3.76	23.38	16.54	1.35	21.53	1.43	0.78	2.99	6.05	1.42	1.52
Oa	6/6	94	2	3	0.53	3.38	43.25	29.87	3.65	21.06	2.33	1.21	4.14	7.10	1.33	1.27
TF	6/7	94	1	1	0.27	3.98	2.09	0.35	1.51	52.23	0.69	1.92	2.08	5.70	2.59	2.34
TF	6/7	94	1	3	0.34	3.95	2.88	0.85	1.36	50.82	0.72	2.09	1.97	6.03	2.51	2.41
TF	6/7	94	1	2	0.36	3.93	2.46	0.45	1.10	49.57	0.62	1.87	2.08	5.09	2.69	2.39
TF	6/7	94	2	1	0.32	4.27	.	0.34	.	168.91	0.83	1.74	1.93	8.17	1.77	1.92
TF	6/7	94	2	2	0.35	4.25	1.85	0.45	1.85	110.44	0.83	1.45	1.62	8.39	1.79	1.79
TF	6/7	94	2	3	0.36	4.54	1.10	0.70	3.14	201.12	1.00	1.48	1.38	10.40	1.62	1.78
TF	6/22	94	1	1	0.19	4.55	1.52	0.05	1.83	75.19	1.20	3.36	2.84	22.55	7.85	4.58
TF	6/22	94	1	3	0.23	4.10	3.19	1.33	1.93	55.13	0.90	2.52	2.32	12.20	4.10	4.28
TF	6/22	94	1	2	0.18	4.60	2.93	1.97	3.75	72.47	1.23	3.64	3.14	21.70	7.70	5.47
TF	6/22	94	2	1	0.25	4.16	1.00	0.07	2.19	74.51	0.81	1.70	1.95	6.63	2.03	2.96
TF	6/22	94	2	2	0.18	4.11	1.89	0.11	2.21	104.36	1.34	2.47	2.69	12.10	2.72	4.20
TF	6/22	94	2	3	0.31	5.09	0.65	0.05	1.89	126.95	1.22	3.91	1.85	15.00	3.43	3.84
TF	6/25	94	1	1	.	4.06	0.93	0.31	0.89	35.27	0.50	1.87	1.59	8.33	3.15	3.99
TF	6/25	94	1	3	.	4.03	1.48	1.10	1.12	36.98	0.51	1.60	1.73	7.66	2.35	4.24
TF	6/25	94	1	2	.	4.01	1.27	0.65	1.07	43.99	0.57	1.80	2.40	8.46	3.17	4.17
TF	6/25	94	2	1	.	4.03	0.73	0.45	0.60	27.65	0.37	1.03	1.35	2.55	1.01	2.87

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	6/25	94	2	2	.	3.97	1.04	0.54	0.68	24.26	0.54	1.11	1.43	3.76	1.16	3.61
TF	6/25	94	2	3	.	4.02	0.85	0.27	0.74	22.46	0.51	0.85	1.03	3.90	0.94	3.22
Oa	6/25	94	1	1	0.87	3.96	0.57	0.11	1.53	56.60	0.86	1.85	2.69	7.42	3.46	3.78
Oa	6/25	94	1	3	0.47	3.71	10.75	9.70	1.99	72.36	0.94	2.46	3.32	6.69	3.29	4.29
Oa	6/25	94	1	2	0.72	3.75	2.04	2.09	1.56	70.70	0.58	2.17	2.73	7.54	4.23	4.52
Oa	6/25	94	2	1	1.64	4.09	0.42	0.19	0.92	39.88	0.80	1.24	1.74	3.78	1.00	2.58
Oa	6/25	94	2	2	1.64	3.81	1.25	0.42	1.56	61.53	0.89	1.79	2.23	5.30	1.53	3.54
Oa	6/25	94	2	3	0.56	3.69	2.74	3.16	1.73	52.70	0.26	1.38	0.62	2.34	1.30	3.06
Oa	7/12	94	1	1	2.56	4.13	0.81	0.09	0.91	37.55	0.57	1.31	1.91	3.50	1.81	2.10
Oa	7/12	94	1	3	2.56	3.65	24.80	17.80	1.68	42.12	1.32	1.37	4.51	5.59	2.02	2.34
