Environmental Pollution

The Fernow Watershed Acidification Study

Edited by
Mary Beth Adams, David R. DeWalle
and John L. Hom

Springer

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ENVIRONMENTAL POLLUTION

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Preface

In the late 1980's, a considerable amount of research addressing the effects of acidic deposition was begun, much of it related to the Congressionally mandated National Atmospheric Precipitation Assessment Program (NAPAP). As a result of the 10-year NAPAP program, effects on human health, materials, structures, visibility and terrestrial and aquatic ecosystems were evaluated. As a result of NAPAP funded research, negative effects of acidic deposition were documented on freshwater lakes in the Adirondacks and on the red spruce of the Adirondacks and northern Appalachians. One of the recommendations of the NAPAP Forest Response Program, however, was that a better understanding of the effects of acidic deposition and its constituents on *processes* within forest ecosystems was needed. In response to this need, the US Environmental Protection Agency (EPA) funded an ambitious program to manipulate the geochemical processes within watersheds in the United States. Originally, there were to be many watersheds to be treated, to encompass the scope of vegetation types, climate and deposition regimes. Ultimately only two such studies, one at on the Fernow Experimental Forest in West Virginia and one at Bear Brook Watersheds in Maine (BBWM) were implemented. Both are ongoing more than fifteen years later.

Work began in 1987 in preparation for the Fernow Watershed Acidification Study. Much attention was initially devoted to issues related to analyses of water chemistry and the quality control/quality assurance of the data coming from the study. A pilot study was conducted on WS9 (Clover Run watershed) to ensure that the project was feasible, and to work out the details and methods to be used. Treatment of Fernow WS3 began in January 1989, and has continued to this time. Funding from EPA was relatively short-lived, and since that time the treatments and measurements have continued through the determination, cooperation, and effort of the scientists and field crew of the Fernow. Timely support in 2000 by the Northern Global Change Research Program of the USDA Forest Service allowed the study to continue. In 2003/4, the Fernow Watershed Acidification Study was selected by the National Science Foundation for funding through the Long-Term Research in Environmental Biology (LTREB) program, ensuring its continuation for at least another 5 years, and expanding the outreach and education opportunities.

This book presents, for the first time, a collection and synthesis of research studies conducted as part of the Fernow Watershed Acidification Study for the period 1989-2004 – the first 15 years. While many of these data have been previously published in peer-reviewed journals and other outlets, this is the first time we have attempted to synthesize the information in a one publication.

The list of research studies, and the researchers involved in the Fernow Watershed Acidification Study, is long, as evidenced by the contributors to this book. The efforts of these researchers have made the Fernow Watershed Acidification Study a success, and much credit goes to these individuals. In addition to these people, particular acknowledgement must be made of the contributions of J. David Helvey for his excellent work in preparing the original proposal, establishing the study, and for his research which provided the setting and background information that was critical in attracting the attention of EPA.

The Fernow Watershed Acidification Study also included contributions from faculty, students and technicians of cooperating academic institutions, notably Fairmont State University, Marshall University, Penn State University, University of Maine, and West Virginia University. Research for many studies has been supported by the USDA Forest Service, Northeastern Research Station as well as numerous grants from other sources cited in original publications. Many of those affiliated with academic institutions are authors in this book, but additional credit should be given to Bryan Swistock, Jeffrey Tepp, Callie Joe Schweitzer, Angela Happel, Agaha Brass, Anthony Buda, and Chad Voorhees from Penn State University, Jeff Bailey, Nicole Turill Welch, Staci Smith Aulick, Dan Evans and Jeff May from Marshall University, and Cassie Jo Foster and Martin Christ from West Virginia University.

Long-term research requires careful, committed technical help, and the Fernow Watershed Acidification Study simply would not have been feasible without dedicated, skillful field technicians including John Campbell, Doug Owens, Melvin Owens, Layne Godwin, Clifford Phillips, Frank Long, and Cloyd Rinehart. For help with the fertilizer applications, we recognize Scott Hockman, Mark Owens, Roy Poling, Jeff Pennington, Alan Myers, and particularly Tim Scherm, our flight coordinator. The reliable work of John Pearce, Emmett Fox, Buck Grey, Lynda Gerath, Jean Cassidy and Joan Pennington in the water quality laboratory is also acknowledged. Frederica Wood has provided very capable data management for all of these years, and provided outstanding support in developing the figures for this volume.

In preparing this book, we have benefited greatly from clerical support provided by Linda Loughry, Linda Plaugher, and Beau Marshall. Susan Wright provided careful editing of an earlier draft, and we acknowledge with appreciation the help of Betty Van Herk of Springer in bringing us through the publication process and assuring quality. We also acknowledge the many people who reviewed individual chapters: Scott Bailey, Ivan Fernandez, Mark Ford, Ray Hicks, Jennifer Knoepp, Steve Norton, Bill Peterjohn, Kathryn Piatek, Tom Schuler. A special acknowledgement goes to the three individuals who reviewed the book in its entirety and provided us with helpful comments: David Grigal, Mark Johnson, and Eric Vance.

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Chapter 1

INTRODUCTION TO THE FERNOW WATERSHED ACIDIFICATION STUDY

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1. INTRODUCTION

The Fernow Watershed Acidification Study in West Virginia dates back to 1987 when experimental additions of ammonium sulfate were first made to the Clover Run watershed (WS9). This pilot experiment was followed two years later by initiation of similar treatments on watershed 3 (WS3), on the Fernow Experimental Forest (FEF) proper, with watershed 4 (WS4) being used as a reference. For purposes of soil and vegetation comparisons watershed 7 (WS7) was used as a reference. (Detailed descriptions of all the watersheds can be found in Chapter 2). Treatment of WS9 has since been terminated, but the WS3 acidification treatment continues to this day. These experiments were planned and conducted largely by personnel with the United States Forest Service, Northeastern Research Station at Parsons, West Virginia. The original objective was to determine impacts of atmospheric deposition on forest ecosystems by determining changes in soil chemistry, soil leachate chemistry and streamflow chemistry resulting from increased applications of nitrogen (N) and sulfur (S). In addition to Forest Service researchers, a number of university researchers and their students have contributed to the knowledge base about the impacts of atmospheric deposition on these areas (see Preface). Lacking a synthesis of this knowledge, a Fernow Watershed Acidification Workshop was held on 20-21 October 2003 at Deep Creek, Maryland to convene scientists to discuss results, with support from the Pennsylvania Water Resources Research Center and the Forest Service. At this meeting, the concept for this book was conceived and an outline was drafted.

M. B. Adams et al. (eds.), The Fernow Watershed Acidification Study, 1 –16.

The Fernow Watershed Acidification Study is quite important in several respects. First, it is the only such experiment that has focused on the Appalachian hardwood forest ecosystems that represent a large fraction of the commercially important forest land in the eastern United States. Secondly, it is one of only a few experiments throughout the world that has been watershed-based; thus deposition impacts on streamflow response rather than just soil leaching can be evaluated. Bear Brook Watershed in Maine is the only other watershed-based acidification study in North America (Norton and Fernandez 1999). Finally, the Fernow Watershed Acidification Study used as treatments ammonium sulfate additions that allowed the simultaneous study of enhanced deposition of both N and S. Experimental additions were distributed throughout the year in amounts that roughly equaled twice the normal ambient load of deposition. It is hoped that the knowledge gained from the Fernow Watershed Acidification Study, when combined with data from other studies, will significantly enhance our understanding of ecosystem response and recovery from acidification by atmospheric deposition.

2. ATMOSPHERIC DEPOSITION AT FERNOW

Comparisons of treated and reference areas as part of the Fernow Watershed Acidification Study should be interpreted in the context of the dynamics of background levels of atmospheric deposition. During the period of the experiments, all of the watersheds were experiencing changing background levels of atmospheric deposition, most notably declining S, calcium (Ca) and magnesium (Mg) deposition.

Atmospheric deposition in the northeastern United States (US) has been diminishing due largely to the Federal Clean Air Act Amendments (CAAA) of 1990. The CAAA of 1990 prescribed a two-phased, market-based system of reductions in emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from power plants. Phase I was to reduce annual emissions from large, high-emission plants in the eastern and midwestern states by 1995. Phase II began in 2000 to impose emission limits on smaller, cleaner power plants and tightened controls on Phase I plants. The impacts of Phase I reductions in 1995 were dramatic, achieving a 45% reduction in SO_2 emissions compared to 1990 levels. Phase II implementation is underway, with some controversy about what constitutes a new power generation source requiring emissions controls, and longer-term results are still being evaluated. Regardless, the effects of the CAAA on deposition have been dramatic during the span of the Fernow Watershed Acidification Study.

Wet deposition of acid ions measured near Fernow through the National Atmospheric Deposition Program/National Trends Network (NADP/ NTN) (see http://nadp.sws.uiuc.edu) has declined significantly. At the Parsons, West Virginia site WV18, approximately 3 km north of FEF, downward trends in sulfate (SO_4) and, to a lesser extent, inorganic N wet deposition and upward trends in precipitation pH were recorded from 1978 through 2003 (Fig. 1-1). Total precipitation amounts during this time have remained relatively constant, averaging about 130 cm annually at WV18, so the downward trends in wet deposition are primarily due to reductions in concentrations of pollutants.

Trends in dry deposition of acidifying substances as determined with the Clean Air Status and Trends Network (CASTNET) (http://www.epa.gov/castnet) are not as consistent. Figure 1-2 shows dry and wet deposition trends for both S and N at the Parsons, West Virginia (PAR107) site located near the NADP WV18 wet deposition site for the 1989-2002 period. Dry deposition of S decreased gradually from 1989-2002, but trends in dry deposition of N are less obvious. Dry deposition of S currently represents about 40% of total wet plus dry S deposition, while dry deposition of N represents about 25-35% of wet plus dry N deposition. Rainfall is greater at higher elevations on FEF, therefore deposition is likely to be greater than at the CASTNET site. For more information on deposition trends, see Chapter 7.

3. THEORY OF ACIDIFICATION BY ATMOSPHERIC DEPOSITION

Forest ecosystem acidification is largely driven by hydrogen ions (H^+) and excess mobile anions such as NO_3^- and SO_4^{2-} that derive directly or indirectly from the atmosphere and that leach cations from the soil. Hydrogen ions directly acidify by their presence in soil solution and can cause increased weathering of aluminum-bearing compounds. Subsequently, the release of Al^{3+} can lead to replacement of nutrient cations, such as Ca^{2+} and Mg^{2+} on soil exchange sites. Nutrient cations are then more available for leaching. Excess anions that are mobile in soil solution can carry available cations out of the soil in order to maintain a charge balance. To the extent that nutrient cations, like Ca^{2+} and Mg^{2+}, are leached and not replaced by weathering, soil fertility can decrease and acidity can increase. Since SO_4 represents the major input of anions from the atmosphere, soil SO_4 dynamics can dominate soil acidification. However, given the reductions in SO_4 deposition occurring in the northeastern US due to the Clean Air Act Amendments, N deposition will assume increasing importance in the future.

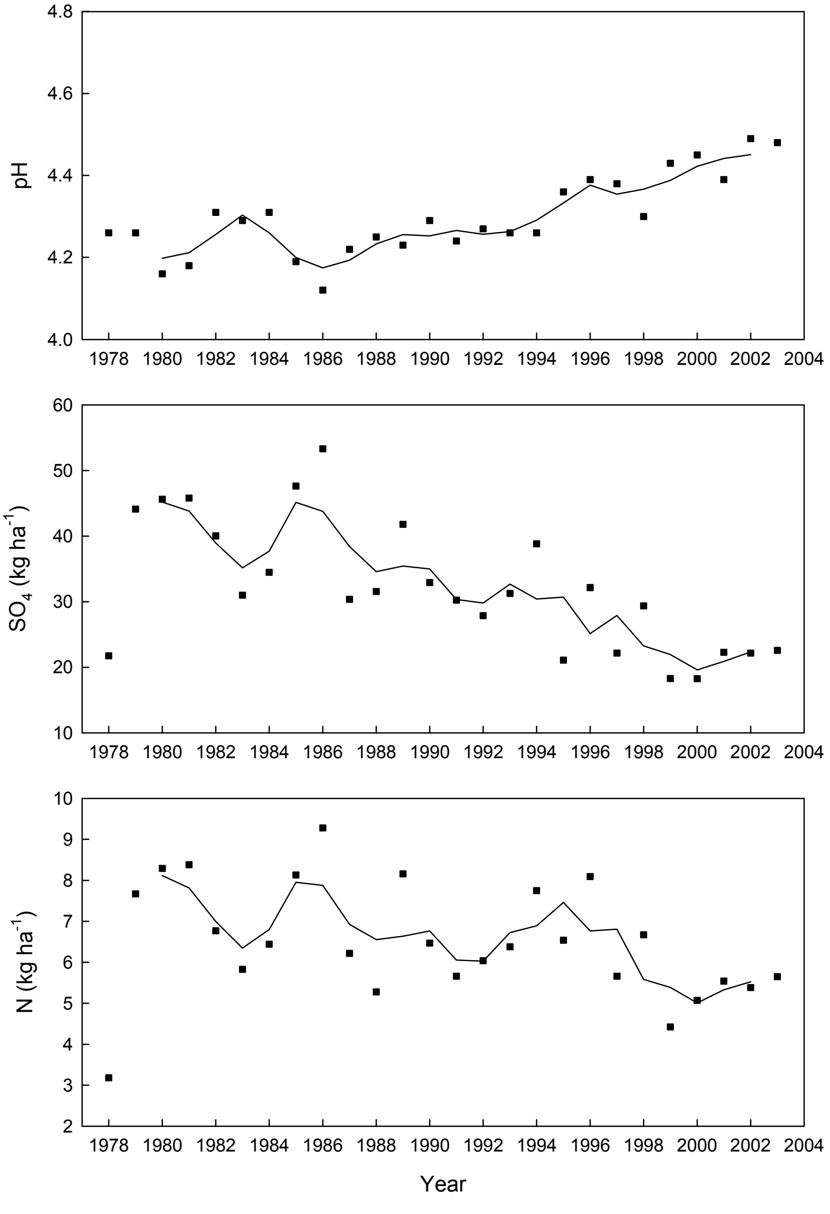


Figure 1-1. Trends in precipitation pH and wet deposition of SO_4 and inorganic N at the WV18 National Atmospheric Deposition Program site near Parsons, WV during 1978-2003.

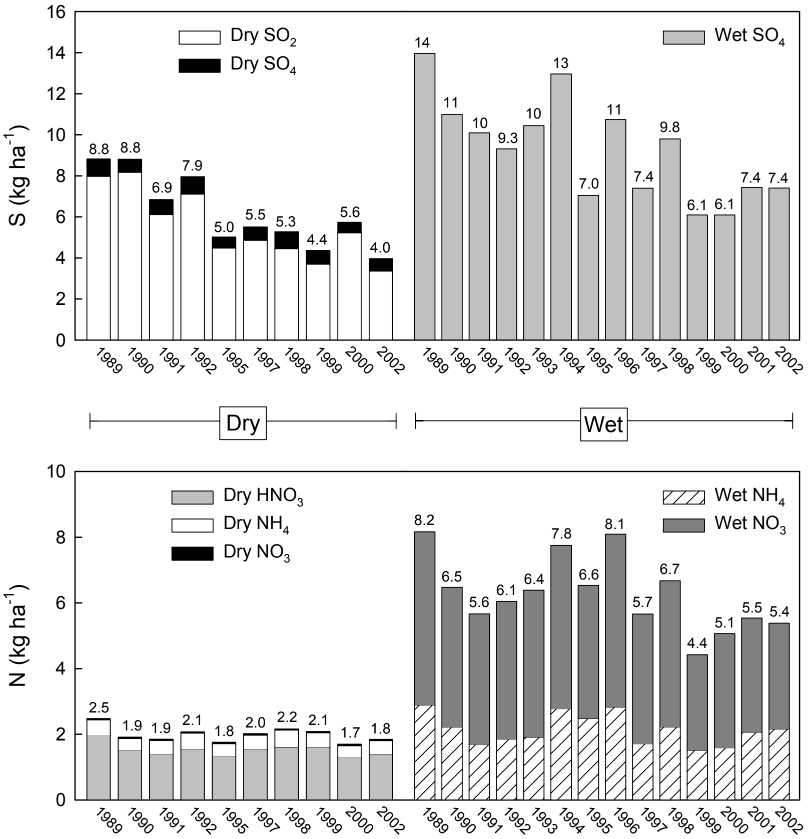


Figure 1-2. Trends in dry and wet deposition of S and N at the CASTNET PAR107 site near Parsons, WV during 1989-2002.