Oa	7/12	94	1	2	2.66	3.72	9.48	5.35	0.69	34.29	0.66	1.14	2.96	5.12	2.11	2.26
Oa	7/12	94	2	1	2.81	4.08	0.54	0.09	0.84	27.74	0.61	0.98	1.30	1.57	1.01	1.92
Oa	7/12	94	2	2	3.24	3.76	12.27	7.27	0.98	26.85	1.06	1.04	3.06	4.11	1.47	1.99
Oa	7/12	94	2	3	2.54	3.81	9.20	6.98	2.04	31.89	0.54	0.83	1.23	2.66	1.05	1.63
TF	7/19	94	1	1	.	3.91	1.51	0.83	0.81	25.75	0.52	0.85	1.92	3.17	1.62	3.61
TF	7/19	94	1	3	.	3.96	1.68	1.27	0.88	26.49	0.52	0.97	1.89	3.35	1.73	3.72
TF	7/19	94	1	2	.	3.97	1.90	1.27	0.97	29.99	0.64	1.02	2.54	3.82	1.82	4.00
TF	7/19	94	2	1	.	4.09	1.06	0.71	0.60	15.83	0.36	0.90	1.57	2.23	1.29	2.68
TF	7/19	94	2	2	.	4.14	1.56	0.87	0.79	21.43	0.59	0.81	1.68	4.27	1.31	3.21
TF	7/19	94	2	3	.	4.20	1.42	0.96	0.78	17.28	0.50	0.80	1.29	4.33	1.37	3.09
Oa	7/19	94	1	1	0.33	3.96	1.27	0.62	1.40	60.99	0.99	1.83	3.51	4.75	2.12	4.09
Oa	7/19	94	1	3	0.30	3.91	7.43	6.77	1.67	57.29	0.87	1.26	2.91	6.04	1.75	4.21
Oa	7/19	94	1	2	0.22	3.72	2.97	1.92	1.58	51.52	0.63	1.45	2.89	3.67	1.87	3.89
Oa	7/19	94	2	1	0.73	4.10	0.84	0.37	1.27	43.13	0.80	0.84	2.47	4.17	1.03	2.88
Oa	7/19	94	2	2	0.46	3.78	1.70	0.40	1.44	47.15	0.87	1.51	2.38	5.53	1.73	4.03
Oa	7/19	94	2	3	0.56	3.68	1.54	1.55	1.82	45.67	0.29	0.91	0.79	2.06	1.01	3.02
TF	7/25	94	1	1	.	4.26	0.56	0.14	0.27	11.49	0.17	0.79	0.66	1.11	0.85	1.17
TF	7/25	94	1	3	.	4.50	0.67	0.35	0.33	13.43	0.20	0.73	0.73	1.51	0.77	1.16

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	7/25	94	1	2	.	4.33	0.62	0.24	0.31	14.99	0.20	0.87	0.93	1.43	0.89	1.28
TF	7/25	94	2	1	.	4.52	0.47	0.28	0.52	22.25	0.33	0.81	1.89	1.59	0.68	0.95
TF	7/25	94	2	2	.	4.73	0.61	0.41	0.73	6.97	0.17	0.71	0.47	1.66	0.73	1.00
TF	7/25	94	2	3	.	4.73	0.54	0.40	0.36	6.16	0.15	0.65	0.35	1.46	0.67	0.92
Oa	7/25	94	1	1	4.10	4.06	0.23	0.12	1.52	72.73	0.49	1.43	2.42	3.09	1.29	1.10
Oa	7/25	94	1	1	1.70	4.19	0.48	0.21	1.80	76.44	0.77	1.37	4.33	1.47	0.98	1.90
Oa	7/25	94	1	1	3.23	3.93	0.32	0.11	1.11	52.82	0.44	1.18	1.71	1.04	1.10	1.50
Oa	7/25	94	1	1	2.23	3.88	0.49	0.20	1.96	86.53	0.81	1.72	3.23	1.76	1.45	1.92
Oa	7/25	94	1	1	3.40	3.86	0.33	0.10	1.29	62.72	0.57	1.47	1.58	1.49	1.38	1.52
Oa	7/25	94	1	3	2.74	3.81	3.40	3.46	2.85	101.05	0.78	1.27	3.21	2.06	0.88	1.82
Oa	7/25	94	1	3	1.26	3.39	12.69	8.08	4.43	104.08	1.07	1.56	3.43	2.35	1.41	2.85
Oa	7/25	94	1	3	1.26	3.64	4.58	2.98	1.37	49.43	0.35	1.13	1.10	1.92	0.93	1.44
Oa	7/25	94	1	3	2.39	3.58	11.27	4.53	2.65	65.93	1.49	0.96	5.58	3.96	1.28	1.79
Oa	7/25	94	1	3	1.33	3.41	7.55	2.43	2.36	86.70	0.77	1.61	2.52	3.39	1.19	2.19
Oa	7/25	94	1	2	1.32	3.50	4.56	1.05	2.16	98.15	0.82	1.98	3.89	1.88	1.93	1.86
Oa	7/25	94	1	2	2.90	3.63	4.72	1.56	1.79	48.60	0.48	1.23	1.63	2.15	0.96	1.36
Oa	7/25	94	1	2	1.60	3.68	3.06	1.38	1.77	59.79	0.31	1.54	2.15	2.14	1.15	1.66
Oa	7/25	94	1	2	4.91	3.64	1.29	0.73	2.12	87.57	0.57	1.55	3.19	1.24	1.44	2.10
Oa	7/25	94	1	2	1.31	3.79	3.34	2.97	1.82	67.90	0.31	1.79	1.43	3.01	1.03	1.89
Oa	7/25	94	2	1	4.52	3.74	0.32	0.20	1.56	53.63	0.48	1.00	0.77	0.49	0.59	1.56
Oa	7/25	94	2	1	2.57	3.83	0.18	0.17	2.35	73.32	1.36	0.90	2.28	0.31	0.71	2.09
Oa	7/25	94	2	1	4.92	3.90	0.22	0.09	1.49	54.88	0.66	0.81	1.23	0.57	0.57	1.10
Oa	7/25	94	2	1	4.80	4.66	0.30	0.07	0.69	25.62	0.46	0.68	1.57	2.72	0.83	1.21
Oa	7/25	94	2	1	5.15	3.66	0.08	0.09	3.12	110.91	0.78	0.98	1.86	0.79	0.52	1.21
Oa	7/25	94	2	2	2.39	3.88	0.35	0.14	1.62	55.39	0.49	0.93	1.58	1.89	0.82	1.11
Oa	7/25	94	2	2	3.19	3.78	0.31	0.06	1.61	64.99	0.33	1.04	1.14	2.23	0.67	0.88
Oa	7/25	94	2	2	5.13	3.77	0.29	0.05	0.99	39.08	0.16	0.72	0.35	0.49	0.72	0.99
Oa	7/25	94	2	2	1.69	3.84	0.39	0.08	0.96	31.61	0.17	0.86	0.44	0.67	0.45	1.17

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	7/25	94	2	2	5.10	3.75	0.44	0.15	1.73	57.69	0.27	0.74	1.04	0.97	0.61	1.03
Oa	7/25	94	2	3	1.02	3.83	0.69	0.13	1.42	44.11	0.23	1.27	0.84	1.50	0.75	1.11
Oa	7/25	94	2	3	2.70	4.05	0.77	1.68	2.00	47.93	0.11	1.30	0.36	0.93	1.01	1.16
Oa	7/25	94	2	3	2.23	3.85	0.49	0.42	1.43	42.05	0.15	1.10	0.43	1.53	0.76	1.09
Oa	7/25	94	2	3	5.21	3.62	0.61	0.15	1.79	54.61	0.14	0.83	0.34	0.30	0.75	0.93
Oa	8/2	94	1	1	2.07	4.12	0.21	0.20	2.20	69.04	0.49	1.19	2.19	1.00	0.96	1.44
Oa	8/2	94	1	3	1.59	3.63	11.25	5.25	1.66	65.35	1.04	1.33	3.73	2.60	1.10	1.30
Oa	8/2	94	1	2	2.33	3.65	6.59	1.34	1.86	56.58	0.63	1.21	3.14	1.43	0.98	1.46