Retention of SO_4^{2-} in Appalachian forest ecosystems occurs by adsorption in the soil and as S storage within living and dead biomass (Lotse 1999). Soil SO_4 adsorption increases with concentration and adsorption can delay leaching until a steady state is reached with inputs. In addition, since this process is at least partially reversible, the soil adsorption of SO_4 can also delay the response to reductions in atmospheric deposition until a new steady state is achieved. Sulfate anion adsorption in many Appalachian forest soils is limited due to low clay content and the capacity to retain SO_4 can eventually be exceeded by long-term deposition.

Gradually increasing N deposition in forest ecosystems can lead to *nitrogen saturation*, a process whereby N limitations on biological functions are removed and increased NO_3 leaching occurs (Aber et al. 1998, Stoddard

1994). Figure 1-3 illustrates the hypothetical response of forests to an increase in N deposition. In N-limited ecosystems, as most forests are believed to be, ammonium (NH_4) and NO_3 deposited from the atmosphere will be assimilated and stimulate biomass production. Aber et al. (1998) argue that soil microbes may play an important role in immobilizing added N even without plant uptake. Indeed, recent research suggests that microbial biomass and diversity may change significantly in response to elevated N deposition (Fisk and Fahey 2001, Frey et al. 2004). Since long-term elevated N inputs from the atmosphere may eventually lead to imbalances with other nutrients and carbon needed to further stimulate growth, gradual declines in growth may occur later. Once saturation is reached, any excess NH_4 is rapidly nitrified to NO_3 and is added to that directly deposited from the atmosphere. At this point, since soil has little NO_3 adsorption capacity (relative to the biological capacity), leaching of NO_3 can then occur and also contribute to base cation leaching. As suggested by Figure 1-3, no steady state in response of net primary productivity (NPP) is suggested by this N saturation theory. McNulty et al. (1996) has suggested that NPP may recover after declining in Stage 3, due to changes in tree species, and varying species tolerance for acidification. A singular pattern of NPP increase followed by a

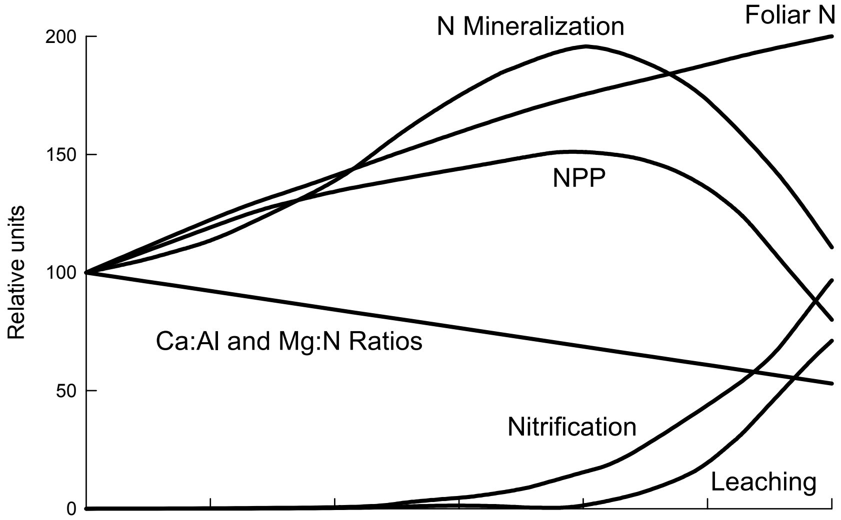
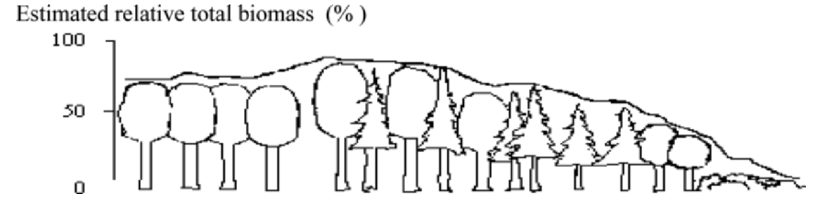


Figure 1-3. Hypothesized response of temperate forest ecosystems to long-term chronic N additions (modified from Aber et al. 1998). NPP = net primary productivity. Stage 0 is pretreatment where growth is N limited, Stage 1 represents high N retention with growth stimulation, Stage 2 represents saturation where leaching of NO_3 begins and NPP peaks, Stage 3 is a decline stage where NPP is declining and leaching accelerates.

decline is also hypothesized for western xeric forests and western high-elevation alpine ecosystems (Fenn et al. 1998). Limited evidence exists for forest growth declines or increased tree mortality due to N saturation, but what does exist has been reported in coniferous stands.

The cations available for leaching in the soil solution vary with the soil buffering regions and minerals available (Fig. 1-4, redrawn from Ulrich 1984). Soils in the carbonic acid/carbonate buffering range have adequate supplies of carbonate to neutralize acidity and resulting soil solutions have relatively high pH and are dominated by high concentrations of Ca^{2+}, Mg^{2+} and HCO_3^-. Within Appalachian forests, such soils typically are residual soil derived from limestone and dolomite, and are relatively uncommon, but tend to be very productive. Interestingly, the relative dominance of cations like Ca^{2+} from carbonate weathering tends to produce some imbalances with cations like K^+, which can reduce biomass growth relative to more acidic systems. Regardless, these soils would take centuries to acidify and therefore acidic deposition is probably not a major threat to the productivity of these soils, and forests.



pH 8.6 6.2 5.0 4.3 3.8 3.0

Buffer region	Carbonic acid/ carbonate	Carbonic acid/ silicate	Strong acid exchanger	Strong acid/Al-oxide to Strong acid/Fe-oxide	
Leaching of nutrients	Mainly Ca	Very limited	Leaching of exchangeable Ca, Mg, K	Base cation leaching complete; Al dominates	Fe^{3+} and H dominate exchangeable cations
Limitations for plant growth	Small limitation by wide Ca:K ratios, and anion surplus in uptake	No limitations by chemical soil factors	Suffering by non-tolerance plants from Al toxicity; exclusion of calicole species	Suffering by all plants from Al toxicity; growth reductions in calicole species	Suffering of all plants by Al-Fe toxicity; only plants rooting in top organic layer survive

Figure 1-4. Buffer systems in soils for ecosystems in steady state (from Ulrich 1984).

Soils derived from the weathering of sandstones and shales, which are much more typical in the Appalachians, initially can buffer acid inputs through the weathering of silicate minerals (Fig. 1-4). In this buffer range, pH in soil solution is somewhat lower and concentrations of dominant ions Ca^{2+}, Mg^{2+} and HCO_3^- are lower, but biomass production is at even higher levels. However, if silicate mineral weathering cannot buffer soil solutions against continuing inputs of atmospheric deposition, then the soil can move into buffer ranges where soil solution pH is even lower, dissolved Al in various forms, Mn^{2+} and eventually Fe^{3+} begin to dominate cations, and anions are dominated by SO_4^{2-} and NO_3^-. Biomass production would eventually also diminish with reducing pH due to metals toxicity according to Figure 1-4. Biomass production includes above- and belowground plant growth, soil microbes and other ecosystem macro-flora and fauna.

Lotse (1999) computed the relationship between soil water Al^{3+} and pH for several forest sites in the Appalachians that included soils at FEF (Fig. 1-5, Fork Mtn.). Data showed that Fork Mountain soils in 1984 on WS3 and WS4 had relatively low exchangeable aluminum compared to the other Appalachian sites and also that large increases in Al^{3+} were possible with relatively small increases in H^+ activity. Elevated concentration of dissolved

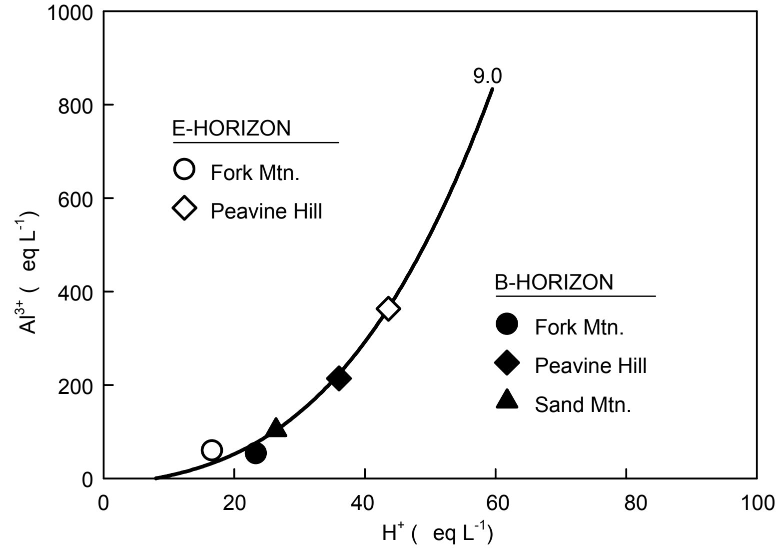


Figure 1-5. Relationship between Al^{3+} and H^+ for five soil leachates at Appalachian forest sites including Fork Mountain at Fernow (Lotse 1999). Plotted trend equivalent to pH-pAl value of 9.0 with assumed activity coefficients of 0.96 and 0.70 for H^+ and Al^{3+}, respectively.

Al^{3+} have direct significance for tree health. Cronan and Grigal (1995) found Ca/Al molar ratios of about 1.0 in soil solution had a 50% chance to produce plant stress and ratios of about 0.4-0.5 a 75% chance to cause stress.

Another way to visualize the effects of atmospheric deposition on stream and lake chemistry is provided by Galloway et al. (1983) who modeled a system dominated by SO_4 adsorption in the soil (Fig. 1-6). In this diagram, the focus is on the chemistry of the receiving waters, rather than soil solution and biomass. As the system experiences increased atmospheric deposition,

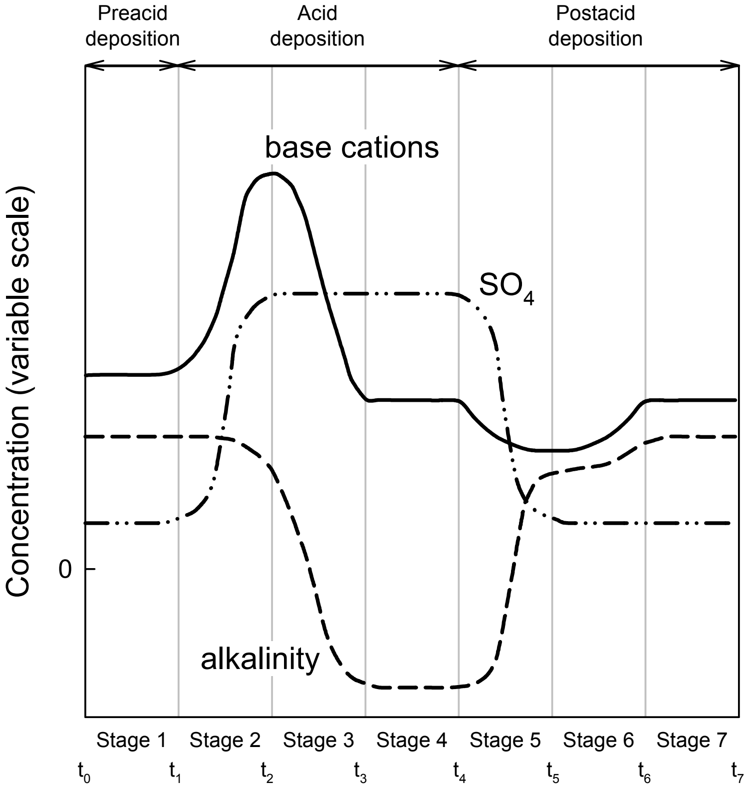


Figure 1-6. Variation in concentration of SO_4, base cations and alkalinity in a stream or lake during seven stages of increased and then decreased acid deposition (modified from Galloway et al. 1983).

Stages 1-4 occur in stream or lake water.

- Stage 1- Pre-acidification with stable base cation, SO_4 and alkalinity levels;

- Stage 2- Initial response stage to a deposition increase, base cations are being replaced by H^+ on the soil exchange complex and base cations are gradually being leached by mobile SO_4 anions into the stream, alkalinity (approx. = cations – anions) declines slightly as both base cations increase and SO_4 increases somewhat more;

- Stage 3- Deposition continues and soil is saturated with SO_4, stream SO_4 reaches steady state, base cations become depleted due to excess SO_4 leaching and begin to decline, stream alkalinity declines and becomes negative as base cations decrease below SO_4;

- Stage 4- Stream SO_4, base cations and alkalinity achieve new steady states with continuing deposition.

A post-deposition scenario is also shown in the diagram with Stages 5-7 occurring after a reduction in atmospheric deposition:

- Stage 5- SO_4 gradually declines assuming only partially reversible adsorption sites in the soil, less base cations are leached to stream due to reduced SO_4, and stream alkalinity recovers due to reduced SO_4;

- Stage 6- New steady state is reached with SO_4 adsorption, a gradual recovery in base cations occurs due to weathering replenishment in excess of leaching demands, alkalinity also gradually rises;

- Stage 7- A new equilibrium at the lower level of deposition is reached but at a lower base cation concentration.

A modified form of the Galloway et al. (1983) model was developed by Norton et al. (2003) to describe the acidification observed in the fertilized West Bear Brook Watershed, part of the Bear Brook Watershed in Maine acidification study. This model considers both N and S as strong acid anions, incorporates the dynamics of Al and Fe, and describes the evolution of acidification/neutralization processes through time (Fig. 1-7). It is clear that as desorption of base cations declines, it is replaced by Al, which is in turn replaced by Fe, either at lower pH and after much acidification, or in Al-deficient soils.

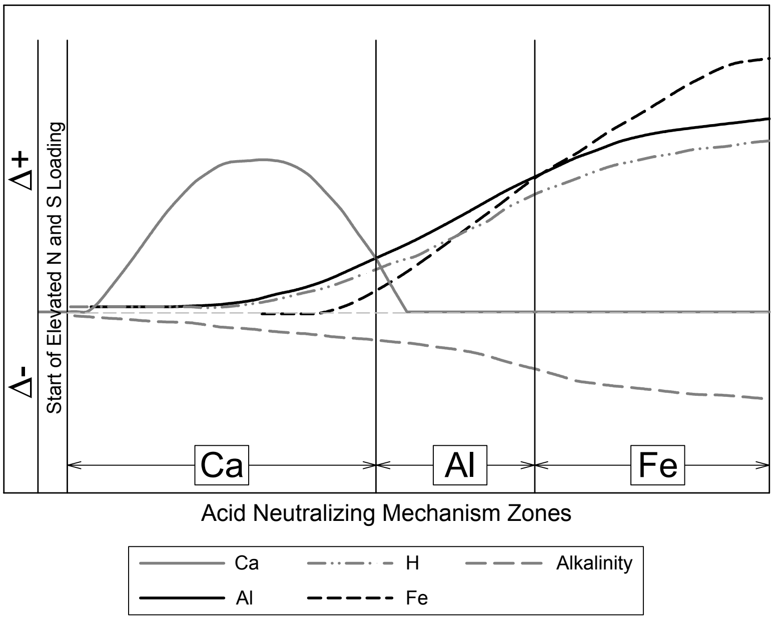


Figure 1-7. Model of cation processes and acidification, based on West Bear Brook Watershed in Maine (redrawn from Norton et al. 2003).

4. FERNOW RESEARCH THEMES

Although forest ecosystem acidification can be viewed from the perspective of N saturation or SO_4 adsorption dynamics, some similar stages or steps in the response to long-term atmospheric deposition are described or implied by each theory. In reality, acidification by both N and S deposition must be considered together and both approaches, of course, share any direct effects of H^+ deposition.

4.1 Nutrient Cation Mobilization

One of the initial changes produced by the acidification process would be mobilization of nutrient cations or so-called "base cations" such as Ca, Mg and K. Although this mobilization is not emphasized with N saturation theory, mobilization would come about by replacement on soil exchange sites by H^+ and possibly NH_4^+ added from the atmosphere, by replacement by Al^{3+} due to increased weathering of Al compounds, and by leaching by mobile NO_3^- and or SO_4^{2-} anions from the soil. Increased mobility of nutrient cations will cause increases in concentrations in soil water and receiving waters, as well as increased acid neutralizing capacity or alkalinity in receiving waters. Foliar and bolewood tissue should also show effects of increased cation availability. The period of mobilization will last until the rate of replacement of nutrient cations exchange and by weathering cannot keep pace with losses. Soil exchange sites may not necessarily show such nutrient cation changes as long as replacement of cations by weathering is sufficient. The occurrence, magnitude, and longevity of such a nutrient cation mobilization is important to understanding the overall impacts of atmospheric deposition on nutrient cycling.

Research questions that arise from the mobilization theory that relate to the Fernow acidification experiments are:

- Will a cation mobilization phase result from ammonium sulfate applications?
- Will soil exchangeable cations show a reduction in base saturation due to mobilization?
- Can plant indicators, such as foliar or bolewood chemistry, be used to detect the mobilization phase?
- Will nutrient cation mobilization cause changes in soil water and stream water chemistry?
- How long will the period for nutrient cation mobilization last on WS3 and WS9?
- How has the retention of applied N and S changed during the cation mobilization phase?