Oa	8/2	94	2	1	3.74	4.00	0.15	0.14	1.71	48.13	0.53	0.74	1.18	0.47	0.82	1.34
Oa	8/2	94	2	2	2.78	3.79	3.25	0.65	1.23	39.66	0.51	0.86	1.25	0.97	0.62	0.82
Oa	8/2	94	2	3	1.49	3.52	12.81	4.12	1.64	36.65	0.95	1.12	1.99	1.49	0.75	0.77
TF	8/6	94	1	1	0.32	4.28	1.78	0.91	1.03	32.14	0.79	1.03	2.58	3.19	1.52	3.27
TF	8/6	94	1	3	0.21	4.07	3.20	1.80	1.38	47.07	1.10	1.27	3.96	4.78	2.06	5.01
TF	8/6	94	1	2	0.26	4.02	2.49	1.39	1.36	38.46	0.86	1.25	3.12	3.79	2.10	4.59
TF	8/6	94	2	1	0.49	4.35	1.04	0.48	0.79	22.95	0.46	0.83	2.03	2.60	0.98	2.50
TF	8/6	94	2	2	0.34	4.38	2.37	1.35	1.85	30.20	0.87	0.98	2.30	6.51	1.26	4.20
TF	8/6	94	2	3	0.42	4.57	1.31	0.85	1.39	23.03	0.65	0.76	1.42	4.88	1.03	3.02
Oa	8/17	94	1	1	0.47	4.19	1.50	2.14	3.46	73.80	0.88	1.35	2.93	4.89	3.06	3.18
Oa	8/17	94	1	3	0.49	3.81	6.44	5.21	1.26	58.89	0.79	1.20	2.98	4.80	2.14	3.82
Oa	8/17	94	1	2	0.24	3.77	3.89	3.03	1.25	68.06	0.68	1.56	3.19	4.18	2.99	3.62
Oa	8/17	94	2	1	0.92	4.14	0.54	0.29	1.60	38.28	0.59	0.84	1.69	3.46	1.14	2.12
Oa	8/17	94	2	2	0.53	4.03	1.54	1.19	.	41.19	0.58	1.10	1.52	6.00	1.42	3.05
Oa	8/17	94	2	3	0.54	3.76	1.20	1.67	1.79	48.78	0.15	0.90	0.49	1.88	1.15	2.38
TF	8/19	94	1	1	.	4.71	0.20	0.08	0.09	7.38	0.09	0.55	0.38	0.59	0.99	0.70
TF	8/19	94	1	3	.	4.63	0.28	0.15	0.28	18.82	0.44	0.79	1.43	1.05	0.98	1.30
TF	8/19	94	1	2	.	4.58	0.25	0.12	0.08	10.87	0.12	0.66	0.62	0.84	0.91	0.87
TF	8/19	94	2	1	.	5.01	0.14	0.07	0.16	11.05	0.13	0.61	0.89	1.16	0.79	0.57
TF	8/19	94	2	2	.	5.10	0.19	0.05	0.10	3.82	0.07	0.48	0.27	0.76	0.72	0.58

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	8/19	94	2	3	.	5.45	0.13	0.09	0.03	2.86	0.07	0.52	0.22	0.91	0.75	0.54
Oa	8/19	94	1	1	3.11	4.05	0.13	0.16	1.69	69.70	0.51	0.84	2.28	0.88	0.97	1.34
Oa	8/19	94	1	3	1.99	3.64	6.79	4.94	2.39	108.97	0.93	1.12	3.61	1.89	1.19	2.05
Oa	8/19	94	1	2	2.27	3.68	3.95	1.36	1.54	64.09	0.46	1.33	2.22	1.36	1.26	1.50
Oa	8/19	94	2	1	3.72	3.97	0.07	0.10	1.30	46.94	0.49	1.14	1.21	0.72	1.05	1.43
Oa	8/19	94	2	2	4.18	4.04	0.09	0.13	0.83	31.89	0.14	0.98	0.46	0.64	1.01	0.69
Oa	8/19	94	2	3	2.02	3.82	0.60	0.47	1.85	52.20	0.16	1.61	0.52	0.79	1.29	0.87
TF	9/20	94	1	1	.	4.13	1.21	0.34	0.52	25.81	0.69	0.72	2.86	2.72	1.12	4.47
TF	9/20	94	1	3	.	4.04	1.92	0.89	0.86	35.09	0.78	0.84	3.24	3.87	1.33	4.79
TF	9/20	94	1	2	.	4.09	1.43	0.78	0.58	24.00	0.55	0.80	2.31	2.59	1.20	4.12
TF	9/20	94	2	1	.	4.34	0.76	0.87	0.71	34.36	0.50	0.69	3.53	3.11	0.94	3.04
TF	9/20	94	2	2	.	4.36	1.00	0.75	0.42	14.54	0.40	0.73	1.35	4.08	0.96	3.32
TF	9/20	94	2	3	.	4.45	0.85	0.96	0.45	10.92	0.33	0.64	0.92	3.30	0.82	3.08
Oa	9/20	94	1	1	0.65	3.83	0.97	0.25	1.90	84.33	1.55	1.13	5.37	4.28	1.90	5.76
Oa	9/20	94	1	3	0.68	3.61	20.17	17.49	2.87	89.22	1.54	1.52	5.84	5.61	1.96	6.83
Oa	9/20	94	1	2	0.41	3.54	9.46	8.03	1.93	63.94	0.78	1.23	4.03	3.92	1.91	6.38
Oa	9/20	94	2	1	1.42	4.06	0.59	0.40	1.35	44.01	0.78	1.49	2.92	4.43	1.46	4.17
Oa	9/20	94	2	2	1.39	3.87	1.43	1.94	1.17	35.27	0.34	0.79	1.05	4.03	1.07	4.03
Oa	9/20	94	2	3	1.01	3.62	3.22	3.56	0.99	39.30	0.22	1.06	0.60	1.73	1.28	4.20
TF	9/28	94	1	1	.	5.27	0.07	0.04	0.18	16.80	0.21	0.69	0.60	1.70	1.14	0.82
TF	9/28	94	1	3	.	4.82	0.67	0.30	0.72	38.17	0.85	0.89	2.46	2.77	1.58	1.88
TF	9/28	94	1	2	.	4.83	0.19	0.13	0.41	18.75	0.19	0.71	0.77	1.57	1.26	1.08
TF	9/28	94	2	1	.	5.25	0.09	0.06	0.41	25.72	0.25	0.79	1.60	2.89	1.00	0.61
TF	9/28	94	2	2	.	5.53	0.17	0.11	0.22	10.41	0.15	0.75	0.44	2.59	1.06	0.81
TF	9/28	94	2	3	.	5.55	0.36	0.20	0.22	7.52	0.13	0.73	0.28	2.16	0.99	0.71
Oa	9/28	94	1	1	2.35	4.07	0.04	0.06	1.78	86.31	0.68	1.29	3.03	0.72	1.32	1.23
Oa	9/28	94	1	1	0.19	.	0.05	0.25	1.56	76.47	0.31	1.64	1.61	0.65	1.50	0.80
Oa	9/28	94	1	1	0.99	4.17	0.05	0.06	0.92	51.02	0.49	1.62	1.72	1.95	1.64	1.65

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	9/28	94	1	1	1.69	3.98	0.04	0.10	2.25	103.82	1.00	1.80	4.05	0.71	1.56	1.78
Oa	9/28	94	1	1	3.33	4.07	0.05	0.07	1.13	59.60	0.53	1.26	1.60	0.79	1.46	1.22
Oa	9/28	94	1	3	2.30	3.76	43.51	33.90	0.03	154.13	3.79	1.88	14.00	5.24	2.21	2.42
Oa	9/28	94	1	3	0.67	3.39	36.43	26.80	0.29	153.55	1.69	1.93	7.51	6.60	2.50	2.61
Oa	9/28	94	1	3	0.62	3.32	48.18	30.11	0.00	68.74	3.40	1.98	9.33	7.82	3.01	1.96
Oa	9/28	94	1	3	1.62	3.51	58.22	48.12	4.02	202.76	3.50	2.12	12.80	7.91	2.83	2.01
Oa	9/28	94	1	3	1.39	3.34	20.70	8.04	0.00	83.92	1.46	1.58	5.02	4.12	2.34	2.89