4.2 Cation Depletion/Aluminum Mobilization

Most forest ecosystems in the Appalachians, including those of the FEF, have soils derived from sandstone and shale parent material and thus probably began soil acid buffering in the silicate weathering regime described by Ulrich (1984). If or when the buffering capacity of silicate weathering is exceeded by acid inputs from atmospheric inputs, then buffering by Al should begin and nutrient cations in drainage waters will gradually be replaced by Al^{3+}. Although not specifically mentioned by Ulrich (1984), Mn^{2+} levels also can rise in drainage waters with mobilization in many Appalachian soils. Soil exchangeable cations during gradual acidification are of special interest. Fernandez et al. (2003) demonstrated a loss of Ca and Mg from exchange sites in the soils that was nearly identical to the excess transport of Ca and Mg measured in streamflow during the first 9 years of acidification of West Bear Brook Watershed in Maine, USA.

The timing of the shift from nutrient cations to Al in drainage waters will depend upon the rate of weathering, the rate of deposition and the rate of cation removal. This shift in mobilization of Al will begin in surface soils and gradually work downward over time through the soil. Toxic effects of Al on terrestrial biomass production and aquatic ecosystems will be discussed later. Hydrologically, it is thus possible for drainage water from the upper soil horizons to be replete with dissolved Al, while water from deeper soil layers and aquifers is more well buffered. Such situations give rise to *episodic acidification* of streams and lakes, where high Al in streams only occurs during large events when additions of water from upper soil zones is occurring. Eventually, acidification of the entire soil profile and deeper aquifers can occur and give rise to *chronic acidification*.

Cation depletion and Al mobilization theory suggest the following questions:

- Do changes in soil chemical properties indicate soil acidification has occurred?
- Can foliar and bolewood chemistry be used to detect the shift from nutrient cation mobilization to depletion?
- Will there be shifts in episodic and baseflow stream chemistry linked to cation depletion and Al mobilization?
- Has the retention of N and S changed during the nutrient cation depletion phase of response?

4.3 Biomass Growth Cycles

Theories of acidification suggest that the timing of biomass growth is dependent upon the shift from nutrient cation mobilization to Al mobilization, although an initial growth increase can be due to added N in these typically N-limited systems. Increased forest growth could result, although soil biomass could also increase. If toxic conditions occur in soil due to Al, then biomass growth will eventually decline. The speed with which the growth cycle occurs and the magnitude of the growth effects are subjects of intense public interest in the Appalachians. The ability to monitor biomass production to detect possible effects of acidification using easily observed indicators of health, such as foliar and bolewood chemistry, as the shift to Al mobilization is occurring, is another area of interest. Streams on Fernow watersheds are too small to support fish populations, but the health of reptiles and amphibians and other fauna that depend on the chemistry of the aquatic ecosystem to some degree, either for habitat or food, is an important topic.

Growth cycle issues to be resolved during acidification experiment were:

- Have the health and growth of both overstory and herbaceous forest vegetation been affected by the acidification experiments?

- Is a cycle of accelerated forest growth followed by a growth decline evident?
- How do such cycles compare among the experiments?
- Have the populations of amphibians and reptiles and other watershed fauna been affected by the acidification treatment?

4.4 Steady States

The S adsorption theory of acidification leads to the conclusion that after a suitable period of response to increased deposition, then a steady state in levels of ecosystem cations and probably growth response to deposition will occur. Nitrogen saturation theory, involving a more dynamic biologic response to deposition, does not immediately lead to a steady state system prediction. Ulrich (1984) describes forest replacement by heath due to atmospheric N deposition in Europe, while McNulty et al. (1996) suggest that NPP (Net Primary Productivity) may decline to a minimum level and then gradually recover with species replacement. Most evidence suggests that hardwood or deciduous forests may have a higher tolerance for atmospheric deposition loads than conifers.

Such questions are ultimately at the heart of Fernow Watershed Acidification Study. Questions of direct relevance are:

- Are periods of growth recovery with species replacement evident in the study watersheds ?
- Do biological and hydrologic indicators of system cation status indicate a steady state has been reached?
- What period of time is needed for steady state conditions to develop?

5. BOOK ORGANIZATION

Chapters in this book have been organized to describe the response of the forest ecosystems at the Fernow Experimental Forest to experimental acidification with ammonium sulfate. Experiments at both Fernow WS3 vs.WS7 and the Clover Run WS9 are included in this book. Chapter 2 describes in detail the history and setting of the experimental areas Chapters 3-6 then describe the soil, soil water and stream water, vegetation, and faunal response to acidification, respectively. In order to synthesize, extrapolate, and generalize these results, Chapter 7 evaluates changes in nutrient cycling processes and Chapter 8 compares Fernow results with those from other experimental areas and uses modeling of observed effects to scale up to the mid-Atlantic region. Finally, in Chapter 9 we summarize the results of the experiments and make some recommendations for future research directions.

Chapter authors are noted in the text and brief biographies are given in Appendix A.

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Chapter 2

FERNOW AND THE APPALACHIAN HARDWOOD REGION

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1. REGIONAL DESCRIPTION

The Fernow Experimental Forest (39.03° N, 79.67° W) is located in north–central West Virginia near the community of Parsons, in the Allegheny Mountain section of the mixed mesophytic forest (Braun 1950). This heavily forested region is located in the central part of the Appalachian mountains which extends 2574 km from Canada to northern Georgia and Alabama traversing 15 degrees of latitude (Brooks 1965). The present Appalachian Mountains are remnants of a higher mountain system that was uplifted during the Appalachian Orogeny which began about 250 million years ago, and has remained above sea level since that time (Cardwell 1975). Practically all exposed rocks in West Virginia are of sedimentary origin, originating during the Paleozoic Era (Core 1966). Late in the Cenozoic Era, less than 100,000 years ago, glaciers crossed the North American continent but did not extend into West Virginia (Cardwell 1975). The cooling climate created by the advance of the ice sheets permitted the southward migration of northern vegetation (Braun 1950). The retreat of the glaciers left relict plant colonies behind, especially on exposed crests or in bogs (Core 1966).

West Virginia is often divided into three physiographic sections: Allegheny Mountains, Ridge and Valley, and the Western Hill section (Core 1966). Maximum relief in the Allegheny Mountains can exceed 600 m along the eastern margin but elevation averages 300 to 500 m over most of the region (Stephenson 1993). The eastern margin west of the Allegheny Mountains is commonly referred to as the Allegheny Front. The Ridge and Valley which lies east of the Allegheny Front is characterized by ridges with lower elevations which run in a northeast–southwest direction often forming a parallel drainage pattern (Stephenson 1993). Most of the Ridge and Valley

M. B. Adams et al. (eds.), The Fernow Watershed Acidification Study, 17–39.

section drains into the Potomac River while the other two physiographic sections drain into the Ohio River system. The Western Hill section includes most of West Virginia located west of the Allegheny Mountain section (Core 1966). Elevations are generally less than 450 m in the northern and western portions of this section and maximum relief usually does not exceed 150 to 250 m (Stephenson 1993). Topography is more rugged in the southern portion of this physiographic section.

Topography and elevation exert a large influence on climatic conditions in West Virginia. Elevations in West Virginia range from 73 m above sea level at Harpers Ferry in the eastern extremity of the state, to 1482 m at the summit of Spruce Knob at the crest of the Allegheny Mountains. In general, precipitation increases and temperatures decrease with increasing elevations. Average annual temperatures in West Virginia range from 9°C in the Cheat River Basin, the coldest part of West Virginia, to 13°C in southern West Virginia (Core 1966). The average length of the growing season ranges from over 150 days in eastern and southern portions of West Virginia to 90 days at higher elevations in the Allegheny mountains. General storm movement is from west to east. The orientation and height of the mountain range creates an orographic effect where precipitation is greatest on the western slopes of the high mountains and lowest in the rain shadows in eastern portions of West Virginia. Annual precipitation ranges from 79 cm to 168 cm in a space of 129 km (Core 1966). Erosion in the high rainfall areas west of the Allegheny Front has resulted in a dense dendritic drainage pattern.

2. DISTURBANCE AGENTS

In addition to climatic and physical features of the landscape, many historical events have helped shape the present condition of the central Appalachian forests. Prior to settlement, forests were shaped by many natural and human caused disturbances such as wind (Lorimer 2001), fire, and agricultural use (Maxwell 1910). These disturbances created “a diverse mosaic of forest stands whose age, tree species, and wildlife varied widely and reflected the disturbance history of the area” (MacCleery 1994). More recently, several insects and diseases (Kuhlman 1978, USDA Forest Service 2003), most of them non-native, have severely impacted Appalachian forests. They include balsam woolly adelgid, butternut canker, dogwood anthracnose, hemlock woolly adelgid, gypsy moth, beech bark disease, Dutch elm disease, and chestnut blight (See Appendix A for scientific names). The chestnut blight, first reported in West Virginia by Brooks (1911), has been the most devastating, virtually eliminating American chestnut which formerly comprised 25 percent of Appalachian forests (Kuhlman 1978).

3. VEGETATION DESCRIPTION

Core (1966) arranged the state of West Virginia into two floristic provinces, the mountain forests, which include the northern evergreen and northern hardwood forest, and at lower elevations, the central hardwood forest, which includes both xeric and mesic mixed hardwood forests. Red spruce and eastern hemlock were dominant trees in the northern evergreen forest which commonly occurred above 915 m in elevation. Red spruce reaches its maximum development in the Appalachians (Korstian 1937). The northern hardwood forest, which often grows in association with the northern evergreen forest, occurs mostly in a zone from 915 m to 1220 m in elevation (Core 1966). Common species are black cherry, American beech, red maple, sugar maple, and yellow birch. Below 915 m in high rainfall areas on the western slope of the Allegheny Mountains, forests are dominated by species such as yellow-poplar, northern red oak, American basswood, cucumber tree, sweet birch, and white oak in addition to several hardwood species that also occur in northern hardwood forests. North-facing slopes and coves support mixed mesophytic or cove hardwoods, whereas drier ridgetops and southern exposures support a forest of oak and pine and oak–hickory. Dense understories of great laurel, an evergreen shrub, often developed on moist sites in both floristic provinces. White pine was often common along stream bottoms growing on sandy loam soils, often forming pure stands (Core 1966). Several species of trees, e.g. balsam fir, paper birch, and red pine, reach the southernmost limits of their range in this region of the Appalachians (Core 1966). Other species, bog rosemary and bog buckbean, which occur in the boreal forests of Canada and northern United States, have restricted ranges in West Virginia, occurring only in high elevation sphagnum bogs in the Allegheny Mountains (McDonald 1993).

The diverse vegetation supported a wide variety of wildlife. Buffalo and elk, the largest herbivores native to this region, were exterminated by 1825 and 1835, respectively (Fansler 1962). Other mammals extirpated from the area were the grey wolf, mountain lion, beaver, fisher, and porcupines (Smith 1993). Both the beaver and fisher have been successfully reintroduced to the mountains of West Virginia. Black bear and wild turkey, once abundant throughout West Virginia during the precolonial period, found refuge in the eastern mountains (Smith 1993) and are still present on the Fernow. The eastern coyote has in relatively recent times expanded its range into West Virginia. Early loggers reported that no deer were present on the Fernow during the 1903-1911 logging era (Kochendefer 1975). This information coincides with DeGarmo and Gill (1958) who reported deer scarcities occurred as early as 1841 and the virtual disappearance of deer in most of West Virginia between 1880-1910. Currently however, overabundant populations of white–tailed deer are adversely affecting forest regeneration on large areas of forestland in the Appalachian Region (Campbell 2003, McWilliams et al. 2003). The occurrence of the endangered Indiana bat on the Fernow has had a major impact on the timing of timber harvesting on research studies, and cutting is now restricted to the period between October 1 – May 1.

4. EARLY SETTLEMENT AND INDUSTRIAL DEVELOPMENT

The first permanent settlement in the vicinity of the Fernow Experimental Forest was established in 1776 (Fansler 1962) but the majority of settlement and land clearing took place later during the 19th century. The mountainous terrain did not lend itself well to agriculture, and as late as 1880 less than 1% of the area surrounding the Fernow was cleared (Maxwell 1884). The arrival of the railroad in 1890 to Parsons (Fansler 1962) stimulated timber harvesting and rapid development of forest-based industries in the immediate area of what is now the Fernow Experimental Forest. The largest sawmill near the Fernow was the Otter Creek Boom and Lumber Company's mill which began operations in 1897 (Fansler 1962). Two tanneries utilizing hemlock and chestnut oak bark and a large pulp mill also were established near Parsons around 1900 (Fansler 1962). In 1902, the Elklick Lumber Co. established a single band sawmill near the mouth of Elklick Run that was used to saw the timber that was harvested on what is now the Fernow Experimental Forest. Most of the larger mills during this period constructed railroads into tracts of timberland and used steam engines to transport logs to their mills. Logs were skidded to railroads with horses and loaded onto railroad cars with steam loaders. Fires resulting from steam-powered equipment, and fires set to promote grazing, were especially prevalent in the highly inflammable slash left after logging in the spruce–hemlock forests (Clarkson 1964).

5. EARLY FERNOW HISTORY

Most of the Elklick watershed, which originated as a land grant to Frances and William Deakins from the State of Virginia in 1783, is now part of the Fernow Experimental Forest (Fig. 2-1). A Deakin heir sold the 1673 ha Big Spring tract to Jonathan Arnold for $4000 in 1856 (Fansler 1962). The tract name refers to a large limestone spring located on the property. A 1932 type map indicated that the entire tract was forested except for about 50 acres of old fields. The fields were located in the vicinity of the Big Spring and on

Fork Mountain near the top of WS3 and WS7 (Fig. 2-1). Old family records indicate that the Henry Irons family occupied an area still referred to as "Irons Sods" between about 1841-1870 on WS7. Early settlement records at Big Spring are less certain but there is evidence of dwellings and cleared fields in the vicinity of the spring. Hopson (1912) reported a 300-acre pole stand growing on an abandoned field in the vicinity of Big Spring. A stand of this size would indicate that clearing and abandonment took place prior to commercial logging. Recent archaeological surveys have uncovered artifacts that indicate that prehistoric people also lived near Big Spring.

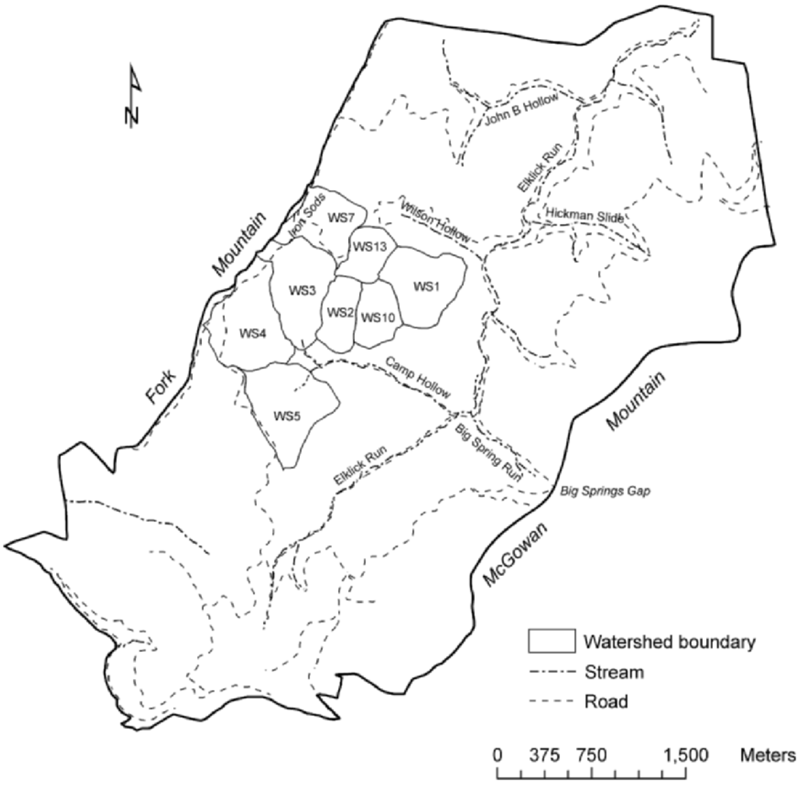


Figure 2-1. The Fernow Experimental Forest.

An heir, Thomas J. Arnold, sold the timber rights to representatives of the Elklick Lumber Co. in 1901. Logging probably started about 1903 and was completed by 1911 (Abell 1933). A railroad was constructed up Elklick

Run adjacent to the stream. Climax and Shay steam engines were used to transport logs to the company's sawmill near the mouth of Elklick Run. Horses and in some cases log slides were used to move logs from the woods to the railroad. Cutting was heaviest near railroads and lighter in more inaccessible areas (Trimble 1977). Place names still used today on the Fernow relate to its early logging history. For example, Camp Hollow, a major drainage on the Fernow, had a logging camp located on it. Hickman Slide Hollow refers to a log slide constructed there by early loggers. John B. Hollow was named after a man who lived in an abandoned lumber camp at the mouth of that hollow.

A land examiner (Hopson 1912) described the property in 1912 as highly productive and well stocked with valuable reproduction. White-tailed deer would not have impacted the development of regeneration because they had been eliminated from the area prior to the logging. It was a common practice to permit hogs to forage for chestnuts and acorns in Appalachian forests (Brooks 1965) and livestock to graze in woodlands. These practices were reported to have occurred on what is now the Fernow Experimental Forest into the 1920s (Bryant 1911, Kochenderfer 1975) but evidently did not adversely impact forest regeneration. In 1915 the USDA Forest Service purchased 2888 ha of land which included the Big Spring tract for $5.50 per acre. The Fernow Experimental Forest, named in honor of Bernard E. Fernow, a well known German-born forester, was established on 28 May 1934. The original boundaries of the Fernow Experimental Forest contained 1473 ha encompassing almost all the entire watershed of Elklick Run, a fourth order tributary of the Black Fork of the Cheat River, and were expanded to 1902 ha in 1974. Many of the main access roads on the Fernow Experimental Forest were constructed by the Civilian Conservation Corps in the 1930s. Like the early railroads, many of the roads are located close to Elklick Run.

Another research area affiliated with the Fernow (WS9 or Clover Run Watershed) is located about 13 km west of the Fernow Experimental Forest. This area was not commercially logged like the Fernow but was cleared for agriculture and by the 1880s most of it was being farmed (Maxwell 1884). In the 1920s the farm, where WS9 is now located, was abandoned largely due to the exhaustion of soil fertility and excessive erosion (Lima et al. 1978). The Forest Service purchased the land in 1941. Two weirs were built in 1957.

6. FERNOW RESEARCH

Research began in earnest when the Northeastern Forest Experiment Station established a branch unit on the Fernow in 1948 (Trimble 1977).

Early work on the Fernow involved collecting inventory data, establishing study compartments and constructing weirs on small watersheds (Trimble 1977). In 1964 headquarters were established at Parsons, West Virginia and named the Timber and Watershed Laboratory. The Fernow serves as an outdoor laboratory where scientists from the Timber and Watershed Laboratory and cooperators address three main problems:

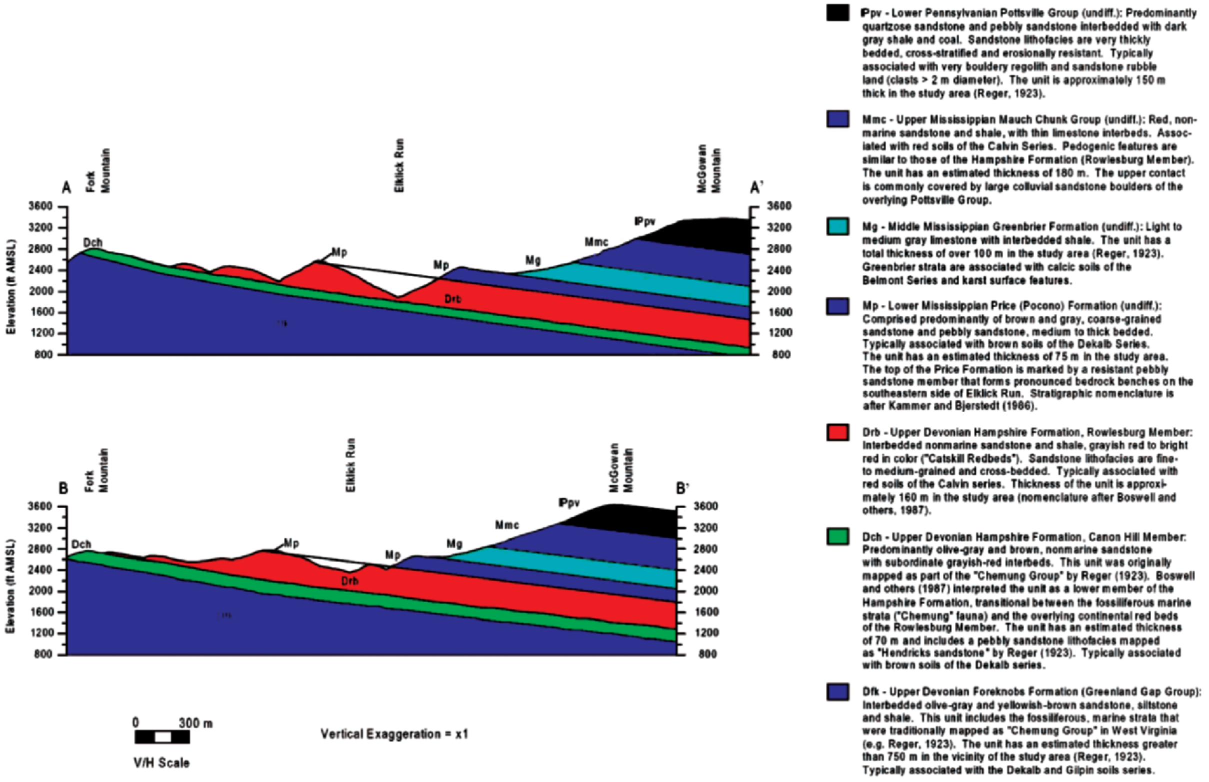
1. The development of ecologically sound silvicultural practices for the intensive management of Appalachian forests.
2. Providing information on basic ecosystem processes and the impacts of chronic acid deposition.
3. The development and evaluation of additional measures to mitigate soil and water impacts associated with timber harvesting activities.

Research on forest hydrology began on the Fernow in 1951 when streamflow and precipitation measurements began on five watersheds ranging in size from 15 to 39 ha. During a 6-year calibration period, data were collected continuously on precipitation, streamflow, water quality and temperatures on the undisturbed watersheds. In 1957-58, studies evaluating four cutting practices ranging from commercial clearcutting using no protection for soil and water resources to a light selection cut with resource protection, were begun on four of the watersheds (Reinhart et al. 1963, Hornbeck and Reinhart 1964). This research used a paired-watershed approach in which relationships developed during the calibration period were used to determine subsequent treatment effects relative to an untreated reference watershed (Reinhart 1958). Later research focused on specific aspects of water yield (Patric and Reinhart 1971) and impacts of forest management practices on erosion and sedimentation (Weitzman and Trimble 1955, Patric 1980, Kochenderfer and Helvey 1987, Kochenderfer et al. 1997). Streamflow and precipitation chemistry measurements began in 1970 and have remained a major focus of Fernow research (Aubertin and Patric 1974, Patric and Smith 1978, Helvey and Kunkle 1986, Edwards and Helvey 1991). In 1987, research on artificial acidification began with the application of ammonium sulfate fertilizer to WS9 (Adams et al. 1993, Adams et al. 1997). Other studies have examined solar radiation (Hornbeck 1970), soil moisture (Patric 1973), evapotranspiration (Tajchman et al. 1997), stormflow (Reinhart 1964, Brewer et al. 1982), and dendroclimatology (Pan et al. 1997, Schuler and Fajvan 1999). The effects of natural reforestation of abandoned farmlands on streamflow were investigated by Lima et al. (1978). Hydrologic data have been collected almost continuously on the five original watersheds that have been instrumented since 1951.

7. FERNOW GEOLOGY AND SOILS

The geologic formations and the soils derived from them are closely related to elevation on the Fernow. Geologic cross-sections of the Fernow by Taylor (1999) are shown in Figure 2-2. The Upper Devonian Hampshire formation (Canon Hill Member) occurs on Fork Mountain between about 762 m and 854 m in elevation. This formation is typically associated with the Dekalb soil series (loamy-skeletal, mixed mesic Typic Dystrochrept). The Upper Devonian Hampshire formation (Rowlesberg Member) occurs near the mouth of Elklick Run and extends to about 823 m above sea level on Fork Mountain. The most common soil on the Fernow, Calvin channery silt loam (loamy-skeletal, mixed, active, mesic Typic Dystrochrept) is derived from this formation. The Lower Mississippian Price (Pocono) formation occurs at about the same elevation on the southeastern side of Elklick Run (Fig. 2-2). The Dekalb soil series is associated with this formation on benches in the headwaters of Elklick Run. The most productive soils on the Fernow are derived from the Middle Mississippian Greenbrier Limestone formation which occurs above the Pocono formation at about 793 m elevation. Belmont silt loam (fine loamy, mixed, active, mesic Typic Hapludalf) is the most common soil associated with this formation on the Fernow. Early settlers recognized the natural fertility of limestone-derived soils and often selected them for agricultural use. A quarry was established on a limestone outcrop in this formation near Big Springs Gap by the Civilian Conservation Corps (CCC) in the 1930s to obtain stone for the Fernow road system.

The Mauch Chunk group occurs above the Greenbrier Limestone at around 854 m (Fig. 2-2). The predominant soil associated with this group is the Cateache series, another highly productive soil (fine-loamy, mixed, active, mesic Ultic Hapludalf). Soils derived from the Greenbrier Limestone and Mauch Chunk groups occur in the upper reaches of Elklick Run and on the eastern side of the Fernow, while soils on the western half of the Fernow are predominantly derived from the acidic sandstone and shale of the Hampshire formation. Early researchers established the experimental watersheds on the western side of the Fernow away from the porous karst topography, so that water balance studies could be conducted. The Lower Pennsylvanian Pottsville group occurs above 915 m on McGowan Mountain. The Dekalb soils series formed in the material weathered from sandstone are often associated with this geologic group. The predominant soil on WS9 is Calvin channery silt loam underlain with fractured sandstone and shale of the Hampshire formation (Losche and Beverage 1967). Elevations on that watershed range from 744 m to 878 m.



■ **Ppv - Lower Pennsylvanian Pottsville Group (undiff.): Predominantly quartzose sandstone and pebbly sandstone interbedded with dark gray shale and coal. Sandstone lithofacies are very thickly bedded, cross-stratified and erosionally resistant. Typically associated with very bouldery regolith and sandstone rubble land (clasts > 2 m diameter). The unit is approximately 150 m thick in the study area (Reger, 1923).**

🟦 **Mmc - Upper Mississippian Mauch Chunk Group (undiff.): Red, nonmarine sandstone and shale, with thin limestone interbeds. Associated with red soils of the Calvin Series. Pedogenic features are similar to those of the Hampshire Formation (Rowlesburg Member). The unit has an estimated thickness of 180 m. The upper contact is commonly covered by large colluvial sandstone boulders of the overlying Pottsville Group.**

🟦 **Mg - Middle Mississippian Greenbrier Formation (undiff.): Light to medium gray limestone with interbedded shale. The unit has a total thickness of over 100 m in the study area (Reger, 1923). Greenbrier strata are associated with calcic soils of the Belmont Series and karst surface features.**

🟦 **Mp - Lower Mississippian Price (Pocono) Formation (undiff.): Comprised predominantly of brown and gray, coarse-grained sandstone and pebbly sandstone, medium to thick bedded. Typically associated with brown soils of the Dekalb Series. The unit has an estimated thickness of 75 m in the study area. The top of the Price Formation is marked by a resistant pebbly sandstone member that forms pronounced bedrock benches on the southeastern side of Elklick Run. Stratigraphic nomenclature is after Kammer and Bjerstedt (1986).**

🟥 **Drb - Upper Devonian Hampshire Formation, Rowlesburg Member: Interbedded nonmarine sandstone and shale, grayish red to bright red in color ("Catskill Redbeds"). Sandstone lithofacies are fine- to medium-grained and cross-bedded. Typically associated with red soils of the Calvin series. Thickness of the unit is approximately 160 m in the study area (nomenclature after Boswell and others, 1987).**

🟩 **Dch - Upper Devonian Hampshire Formation, Canon Hill Member: Predominantly olive-gray and brown, nonmarine sandstone with subordinate grayish-red interbeds. This unit was originally mapped as part of the "Chemung Group" by Reger (1923). Boswell and others (1987) interpreted the unit as a lower member of the Hampshire Formation, transitional between the fossiliferous marine strata ("Chemung" fauna) and the overlying continental red beds of the Rowlesburg Member. The unit has an estimated thickness of 70 m and includes a pebbly sandstone lithofacies mapped as "Hendricks sandstone" by Reger (1923). Typically associated with brown soils of the Dekalb series.**

🟦 **Dfk - Upper Devonian Foreknobs Formation (Greenland Gap Group): Interbedded olive-gray and yellowish-brown sandstone, siltstone and shale. This unit includes the fossiliferous, marine strata that were traditionally mapped as "Chemung Group" in West Virginia (e.g. Reger, 1923). The unit has an estimated thickness greater than 750 m in the vicinity of the study area (Reger, 1923). Typically associated with the Dekalb and Gilpin soils series.**

Figure 2-2. Northern view of the geologic cross-section of the Fernow Experimental Forest (after Taylor 1999).

8. FERNOW FOREST COMPOSITION

The forest composition that existed on the Fernow near the beginning of the 20th century has been changed significantly through harvesting and the accidental introduction of exotic diseases. During the exploitive logging practices of the early 20th century, species preferences and merchantability standards influenced the structure and composition of the residual stands. Preferred species included American chestnut (Fig. 2-3), larger and better quality black cherry, white and red oak, yellow-poplar, and black walnut. Sugar maple, birch spp., American beech and hickory spp. were seldom harvested and accounted for a large percentage of the older residuals present when treatments on the Fernow began in 1951. Sawtimber volumes on the Fernow prior to the beginning of treatments in 1951 averaged 129 m^3 ha^{-1} (Weitzman 1949). Preferential harvesting in Appalachian forests may have significantly depleted some species such as black walnut, butternut and white oak (Carvell 1986). According to interviews with early loggers, black walnut may be the best example of a species that was reduced in importance on the Fernow because of extensive harvesting circa 1910 (Kochenderfer 1975). In some cases, black walnut growing on limestone-derived soils reportedly was harvested with roots attached to the boles because the wood was so highly valued. Today only a few scattered walnut trees remain on the Fernow. The heavy uncontrolled cutting of the hardwood stands at the turn of the century also had beneficial effects on several plant species. In the Appalachians it often resulted in a high proportion of shade-intolerant species such as yellow-poplar, black cherry and northern red oak on good and excellent sites (Trimble 1965). The high percentage of valuable shade-intolerant species in the overstories of many Fernow stands today originated in the absence of deer in the openings created by the early logging.

Following the initial logging of the Fernow, the next major disturbance was the widespread death of American chestnut due to the chestnut blight. Weitzman (1949) estimated that 25% of the timber volume on the Fernow was comprised of American chestnut prior to the blight. Another study using old land surveys and early timber cruises estimated American chestnut importance value as 8.3 percent in the 1856 old-growth forest, 15.1 percent in 1915 following first logging, 5.5 percent in 1922 after the onset of the blight, and completely absent from the overstory by 1948 (Schuler and Gillespie 2000). Because of the rot resistance of the wood, American chestnut coarse woody debris is still a major constituent in some watersheds (Adams et al. 2003).

Figure 2-3. Cutting a large American chestnut tree on the Fernow at Fork Mountain circa 1905. (Courtesy William Pennington)

Research cutting treatments on the Fernow are also affecting species composition. From these studies it is possible to gauge the impacts of several management practices and the effects of time alone on species composition. In the early 1950s, northern red and chestnut oak were the two most abundant species on the Fernow; in contrast, sugar and red maple are most abundant today (Schuler 2004). Trimble (1965) predicted partial cutting practices would increase the proportion of shade-tolerant sugar maple and decrease the proportion of shade-intolerant species. Species diversity through the decades has undergone the greatest change on the most productive sites and in areas that are either unmanaged or are managed using single-tree selection. Small canopy gaps in the overstory combined with recent high deer density and no control of shade tolerant species in the understory has heavily favored red maple, sugar maple, and an understory of American beech and striped maple at the expense of most other species.

Variation in aspect, elevation, soils, geology, landform and other physical features of the landscape give rise to numerous understory and overstory communities. Vegetation on the Fernow fits into Core's (1966) mixed central hardwood forests floristic province. Common tree species on the better sites are yellow-poplar, sugar maple, black cherry, white oak, basswood and red oak. Understories often include striped maple, sugar maple, American beech and great laurel. Herbaceous plants on these sites often include stinging nettle, black snakeroot, blue cohosh, violets, white snakeroot and Christmas fern. A profusion of spring wildflowers also occur on these good sites, especially those associated with limestone. Dominant tree species on the poorer sites include white oak, chestnut oak, hickory, red maple, sourwood, American beech, and sassafras. Common understory woody plants on these more xeric sites include blueberry, greenbrier, serviceberry, red maple and mountain laurel. A partial list of species found on the Fernow Experimental Forest was recently completed and includes over 500 species of vascular flora (Madarish et al. 2002). Running buffalo clover, a federally endangered species, occurs on the Fernow on areas that are periodically disturbed, such as logging roads (Madarish and Schuler 2002), especially on limestone-derived soils on the eastern portion of the Fernow.