Oa	9/28	94	1	2	0.59	3.43	12.58	2.21	2.32	85.13	1.44	2.38	6.95	2.05	2.35	1.85
Oa	9/28	94	1	2	1.99	3.68	10.96	5.36	0.61	38.65	0.76	0.97	2.48	2.13	1.50	1.16
Oa	9/28	94	1	2	0.63	3.49	13.65	3.44	1.47	59.83	0.82	2.25	6.34	2.05	1.79	1.43
Oa	9/28	94	1	2	2.99	3.35	27.86	13.56	2.47	120.32	1.99	2.73	11.60	1.60	2.48	1.97
Oa	9/28	94	2	1	0.91	4.10	0.07	0.08	0.72	23.56	0.27	1.36	0.44	0.29	1.60	1.68
Oa	9/28	94	2	1	1.66	4.01	0.09	0.10	1.50	42.88	0.52	1.00	0.96	0.21	1.09	1.27
Oa	9/28	94	2	1	1.86	3.83	0.06	0.12	2.19	84.93	0.95	1.18	1.90	0.39	1.24	1.69
Oa	9/28	94	2	1	2.17	4.92	0.11	0.12	0.83	18.52	0.21	1.81	0.86	3.24	1.87	0.91
Oa	9/28	94	2	1	4.53	4.06	0.03	0.09	1.50	54.33	0.42	0.70	2.23	1.16	0.86	1.42
Oa	9/28	94	2	2	0.38	.	0.43	0.27	0.73	24.10	0.21	1.52	0.37	0.68	1.51	0.55
Oa	9/28	94	2	2	2.05	3.78	3.33	0.36	0.77	36.93	0.43	1.36	1.11	1.68	1.50	0.76
Oa	9/28	94	2	2	1.18	3.62	10.60	7.12	0.00	50.92	0.69	0.88	1.29	2.92	2.75	1.07
Oa	9/28	94	2	2	5.25	3.69	11.64	6.57	0.77	35.04	0.63	0.91	2.10	2.49	1.44	0.87
Oa	9/28	94	2	3	0.72	3.59	14.37	7.03	0.30	41.16	1.37	1.66	3.98	2.02	1.52	1.25
Oa	9/28	94	2	3	0.72	3.51	30.65	19.69	0.00	35.99	1.33	1.65	2.75	1.81	1.68	1.14
Oa	9/28	94	2	3	0.42	3.46	12.57	6.84	0.55	55.54	0.68	2.71	1.34	1.69	2.18	0.99
Oa	9/28	94	2	3	1.76	3.45	12.11	5.98	0.00	47.21	0.67	0.95	1.37	0.85	1.25	0.94
TF	10/21	94	1	1	1.07	4.34	0.90	0.10	0.34	21.29	0.24	1.04	0.95	2.41	1.58	1.27
TF	10/21	94	1	1	1.17	5.00	0.73	0.06	0.31	22.15	0.38	0.90	0.79	4.14	1.52	1.12
TF	10/21	94	1	1	1.38	4.54	0.44	0.07	0.13	10.19	0.13	0.75	0.41	0.85	0.99	0.83
TF	10/21	94	1	1	1.20	4.83	0.58	0.06	0.14	8.68	0.30	0.92	0.63	0.86	1.13	0.86

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
TF	10/21	94	1	1	1.07	4.75	1.07	0.08	0.57	31.10	0.53	1.21	1.50	3.32	1.44	1.17
TF	10/21	94	1	3	1.16	4.34	1.69	0.20	0.57	28.80	0.44	1.02	1.10	4.45	1.58	1.10
TF	10/21	94	1	3	0.32	.	2.54	0.33	0.92	50.27	0.52	1.69	1.89	1.49	1.64	1.35
TF	10/21	94	1	3	1.04	4.50	1.43	0.23	0.98	45.05	0.54	1.18	1.82	6.90	2.75	1.48
TF	10/21	94	1	3	1.29	4.28	1.20	0.22	0.41	14.33	0.22	0.98	0.86	2.30	1.33	1.19
TF	10/21	94	1	3	1.49	4.23	0.98	0.13	0.20	15.26	0.21	0.97	0.72	1.45	1.21	1.10