9. FERNOW CLIMATE

The growing season on the Fernow extends from May through October, and the average length of the frost-free season is 145 days. There are four distinct seasons on the Fernow. Leaves begin emerging in late April, are fully developed by the beginning of June, and begin to fall in October. Annual precipitation is about evenly distributed between growing and dormant seasons, averaging 145.8 cm. The maximum average monthly precipitation (14.4 cm) occurs in June and the lowest monthly precipitation in October (9.7 cm). Precipitation often occurs in the form of snow during the winter but a snowpack usually does not develop for extended periods. Annual runoff for the reference watershed (WS4) averages 64 cm; 17 cm occurs during the growing season and 47 cm in the dormant season (Adams et al. 1993). The average annual air temperature is 9.2° C, with a minimum of 7.0° C occurring in 1958 and a maximum of 11.3° C in 1921 (Pan et al. 1997). Mean monthly temperatures range from –18° C in January to 20.6° C in July. Potential evapotranspiration on the Fernow was estimated to be 56 cm per year (Patric and Goswami 1968).

10. STUDY WATERSHEDS

The watershed treatments are summarized in Table 2-1. Two catchments, WS9 and WS3, were treated with ammonium sulfate fertilizer beginning in 1987 and 1989, respectively (Adams et al. 1993). Three untreated reference or control watersheds, WS4, WS10 and WS13, also were established on the Fernow. WS4 was employed as a paired reference for stream water and soil water comparisons with WS3 and as a paired reference for

Table 2.1. Treatment description for the Fernow watersheds.

WS	Area	Treatment	Treatment Date	Basal Area Cut	References
	ha			%	
3	34	Intensive selection cut, including cull trees > 12.7 cm dbh	10/1958-2/1959	13	Aubertin and Patric 1974, Kochenderfer et al. 1990
		Repeat treatment	9/1963-10/1963	8	Adams et al. 1997
		0.16 ha patch cuttings totaling 2.3 ha, cut down to 12.7 cm, 2-12 cm stems sprayed with herbicide	7/1968-8/1968	6	Edwards et al. 2002
		2-12 cm stems treated with herbicide then clearcut to 2.5 cm dbh., except for a partially cut 3.0 ha shade strip along the stream channel	7/1969-5/1970	91	
		Shade strip clearcut	11/1972	9	
		Natural recovery	11/1972-present		
		Ammonium sulfate fertilizer applied	12/1989-present		
4	39	No treatment/natural recovery since 1905		0	Reinhart et al. 1963
7	24	Upper 12 ha clearcut	11/1963-3/1964	49	Patric and Reinhart 1971
		Maintained barren with herbicides	5/1964-10/1969		
		Lower 12 ha clearcut	10/1966-3/1967	51	
		Entire watershed maintained barren with herbicides	5/1967-10/1969		Kochenderfer and Wendel 1983
		Natural recovery	10/1969-present		Adams et al. 1995
9	18	No treatment/natural regeneration since 1920's			Lima et al. 1978
		Cut trees ≥ 15 cm dbh (8.9 ha) Mechanical site prep (8.9 ha)	8/1983-11/1983	70	Kochenderfer and Helvey 1989
		Planted Japanese larch (8.9 ha)	4/1984		Kochenderfer et al. 1995
		Ammonium sulfate fertilizer applied (11 ha)	4/1987-7/1994		Pickens et al. 1995
10	15	No treatment/natural recovery since 1905		0	Christ et al. 2002
13	14	No treatment/natural recovery since 1905, except for minor cutting 1951		0	Weitzman et al. 1949

stream water for WS9. There was no paired watershed soil water analyses for WS9 because untreated control plots were established within the boundaries of WS9 (described in Chapter 4). WS7 was the vegetative reference for WS3 and was selected because the stands are the same age.

After the clearcut harvest in 1969 – 1970, a dense and vigorous hardwood stand quickly became established on WS3. Aubertin and Patric (1974) reported that streamflow increased 20.3 cm during the first year after treatment, but rapid regrowth reduced water yield increases to 6.4 cm by the second year after cutting. This clearcutting-only treatment had only minimal, short-term effects on streamflow chemistry (Fig. 2-4). In contrast to WS7, the already low nitrate (NO_3) concentrations on WS3 did not decline when regrowth began in 1970 and remained stable until the fertilizer treatments began in 1989. A stand inventory conducted in the 2004 dormant season indicated that WS3 supported a young hardwood stand dominated by black cherry, red maple, and American beech with a mean stand density of 1883 stems ha^{-1} in stems $\geq$2.54 cm in diameter (Table 2-2). Black cherry accounted for 51% of the stand basal area in trees $\geq$2.54 cm in 2004.

Treatment effects on both streamflow chemistry and vegetation following herbicide treatments on WS7 were larger and persisted for a much longer period than they did on WS3 (Fig. 2-4). Recovery of vegetation on both WS3 and WS7 began with the 1970 growing season. Natural plant succession on WS7 began at the grass and herbaceous stage (Kochenderfer and Wendel 1983) whereas on WS3 vegetation regrowth began at a more advanced successional stage consisting mainly of *Rubus* spp. and woody vegetation. Water yields from WS7 increased more than 25.4 cm after complete deforestation (Patric and Reinhart 1971), declining as regrowth occurred to between 5 cm to 10 cm above preharvest levels, where they persisted for 14 years (Hornbeck et al. 1993). Nutrient export data are not available for the herbicide treatment period but specific conductance of WS7 stream water almost tripled, increasing from a pretreatment mean of about 19 $\mu S\ cm^{-1}$ to 57 $\mu S\ cm^{-1}$ in 1969, the last year of treatment. It then decreased to about 24 $\mu S\ cm^{-1}$ in 1979, 10 years later (Kochenderfer and Wendel 1983). Edwards and Helvey (1991) attributed specific conductance increases observed on another Fernow watershed (WS4) to increased concentrations of NO_3 and calcium (Ca). Stream water NO_3 concentrations in 1970 on WS7 were about eight times higher than concentrations on WS3 (Fig. 2-4) indicating that NO_3 leaching was accelerated on WS7 by the herbicide treatments which maintained the watershed barren of vegetation. Stream NO_3 concentrations declined rapidly with regrowth and by 1980 had leveled off but remained elevated above WS3 until fertilization began in 1989. A 2004 inventory indicated WS7 supported a young hardwood stand dominated by sugar maple, sweet birch, and red maple with a mean stand density of

1473 stems ha^{-1} (Table 2-2). Yellow-poplar accounted for the largest percentage of stand basal area (26%) in 2004. Stand density has been higher on WS3 than WS7 for the entire study period remaining at or above full stocking levels. In 2004, mean stand basal area was 22 percent greater on WS3.

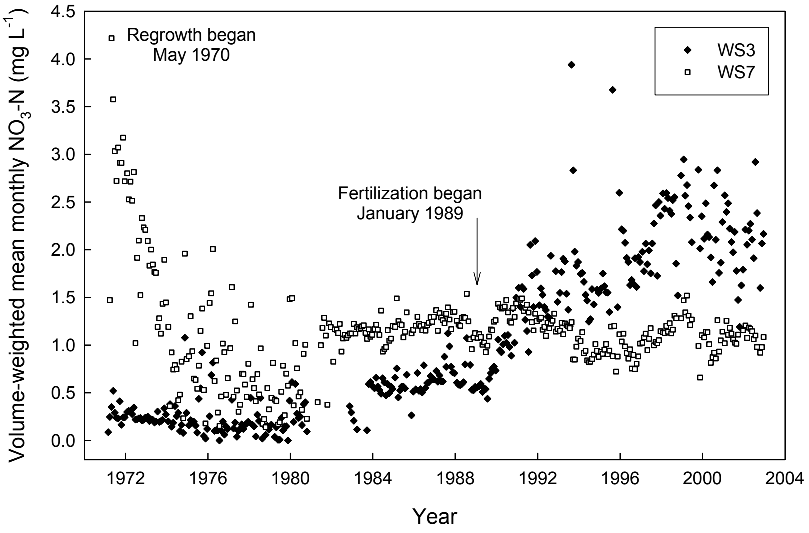


Figure 2-4. Volume-weighted mean monthly NO_3-N concentrations in stream water for WS3 and WS7 between 1970-2004.

After farming ended on WS9 in the 1920s, natural revegetation proceeded until August 1983. A vegetation survey taken in September 1983 classified 39 percent of the watershed as "open" – not shaded by other vegetation, 3 percent still in old fields and the remaining area in poor quality hardwoods. The trees on the watershed were cut in 1983, except for a 1.42-ha buffer strip (~20 m wide on each side) around the entire length of the stream. Following cutting, WS9 was prepared for planting by mechanical root-raking and windrowing slash on the contour with a bulldozer in November 1983 (Kochenderfer and Helvey 1989). The site preparation treatment exposed bare soil on 45 percent and created a litter-soil mixture on an additional 38 percent of the watershed. There was a 28 percent increase in average annual specific conductance and a small increase in stream water NO_3 export (1.68 kg ha^{-1}) after site preparation. WS9 was planted with 2-0 Japanese larch in the spring of 1984 at a 1.8 x 1.8 m spacing (Kochenderfer et al. 1995).

Table 2-2. Some characteristics of the study watersheds. Stand parameters are based on the 1990 inventory for WS4, 2004 for WS3 and WS7.

Characteristic	WS3			WS7			WS4		
Area (ha)	34			24			39		
Aspect	South			East			Southeast		
Mean elevation (m)	792			792			792		
Mean annual precipitation (mm)	1473			1448			1473		
Mean stand density (stems ha^{-1})	1883			1473			1206		
Mean stand basal area (m^2 ha^{-1})	36.0			28.0			38.6		
Mean stand biomass (mt ha^{-1})	203.4			157.5			310.7		
Site index 50 yr NRO (m)	23			23			23		
Dominant tree species stems ha^{-1} (% basal area)	Black cherry	442	(51.0)	Sugar maple	334	(4.9)	Sugar maple	336	(11.3)
	Red maple	366	(11.5)	Sweet birch	319	(20.5)	Red maple	188	(8.9)
	Am. beech	245	(2.5)	Red maple	274	(8.2)	Am. beech	183	(6.5)
	Sweet birch	161	(5.1)	Yellow-poplar	143	(26.2)	N. red oak	69	(29.8)
	Sugar maple	119	(1.3)	Black cherry	143	(20.5)	Sweet birch	42	(3.6)

Reference watersheds 4, 10, and 13 (WS4, WS10, WS13) have remained relatively undisturbed since the original cutting between 1905 and 1910. Some chestnut trees killed by the chestnut blight were salvaged in the early 1940s (Trimble et al. 1986). Most of WS4 and WS13 are located on mesic sites while WS10 represents a more xeric site. Species composition on WS4 and WS13 is very similar. Sugar maple is the dominant tree species on both watersheds. Stand characteristics for WS4 are shown in Table 2-2. Chestnut oak is the dominant tree species on WS10 (Christ et al. 2002).

11. WATER INSTRUMENTATION

The hydrometeorologic network used on the Fernow is described by Adams et al. (1993). WS3, WS4, WS7, and WS9 are instrumented with 120° V-notch weirs and WS10, WS13 with 0.61-m H-type flumes, all equipped with FW-1 water level recorders and 7-day strip charts to measure streamflow continuously.

Stream water grab samples have been collected from WS3, WS4, WS7, and WS9 on a weekly or bi-weekly basis since 1960 and from WS10 and WS13 since 1984. Samples were analyzed for pH and specific conductance only prior to 1970. Since then Ca, magnesium (Mg), potassium (K), sodium (Na), sulfate (SO_4), NO_3, chloride (Cl), ammonium (NH_4), and alkalinity have been analyzed on these samples. Zero-tension pan lysimeters were installed on WS3 and WS4 in 1988, and WS9 in 1986 to sample soil water for chemical analyses. In addition to grab sampling, stream water also was sampled during storm runoff events using automatic pumping samplers.

The precipitation monitoring network on the Fernow consists of eight 20-cm diameter standard rain gages and five weighing-type rain gages. Precipitation catch is measured and strip charts changed weekly. Two wet deposition collectors and 2 bulk (wet/dry) collectors also are located on the Fernow. Chemical analyses of stream water samples and precipitation samples are performed at the Timber and Watershed Laboratory at Parsons. Clean Air Status and Trends (CASTNET) and National Atmospheric Deposition Program (NADP) monitoring sites also are located at the Timber and Watershed Laboratory.

12. WATERSHED ACIDIFICATION TREATMENTS

Acidification treatments on WS3 and WS9 consisted of three applications of ammonium sulfate fertilizer annually. Fertilizer applications were made at a rate that was approximately double the bulk nitrogen (N) and sulfur (S) deposition inputs estimated from throughfall concentrations determined by Helvey and Kunkle (1986). Because deposition varies seasonally, fertilizer application rates were made at levels to reflect that variability. Applications were made in spring, summer, and autumn (usually in March, July, and November) each year. Spring and autumn application rates of 34 kg fertilizer ha^{-1} (7.1 kg N ha^{-1} and 8.1 kg S ha^{-1}), were approximately double the deposition rates for January to April and September to December, respectively. Summer application rates of 101 kg fertilizer ha^{-1} (21.3 kg N ha^{-1} and 24.4 kg S ha^{-1}) were approximately double the deposition between May and August. Multiple applications per year using relatively low rates avoids inducing toxicity and reduces the potential for altering the proportions of N and other nutrients (Schleppi et al. 1999). Annual application rates were 40.6 kg S ha^{-1} and 35.4 kg N ha^{-1}, which resulted in a 3x ambient (ambient + 2x ambient) treatment. Fertilizer application rates did not vary among years.

Fertilizer treatments on WS9 began in April 1987 and were terminated in July 1994. The rates and timing of application were identical to those described for WS3. Treatments on WS3 began in January 1989 (in place of the March application) and continue. The first two applications on WS9 were made manually by applying pre-weighted amounts of fertilizer to the entire watershed after it was gridded into small areas of known acreage. All other applications on WS9, and all applications on WS3 during the first 9 years, were made by helicopter; beginning in July 1998 all applications to WS3 have been made by low flying fixed-wing aircraft equipped with a global positioning swathing system to ensure accurate coverage.

To reduce the possibility that fertilizer would reach control lysimeters on WS9 either by leaching or during fertilization, large plots (30.5 m x 30.5 m) were established and the lysimeter in each plot was located in the middle of each plot (width) approximately two-thirds of the way downslope from the top of the plot. During each aerial treatment on WS9, fertilizer was applied by hand to a 9.1-m wide area around the entire perimeter of each control plot and the helicopter operated outside this area, applying fertilizer to the rest of the watershed.

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Chapter 3

SOIL CHEMICAL RESPONSE TO EXPERIMENTAL ACIDIFICATION TREATMENTS

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1. INTRODUCTION

One of the conclusions reached during the Congressionally mandated National Acid Precipitation Program (NAPAP) was that, compared to ozone and other stress factors, the direct effects of acidic deposition on forest health and productivity were likely to be relatively minor. However, the report also concluded "the possibility of long-term (several decades) adverse effects on some soils appears realistic" (Barnard et al. 1990). Possible mechanisms for these long-term effects include: (1) accelerated leaching of base cations from soils and foliage, (2) increased mobilization of aluminum (Al) and other metals such as manganese (Mn), (3) inhibition of soil biological processes, including organic matter decomposition, and (4) increased bioavailability of nitrogen (N).

Sulfate-induced acidification occurs as the sulfate (SO_4) adsorption potential of a soil is reached, and excess SO_4 ions are leached from the soil into surface and ground waters (Reuss and Johnson 1986). Unlike nitrate (NO_3), SO_4 is often strongly adsorbed in the soil. Nonetheless, when excess SO_4 appears in percolating soil water, charge balance dictates that a counter ion such as calcium (Ca) must also be present. Consequently, continual leaching of excess SO_4 can gradually decrease exchangeable base cation

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pools in the soil if the rate of base cation supply to the soil is not able to keep up with the new equilibrium.

Although NO_3 is poorly adsorbed in soil systems by abiotic mechanisms, soils represent the largest storage pools for N inputs (Fenn et al. 1998), although plant uptake is also important. Nitrogen saturation occurs when the combination of external and internal sources of N exceeds biological demand, resulting in NO_3 leaching (Ågren and Bosatta 1988, Aber 1992, Stoddard 1994). Other symptoms of N saturation include: increased rates of N cycling, leaching of base cations from the soil, increases in foliar N, and changes in vegetative productivity (Fig. 1-3; Aber 1992, Magill et al. 1997, Fenn et al. 1998, Lovett et al. 2000).

The original study design for the Fernow Acidification Study did not include evaluating impacts on soils, focusing instead on solution chemistry. Soils were fully incorporated into the study beginning in 1994, in an effort to better document changes in ecosystem processes at all levels. Results from sampling for the Direct Delayed Response Program suggested that the soils on the Fernow watersheds were relatively low in SO_4 adsorption capacity, that effects of the additions of ammonium sulfate fertilizer would manifest fairly rapidly, and would most likely be an acidification response to sulfur (S) (Herlihy et al. 1993). However, N appeared to be as important as S in defining acidification processes, based on early stream chemistry responses. Therefore, a number of studies evaluating N cycling processes in the soil also were conducted, and will be discussed in this chapter. We will present information on soil chemistry for WS3, WS4, WS7 and WS9 (Table 3-1, See Chapter 2 for more detailed watershed descriptions.), and will focus on those chemical constituents believed to be most sensitive to acidification or N saturation: pH, N, Ca, magnesium (Mg), Al and Mn. Other data will be included as needed for supporting arguments.

2. METHODS

2.1 Comparisons between WS3 and WS4

In 1988, as the study was being planned, 15 sites per watershed on WS3 and WS4 were selected for the measurement of soil solution by lysimetry (Fig. 3-1). WS3 serves as the treatment watershed and WS4 is the reference watershed. (See Chapter 2 for detailed descriptions of the watersheds.) At each site, prior to lysimeter installation, a soil pit was excavated and the major horizons were described. Mineral soil samples were collected from each pit and each horizon for analysis; the forest floor was not sampled. Unfortunately, most of these soil samples and the associated chemical and physical data were lost. The few archived soil samples that were retained were analyzed in 1994 for chemical properties at the University of Maine Plant and Soil Testing Laboratory, using analytical methods described below. These data will be used to provide insights on pretreatment conditions, and to evaluate changes over time.

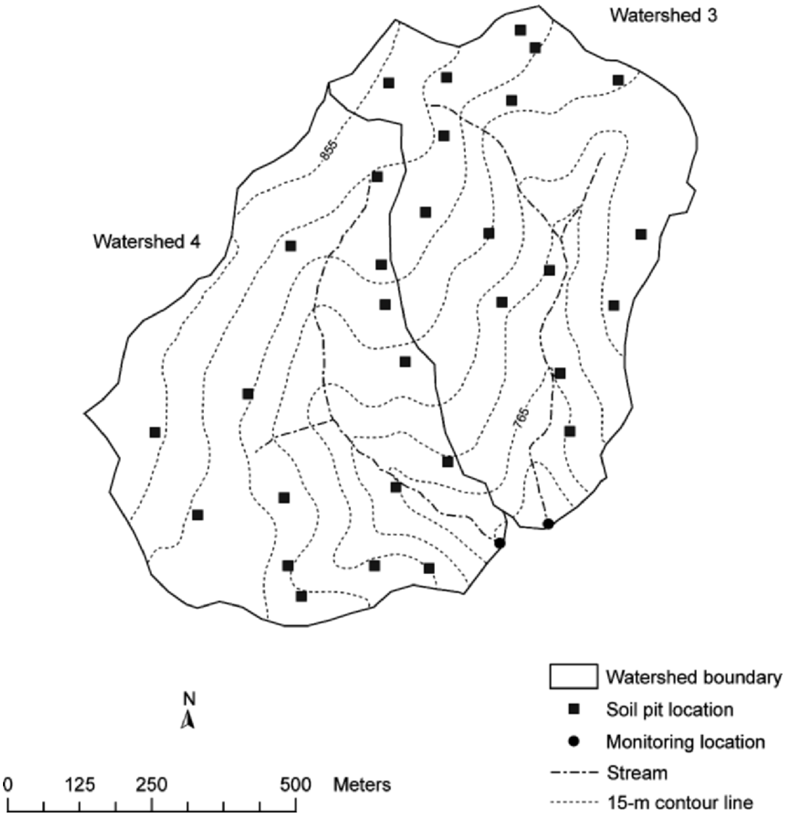

Figure 3-1. WS3 and WS4 soil pit locations.

These 15 lysimeter sites per watershed were resampled in adjacent, undisturbed soil in 1994 and 2002. On each of these sampling dates, soil samples were collected a short distance away from the lysimeters, along the contour (e.g. at the same elevation and aspect). Samples were collected from the O horizon (Oa and Oe horizons were not separated), and the mineral soil by depth (0-10, 10-20, 20-30 and 30-45 cm), which approximately correspond to the A, AB, BW1 and BW2 horizons as described in 1988.

Samples were air-dried, sieved (2 mm) and analyzed for chemical constituents. Soil pH was measured in distilled water (1:1 ratio). Organic matter concentration was estimated by loss-on-ignition (LOI) at 550°C (Page et al. 1982). Total N was measured by the macro Kjeldahl method in 1994 and by combustion in 2002. The two methods give comparable results in these types of soils (Bruce Hoskins, Univ. Maine Soil Testing Laboratory, pers. comm., 1998). All other nutrients were extracted with 1N ammonium chloride and measured by plasma emission, or in the case of potassium (K) and sodium (Na), by flame emission. Exchangeable acidity was extracted by 1N potassium chloride and measured by titration (Page et al. 1982). Base saturation was calculated as the percentage of the effective cation exchange capacity (ECEC) occupied by exchangeable bases, whereas Ca or Mg saturation was the percentage of the ECEC occupied by these individual exchangeable cations.

Data were analyzed using "Proc Mixed" (SAS Institute, Inc. 1988) with a restricted maximum likelihood estimation technique. Year was a repeated variable in the analysis and was modeled using an autoregressive order 1 covariance structure. Data were log-transformed to the meet the assumptions of normality and equality of variances. Base saturation and LOI data were transformed using the arcsine transformation, which is more appropriate for percentage data. Note that for soil Ca, no transformations were successful in meeting the assumptions of normality and equality of variances and therefore results should be interpreted with extreme caution. Other watersheds were sampled for related studies; those data are included here for comparative purposes.

2.2 Comparisons between WS3 and WS7

Two sets of soil samples were collected during the acidification experiments that allowed comparison of soil conditions on WS3 and WS7. For these comparisons, WS7 serves as the vegetative reference for the treated WS3. See Chapter 2 for details on the watersheds' characteristics. Tepp (1995) sampled soil in the vicinity of 25 randomly located litter collectors on WS3 and WS7 in May 1995, after approximately 7 years of ammonium sulfate treatments. Tepp collected samples from soil A horizons (mean depths 5.9 and 7 cm on WS3 and WS7, respectively) and soil B horizons (mean depths 18.6 cm and 22.1 cm for WS3 and WS7, respectively) within 2 m of the litter collectors (Fig. 3-2). Soil samples were analyzed for available phosphorus (P), K, Ca, and Mg using the Mehlich 3 method (Wolf and Beegle 1991) at The Pennsylvania State University Agricultural Analytical Services Laboratory. Available metals (Mn, iron (Fe), copper (Cu), zinc (Zn), Na, Al, lead (Pb), nickel (Ni), cadmium (Cd)) were analyzed at the same facility using the Diagnostic Soil Test Methods (ASTM D5435-93) and pH using the water method (Eckert and Sims 1991). Odenwald (2002) sampled soil O, A, and B horizons in the vicinity of 10 trees sampled for growth cores and dendrochemistry on WS3 and WS7 in 2000. (See Chapter 5 for further details), 12 years after the initiation of treatments. These samples were also analyzed for soil chemical parameters at the Penn State Agricultural Analytical Services Laboratory using methods described above. In addition, a strontium chloride ($SrCl_2$) extraction aluminum stress test analysis was used to determine plant available Ca and Al at The Pennsylvania State University Agricultural Analytical Services Laboratory (Odenwald 2002).

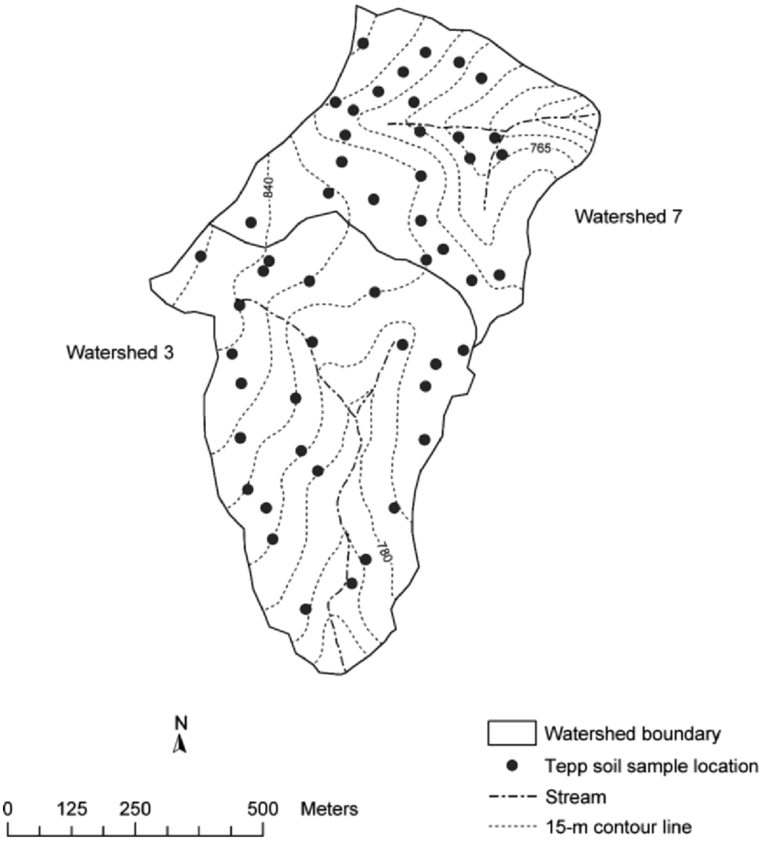

Figure 3-2. Tepp (1995) soil sampling locations.

2.3 Effects on Soils on WS9

Each year from 1992-1994, soil samples were collected from one control plot and one treatment plot (Fig. 3-3) in July (prior to the July fertilizer application) and in August (post-fertilization). In 1992, six control and six treated soil pits (approximately 20 x 20 cm) were excavated in each plot. In 1993 and 1994, 12 pits on each plot were hand excavated and soil samples were obtained from each. All soil samples were collected from the 0-2 cm layer (O horizon) and the 2-10 cm layer (A horizon). These horizons were chosen to represent the effective rooting horizons for this soil (Kochenderfer

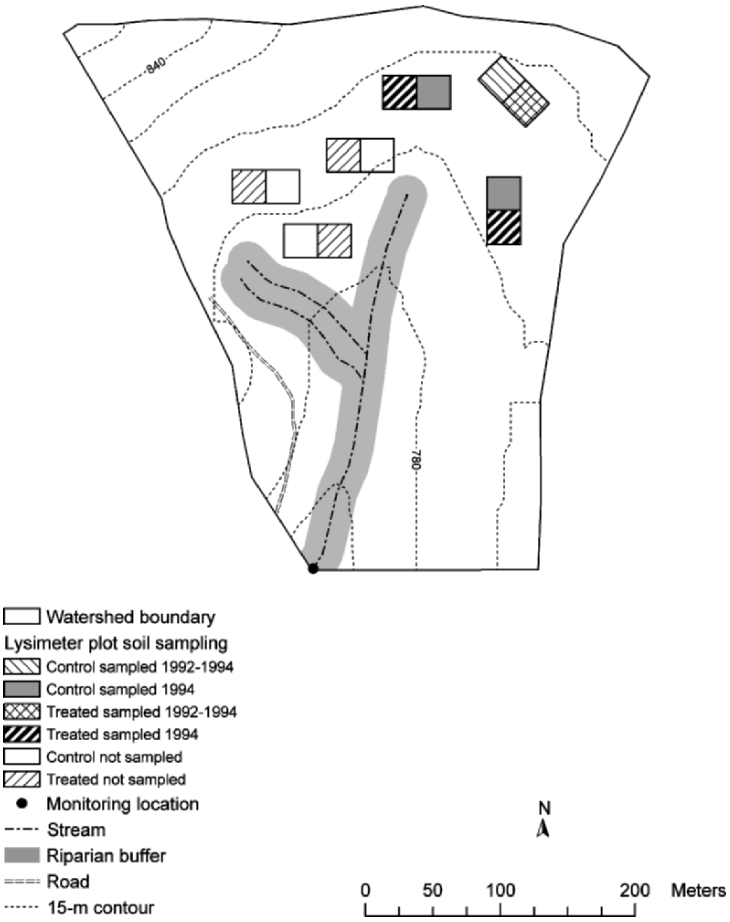

Figure 3-3. Soil sampling locations on WS9.

1973). All analyses were conducted on air-dried soil sieved to 2 mm, at the Environmental Resources Research Institute Soil Chemistry Laboratory at The Pennsylvania State University. Soil pH was determined in water with soil-to-solution ratios of 1:1 for both soil horizons (Black 1964). The base cations, Ca, Mg, and K, and metal cations Al and Mn were determined by atomic absorption spectrophotometry following 0.01 M $SrCl_2$ extraction and preparation as outlined by Joslin and Wolfe (1989). In 1992, soil carbon (Schulte 1991), NO_3-N (Isaac and Johnson 1976) and SO_4-S (Black 1964) analyses were performed by the Agricultural Analytical Laboratory at The Pennsylvania State University. In 1993 and 1994, total carbon (C) and total N were analyzed by combustion using an elemental analyzer and total S by combustion using an elemental analyzer with an electron capture detector (Baccanti et al. 1993, Carlo Erba Instruments 1990) at the USDA Forest Service's Timber and Watershed Laboratory in Parsons, West Virginia.

Statistical analysis followed a Model I two-treatment ANOVA for a fixed treatment, incorporating t-tests for means comparisons (SAS Institute 1988). All significant differences are reported at $p \leq 0.05$.

3. RESULTS

3.1 Pretreatment Soil Characteristics – WS3, WS4, WS7

A rock layer composed of fractured hard sandstone and shale underlies most of the Fernow watersheds. Slopes ranging from 20 to 50 percent are common. The soils are predominantly from the Calvin and Dekalb soil series, which originated from these rocky materials (loamy–skeletal mixed mesic Typic Dystrochrepts). The Calvin series consists of moderately deep, well-drained soils formed in material weathered from interbedded shale, siltstone and sandstone. Dekalb soils are also acidic, deriving from acidic sandstones. Average soil depth is about 1 m, and the soil contains a considerable amount of stones and large gravels, as much as 70% by volume (Adams et al. 2004). Average bulk density of the whole soil ranges from 1.2 to 1.5 g cm^{-3}, with average porosity 43 to 55% (Adams et al. 2004).

From the relatively few pretreatment samples, we may conclude that there were few pretreatment differences (1988) between the upper mineral horizon (0-10 cm) on WS3 and WS4 (Table 3-1). Edwards et al. (2002a) reported that WS3 had a significantly greater A horizon (approximately 0-10 cm) soil pH than WS4, and significantly lower exchangeable Al than WS4, but noted no other statistically significant differences in the upper horizon chemistry. Base saturation of the A horizon soil on WS3 was more than twice that of WS4 A horizon, and indeed, almost twice that of the other watersheds, but the differences were not statistically significant (Table 3-1). Some of this is due to very high Ca values within one location on WS3, and thus is attributed to high spatial variability. Within-watershed variability was large and the number of samples was fairly small.

The soils of all watersheds were fairly acidic, with moderately low ECEC and base saturation. Based on work by Reuss (1983), these soils are at the thresholds where an abrupt change from Ca to Al mobilization should occur with acidification. Overall, the variability in soil chemical properties among watersheds was not great. The watersheds designated to be treated, WS3 and WS9, had the highest base saturation levels, suggesting a relationship with stand age perhaps. However, mean base saturation on WS7, also a young stand, was the lowest (Table 3-1). Gilliam and Adams (1995) evaluated the relationship between soil chemical properties and stand age for these watersheds, but found no statistically significant relationship. However, exchangeable nutrients were more highly correlated with organic matter content and texture in the young stands than in the mature stands that they studied, which the authors interpreted to mean that the importance of soil organic matter as a source of nutrients or cation exchange sites might decrease with stand age.

Table 3-1. Soil chemistry means and standard deviations (in parentheses) for Fernow watersheds for upper mineral soil horizon (0–10 cm on average), selected parameters. Data for WS3 and WS4 are mean pretreatment soil levels (n = 12 and n = 6, respectively). Data for other watersheds represent different sampling dates. NA= data not available.