TF	10/21	94	1	2	1.42	4.30	0.86	0.06	0.24	15.13	0.23	0.91	0.86	1.46	1.18	1.09
TF	10/21	94	1	2	1.23	4.41	0.80	0.20	0.13	8.41	0.14	0.80	0.46	1.45	1.19	0.90
TF	10/21	94	1	2	0.89	4.23	0.91	0.10	0.25	15.63	0.25	1.09	0.84	1.59	1.46	1.23
TF	10/21	94	1	2	1.66	4.28	0.81	0.10	0.21	15.08	0.20	0.72	0.85	1.16	1.10	1.16
TF	10/21	94	1	2	1.41	4.34	0.73	0.08	0.15	9.36	0.14	0.77	0.54	0.86	1.02	0.92
TF	10/21	94	2	1	1.30	4.61	0.51	0.08	0.06	7.29	0.16	0.78	0.50	1.37	1.13	0.81
TF	10/21	94	2	1	1.60	4.88	0.42	0.08	0.16	6.04	0.15	0.74	0.33	1.63	1.01	0.74
TF	10/21	94	2	1	1.25	4.73	0.34	0.08	0.01	3.48	0.12	0.74	0.19	0.61	0.93	0.62
TF	10/21	94	2	1	0.93	4.46	0.85	0.16	0.31	7.86	0.13	0.93	0.57	2.05	1.32	1.00
TF	10/21	94	2	1	1.11	4.60	0.26	0.17	1.59	89.60	0.82	0.95	7.98	6.27	1.45	0.99
TF	10/21	94	2	2	1.05	4.54	0.71	0.11	0.31	15.41	0.19	0.92	0.55	2.29	1.32	0.84
TF	10/21	94	2	2	0.97	4.61	0.89	0.13	0.43	19.30	0.33	1.09	0.87	3.63	1.52	1.15
TF	10/21	94	2	2	1.14	4.75	1.47	0.06	0.59	39.46	0.71	0.94	1.16	9.15	2.56	1.22
TF	10/21	94	2	2	1.29	5.54	0.71	0.08	0.57	16.17	0.18	0.66	0.56	7.04	1.87	1.06
TF	10/21	94	2	2	1.57	4.60	0.56	0.07	0.10	7.81	0.17	0.64	0.49	1.35	0.91	0.80
TF	10/21	94	2	3	1.34	4.65	0.54	0.16	0.15	5.32	0.11	0.61	0.28	1.41	1.04	0.74
TF	10/21	94	2	3	1.40	4.61	0.77	0.17	0.27	13.90	0.24	0.67	0.53	1.88	1.04	0.79
TF	10/21	94	2	3	1.05	4.55	0.62	0.14	0.06	5.03	0.18	0.82	0.44	1.06	1.01	0.75
TF	10/21	94	2	3	1.10	4.71	1.18	0.43	0.37	12.30	0.26	0.83	0.61	3.72	1.39	1.06
TF	10/21	94	2	3	1.20	4.68	0.66	0.05	0.21	16.82	0.22	0.82	0.51	2.72	1.20	0.81
Oa	10/21	94	1	1	0.42	4.01	0.55	0.07	1.20	63.03	0.66	1.23	2.52	3.98	2.48	1.91
Oa	10/21	94	1	3	0.38	3.77	8.59	7.18	1.00	60.15	0.43	0.98	1.83	2.84	2.05	1.69

ST	date	yr.	sta.	tmt.	amt. [cm]	pH	NO3-N [mg/L]	NH4-N [mg/L]	DON [mg/L]	DOC [mg/L]	Mg [mg/L]	Na [mg/L]	Ca [mg/L]	K [mg/L]	Cl [mg/L]	SO4-S [mg/L]
Oa	10/21	94	1	2	0.36	3.78	2.16	1.25	1.27	48.48	0.22	1.07	1.35	1.68	2.35	1.41
Oa	10/21	94	2	1	0.69	4.04	0.33	0.06	0.97	39.68	0.40	0.84	1.24	2.77	1.70	1.35
Oa	10/21	94	2	2	0.72	3.89	0.84	0.10	1.02	39.14	0.25	1.00	0.61	3.14	2.49	1.35
Oa	10/21	94	2	3	0.54	3.85	1.33	1.56	.	41.23	0.14	0.93	0.37	0.50	2.19	1.16