Analyte	Watershed, stand origination date, and treatment				
	WS3 1969 Fertilization	WS4 ~1911 Reference	WS7[a] 1969 Vegetative Reference	WS10[b] ~1911 Reference	WS9[c] 1984 Fertilization
pH	4.48	3.95	4.68	3.96	4.56
Total C (g kg^{-1})	91 (54)	112 (53)	NA	62 (23)	33 (13)
Total N (g kg^{-1})	4.79 (1.38)	2.6 (1.4)	4.5 (1.3)	3.1 (0.8)	NA
Exch. Ca (meq 100g^{-1})	4.79 (8.72)	0.49 (0.22)	1.28 (1.82)	0.5 (0.3)	0.64 (0.57)
Exch. Mg (meq 100g^{-1})	0.59 (0.88)	0.23 (0.10)	0.28 (0.20)	0.22 (0.08)	0.17 (0.12)
Exch. Al (meq 100g^{-1})	1.39 (1.81)	8.70 (3.79)	1.88 (0.53)	0.50 (0.03)	4.23 (0.85)
Base saturation (%)	34 (33)	14 (4)	13 (14)	14 (7)	21 (12)
ECEC (meq 100g^{-1})	11.77 (7.86)	9.35 (3.41)	14.6 (1.83)	8.50 (2.1)	6.50 (1.0)

[a] Data from Tepp (1995) .

[b] Note that 0-10 cm in WS10 includes Oe and Oa horizons, where present, but not in WS3 and WS4. WS10 was sampled in 1997 (Christ et al. 2002).

[c] Data from Edwards et al. (2002b).

Helvey and Kunkle (1986) demonstrated that much more SO_4 entered WS4 as throughfall than was lost in streamflow on an annual basis, suggesting net watershed accumulation, and significant SO_4 buffering capacity by the soil. However, Polk (1991) examined Berks and Dekalb soils from Fork Mountain and concluded that the soils had little further ability to absorb SO_4. Helvey and Kunkle (1986) also demonstrated that NO_3-N inputs were approximately equal to outputs. Nitrate was generally the dominant form of available N on both watersheds (Gilliam and Turrill 1993).

3.2 Pretreatment Soil Characteristics – WS9

The predominant soil on WS9 is Calvin channery silt loam (loamy-skeletal, mixed mesic Typic Dystrochrept), similar to that of WS3, WS4, and WS7. However, WS9 was farmed for many years before 1930 (Lima et al. 1978), and soils on the watersheds were nutrient-poor even 50 years later (Table 3-1), with relatively high exchangeable Al levels, and the lowest exchangeable Mg and ECEC of the watersheds evaluated. Much of the original A horizon soil has been eroded from the slopes of WS9 (Kochenderfer and Helvey 1989).

3.3 Treatment Effects

3.3.1 Comparisons between WS3 and WS4

The effect of Horizon was statistically significant for all the variables, as might be expected. There is an order of magnitude difference in soil carbon, for example, between the O horizon and the 30-45 cm horizon. The differences among horizons were largely driven by higher concentrations and nutrient values in the O horizon, due to the greater organic matter content. The 0-10 cm horizon usually differed significantly from the O horizon and from the deeper horizons, and there were few significant differences among the lower horizons (10-20, 20-30 and 30-45 cm horizons). This trend of decreasing nutrient concentrations and organic matter with depth is common in these soils, and points to the importance of annual litter inputs in nutrient cycling, and to the role of uptake by vegetation.

Year was a statistically significant effect for all variables except for acidity and Mg, although lack of data for the O horizon in 1988, and the relative paucity of data for 1988 in general, made interpretation of these data difficult. The horizon*year interaction was statistically significant for all variables, again due to the influence of the O horizon, and in particular, changes in O horizon nutrient concentrations between 1994 and 2002 (Tables 3-2 and 3-3). Total carbon, total N, pH base saturation, Ca saturation, ECEC, and K all increased significantly in the O horizon between 1994 and 2002. The lowest horizons showed little (20-30 cm) or no change (30-45 cm) over time.

Table 3-2. Chemical characteristics of soils on WS3 and WS4, 1994. Values are means of 15 samples; values within an horizon followed by different letters indicate significant differences between watersheds at $p < 0.05$.

	Depth (cm)									
	O horizon		0-10		10-20		20-30		30-45	
Characteristic	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4
pH	4.22	4.07	4.34	4.34	4.57	4.55	4.55	4.51	4.50	4.54
Total C (g kg^{-1})	108	189	57	53	28	26	20	17	9	7
Total N (g kg^{-1})	5.97a	8.75b	3.84	3.11	1.68	1.25	1.07	0.72	0.91	0.54
C:N	18.1	20.4	15.6	18.0	18.3	22.1	22.0	24.6	10.8	15.4
Ca (meq 100g^{-1})	3.32	4.56	1.55	0.48	0.32	0.14	0.32	0.11	0.36	0.12
K (meq 100g^{-1})	0.39	0.74	0.26	0.20	0.14	0.12	0.14	0.11	0.14	0.12
Mg (meq 100g^{-1})	0.63	1.07	0.33	0.22	0.11	0.09	0.09	0.08	0.09	0.08
Na (meq 100g^{-1})	0.08	0.11	0.06	0.04	0.03	0.04	0.03	0.03	0.03	0.03
Base saturation (%)	29.6	40.9	20.1	12.8	11.7	7.8	12.0	7.1	11.1	7.5
Ca saturation (%)	21.4	28.9	13.4	6.5	6.2	2.8	6.8	2.5	6.3	2.6
Mg saturation (%)	4.6	6.7	3.3	2.9	2.1	1.8	1.9	1.6	1.8	1.7
Exch. acidity (meq 100g^{-1})	8.4	9.2	7.2	6.7	4.6	4.9	4.5	4.6	4.8	4.8
ECEC (meq 100g^{-1})	12.9	15.7	9.4	7.6	5.3	5.3	5.1	4.9	5.4	5.1

The Watershed effect was statistically significant only for Ca and ECEC, suggesting that the treatments may have altered Ca throughout the soil profile, and therefore ECEC. Generally, WS3 mean Ca and ECEC values were greater than for WS4. However, because of the variability of these data, and because the Ca data did not meet the assumptions of normality and equality of variances, this conclusion cannot be made with confidence. A significant watershed*horizon effect was detected only for K and total C. Significant watershed*year effect was detected for acidity, Mg, and Ca saturation. The watershed*horizon*year effect was statistically significant only for pH, total N, Mg, K, and total C.

Table 3-3. Chemical characteristics of soils on WS3 and WS4, 2002. Values are means of 15 samples; values within an horizon followed by different letters indicate significant differences between watersheds at $p < 0.05$.

	Depth (cm)									
	O horizon		0-10		10-20		20-30		30-45	
Characteristic	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4	WS3	WS4
pH	4.10	4.14	4.20	4.13	4.61	4.54	4.74	4.71	4.78	4.72
Total C (g kg^{-1})	268	249	73	60	40	37	18	18	9	8
Total N (g kg^{-1})	13.84	10.38	4.35	3.61	2.45	2.37	1.22	1.20	0.71	0.69
C:N	19.4	23.8	15.4	15.7	14.5	16.8	20.8	18.1	13.0	11.6
Ca (meq 100g^{-1})	11.93	12.86	1.47	0.83	0.46	0.29	0.19	0.17	0.21	0.11
K (meq 100g^{-1})	1.11	1.13	0.30	0.34	0.22	0.19	0.14	0.15	0.12	0.10
Mg (meq 100g^{-1})	1.85	1.93	0.24	0.24	0.10	0.12	0.05	0.09	0.05	0.05
Na (meq 100g^{-1})	0.08	0.07	0.01	0.06	0.01	0.02	0.01	0.02	0.01	0.01
Base saturation (%)	61.1	67.0	19.9	22.8	12.6	11.6	8.1	9.5	7.4	5.4
Ca saturation (%)	48.3	53.7	13.6	13.6	7.1	5.7	4.0	3.9	4.1	2.2
Mg saturation (%)	7.7	8.2	3.5	5.1	3.7	3.4	2.8	3.2	2.2	1.9
Exch. acidity (meq 100g^{-1})	8.3	7.3	7.0	5.9	5.6	5.1	4.8	4.2	5.4	4.8
ECEC (meq 100g^{-1})	23.4	23.3	9.1	7.3	6.4	5.7	5.2	4.6	5.8	5.1

Thus, we may conclude that there are significant differences in most chemical parameters among the upper two horizons (O and 0-10 cm), and the mean values of some chemical variables changed over time. In general, the differences among watersheds were not statistically significant, and did not provide strong evidence of decreases in base cation concentrations. The O horizon showed significant changes between 1994 and 2002, particularly related to changes in organic matter content. During this time period, organic matter increased more on WS3 (150%) than on WS4 (32%), although initial C levels were greater on WS4. The increase in total N also was greater on

WS3 (125%) relative to the changes on WS4 (20%), resulting in lower C:N ratios on WS3 than WS4 in 2002 (Fig. 3-4).

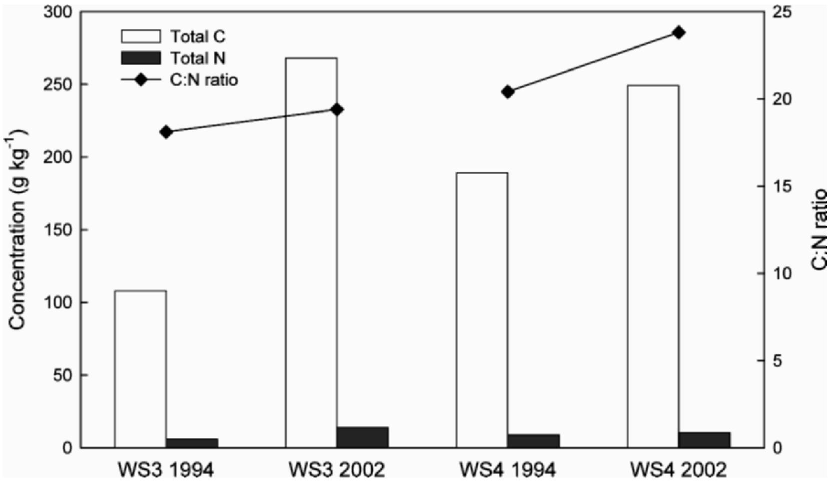

Figure 3-4. Total soil C, total soil N and C:N ratios for O horizon, WS3 and WS4, sampled in 1994 and 2002.

ECEC also increased significantly in the O horizon for both watersheds, but exchangeable acidity did not (Fig. 3-5). In addition, WS3 O horizon concentrations of Ca, K, and Mg, all increased significantly between 1994 and 2002, perhaps reflecting increased uptake of nutrients by the vegetation and storage in leaves, and eventually increased concentrations in leaf litter. Fertilizer additions also may have increased litter mass and organic matter delivery to the soil surface, although litterfall data do not show increases in litterfall mass on WS3 over time. Higher quality litter (that with more soluble N, more easily decomposed) would mineralize more quickly, which could result in more organic matter but in a more mature state of humification with higher surface charge.

There were fewer statistically significant differences in the O horizon between the two watersheds in 2002 relative to 1994, suggesting the O horizons of the two watersheds may be becoming more similar with time and perhaps treatment. Gilliam et al. (2001a) concluded that the acidification treatment appeared to decrease the spatial and temporal variability of some soil properties within WS3, particularly those related to N cycling. Decreased spatial heterogeneity within a watershed might lead to greater ability to detect differences between watersheds.

Based on these data, the O horizon appears to be the most sensitive to change over time, as statistically significant changes in most nutrient concentrations, generally increases, were observed for both watersheds between 1994 and 2002. The O horizon showed the most changes over time probably because of differences in total C, and given the reactivity of organic matter in these soils it is reasonable to expect that many other things would also change in concert with organic matter. A similar responsiveness in the O horizon was reported for the Bear Brook Watershed Manipulation study in Maine (Fernandez et al. 2003).

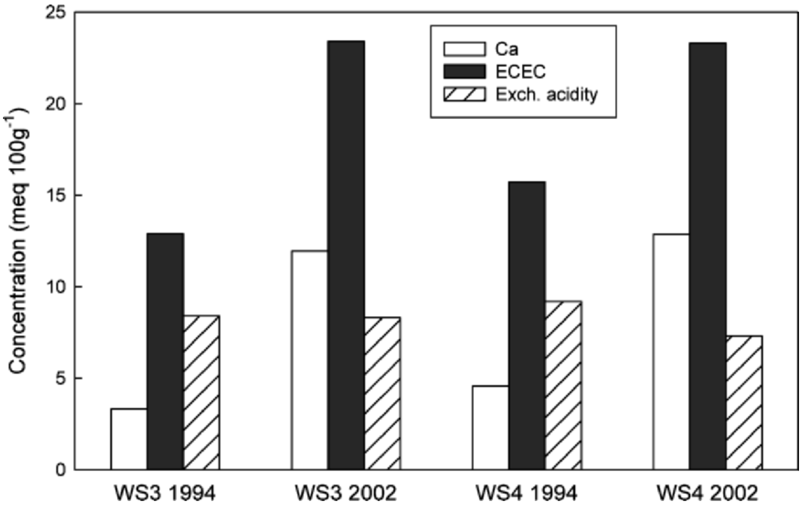

Figure 3-5. Exchangeable soil Ca, ECEC and exchangeable soil acidity for O horizon, WS3 and WS4, sampled in 1994 and 2002.

To further extend these temporal trends, and allow some evaluation of possible treatment effects on soil chemistry, we evaluated changes in average values for a number of soil parameters for the locations sampled in each of 1988, 1994 and 2002 (four pits in WS3 and three in WS4). We focus on the 0-10 cm and 10-20 cm horizons for clarity of presentation (Figs. 3-6 through 3-10), and because the changes in the lower horizons were subtle to nonexistent. There is a trend of increasing mean organic matter content, as measured by LOI, over the 14-year period, on both watersheds, with the exception of the 0-10 cm horizon of WS4 (Fig. 3-6) where organic matter content is decreasing slightly over time. Calcium and Mg concentrations generally declined over time in the upper mineral horizons of both watersheds (Figs. 3-7 and 3-8, respectively), although there were slight increases in the mean Ca concentration between 1994 and 2002 in the 0-10 cm of WS3. The greatest changes in mean values occurred between 1988 and 1994, in the upper 10 cm of soil. Variability in Ca and Mg

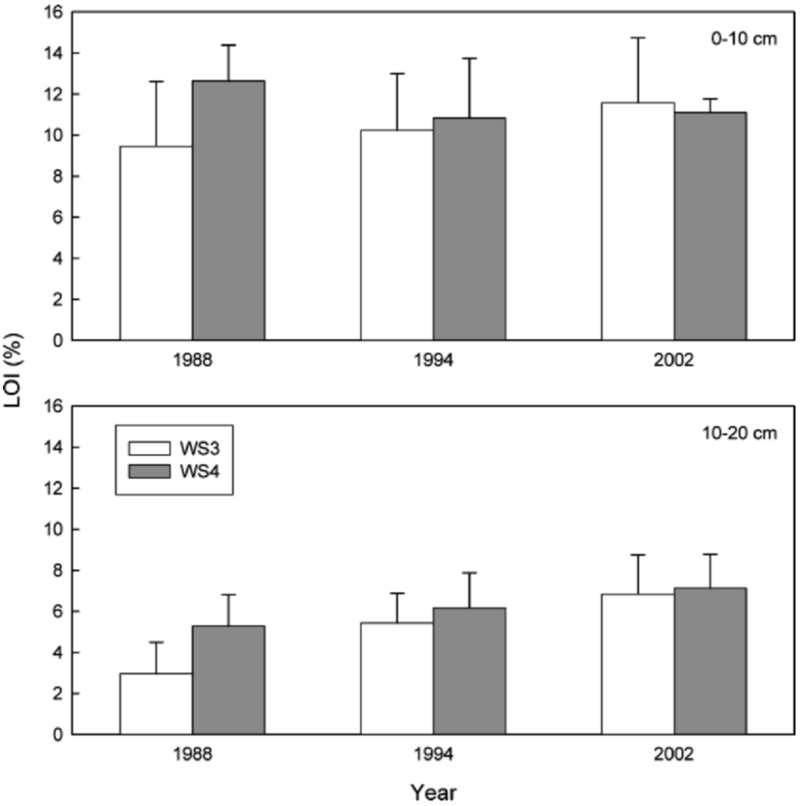

Figure 3-6. Changes in LOI over time, WS3 and WS4.

concentrations was also quite large in the 0-10 cm horizon for the 1988 sampling in particular. ECEC decreased for both watersheds, although most consistently in WS3 (Fig. 3-9). Base saturation increased over time for WS4 while decreasing on WS3 (data not shown), while exchangeable acidity showed the reverse pattern, increasing in WS3 0-10 and 10-20 cm horizons, and decreasing in WS4 (Fig. 3-10). Note that Ca concentration values from a single location in WS3 (1988) are quite high and are strongly influencing the means and variability. This represents the significant spatial variability discussed earlier. Overall, however, these data suggest a trend on WS3 of increasing acidity and organic matter over time, and decreases in base cations and ECEC, mostly in the upper mineral horizon. Although the data available to examine changes through time are very limited, the general patterns seem to suggest that more change occurred on WS3 between 1988

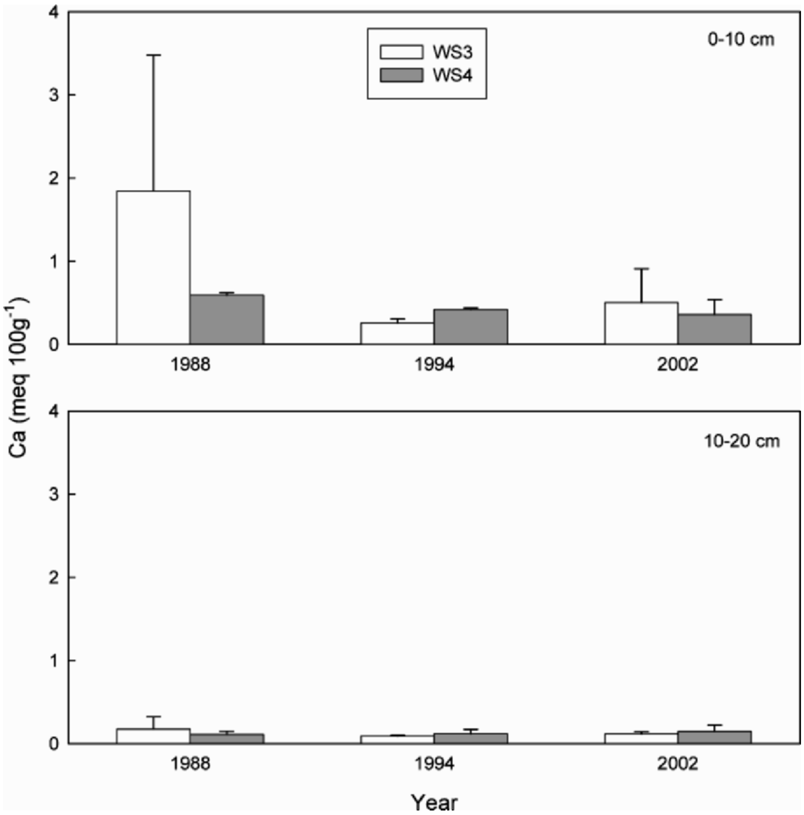

Figure 3-7. Changes in exchangeable soil Ca with time, WS3 and WS4.

and 1994 than between 1994 and 2002. In addition, the direction of the apparent change is what might be expected if soil acidification is occurring, supporting the hypothesis that the treatments are affecting soil processes. The trend of increasing nitrogen in the organic horizon (Tables 3-2 and 3-3) also provides evidence for a treatment effect, as we would expect soil N to increase as a result of chronic N fertilization. However, the effects are difficult to detect with existing data sets. The apparent trends of increasing organic matter in the O horizon (Fig. 3-4), and in the upper mineral soil (Fig. 3-6) of WS3 are intriguing and worthy of further examination and sampling, as organic matter is undoubtedly an important source of nutrients in these soils.

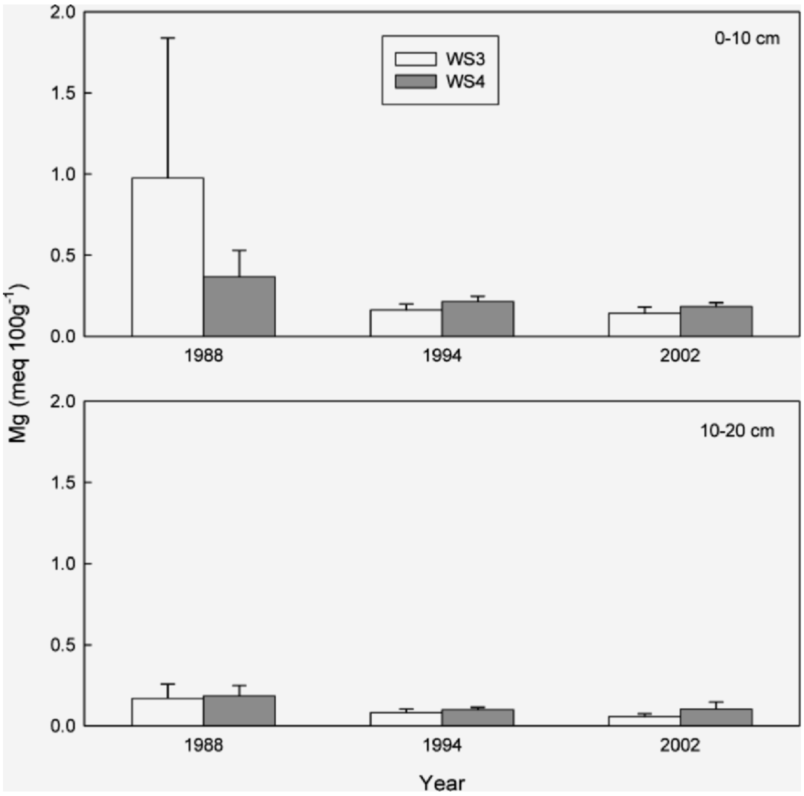

Figure 3-8. Changes in soil Mg over time, WS3 and WS4.

3.3.2 Comparisons between WS3 and WS7

Soil on the treated WS3 had lower soil pH and exchangeable base cation concentrations and higher Al concentration than the vegetative reference WS7, after both 7 and 12 years of treatment (Figs. 3-11 through 3-13), although not all differences were statistically significant. Differences in soil pH and A horizon Ca concentrations between the two watersheds were statistically significant in both studies, while Mg and Al levels did not differ significantly in the Tepp (1995) study (Figs. 3-11 and 3-12). Odenwald's (2002) study showed significantly higher Al levels in the soil of WS3. Ca/Al ratios in A and B horizons on the treated basin were at or below unity (Fig. 3-13), a level below which some trees may experience growth stress (Cronan and Grigal 1995).

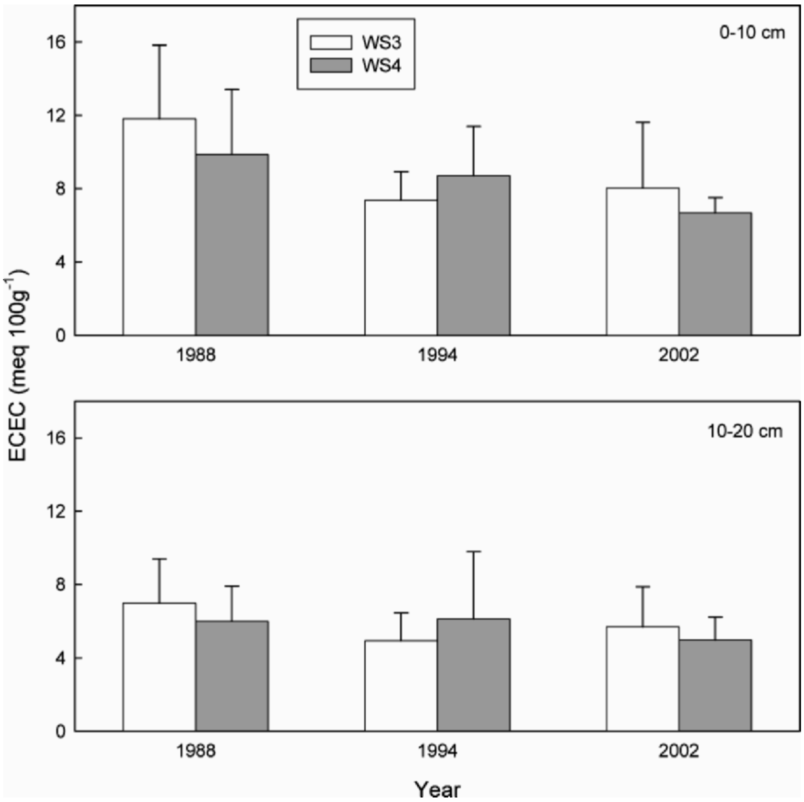

Figure 3-9. Changes in ECEC over time, WS3 and WS4.

Levels of Mn in soil differed between WS3 and WS7 (Tepp 1995), with mean Mn concentrations significantly less on WS3 relative to WS7 after 7 years of treatment. Soil Mn concentrations on the treated watershed in A horizon samples were lower (142.6 mg kg^{-1} on WS3 compared to 174.0 mg kg^{-1} on WS7), although not significantly so, but B horizon samples showed significantly lower levels of Mn on the treated basin (31.6 mg kg^{-1} on WS3 compared to 48.7 mg kg^{-1} on WS7; Tepp 1995). This was somewhat surprising, as soil acidification was expected to eventually increase Mn availability. On the treated watershed, vegetation also showed lower concentrations in bolewood Mn concentrations after 4 years of treatment in two of four species, but after 8 years of treatment all four tree species showed a higher Mn and lower Ca and Mg in bolewood samples (see Chapter 5). Thus, mineral soil Mn levels were lower 7 years after treatment, while

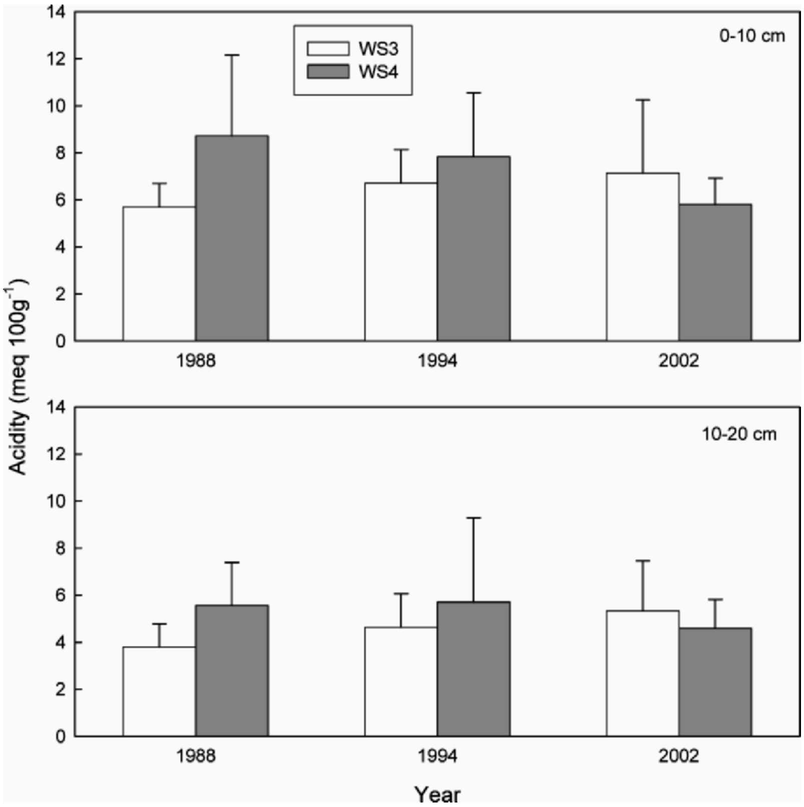

Figure 3-10. Changes in exchangeable soil acidity over time, WS3 and WS4.

vegetation bolewood Mn levels were elevated after 8 years of treatment. These results presumably reflect some complex combination of soil depletion and increased availability due to mobilization, playing itself out in the soil over time and depth.

3.3.3 Treatment Effects WS9

Soil on the treated plots sampled in August 1992 had significantly greater N and C concentrations compared to soil from the control plots; for the A horizon these differences were statistically significant. Soil from the A horizon on the treated plots also showed significantly greater SO_4-S concentrations than those of the control plots. The 1993 July total S concentration in the A horizon was significantly greater than the control. In

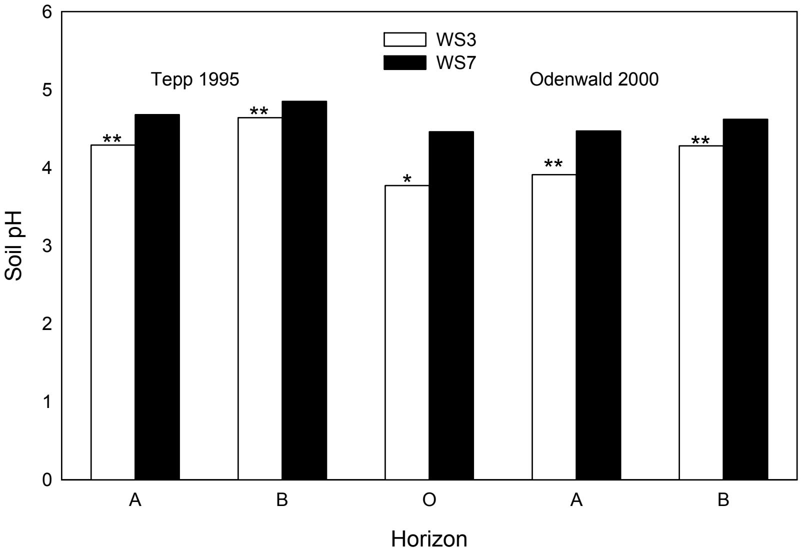

Figure 3-11. Comparisons of soil pH between Fernow WS3 and WS7 by soil horizon after 7 years of treatment (Tepp 1995) and 12 years of treatment (Odenwald 2002). Significant differences are indicated above bars; * 0.05 level, ** 0.01 level.

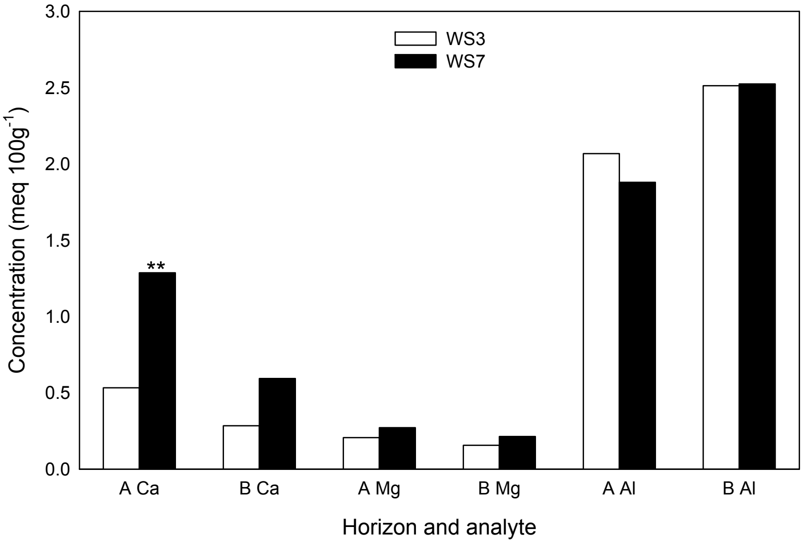

Figure 3-12. Comparison of soil exchangeable Ca, Mg, and Al on Fernow WS3 and WS7 after 7 years of treatment by horizon (Tepp 1995). Significant differences are indicated above bars; * 0.05 level, ** 0.01 level.

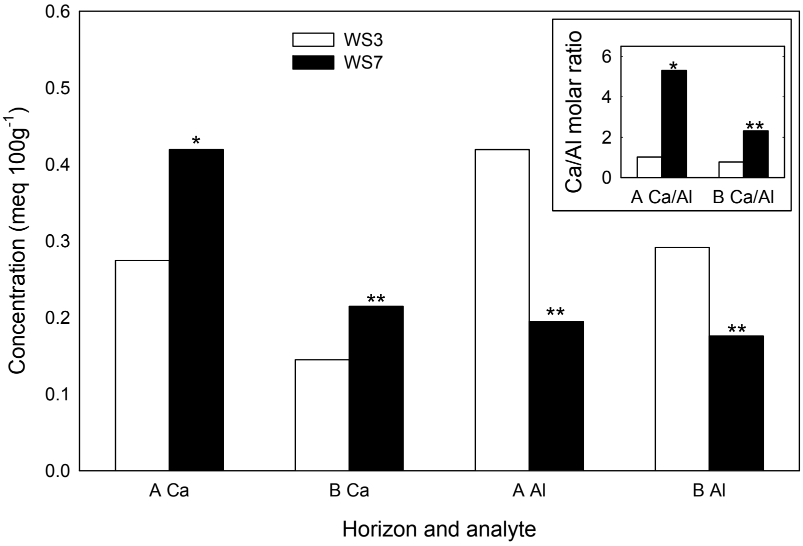

Figure 3-13. Comparison of soil exchangeable Ca and Al and Ca/Al molar ratios on Fernow WS3 and WS7 after 12 years of treatment by horizon (Odenwald 2002). Significant differences are indicated above bars; * 0.05 level, ** 0.01 level.

August 1994, O horizon concentrations of C and N were significantly greater in the treated plots compared to the control plots.

Base cation concentrations also varied between the treatment and control plots in WS9. In 1992, the O horizon Ca concentration was significantly greater in the control plots compared to soil in the treated plots both in July and August (Table 3-4). For the same year, values of $SrCl_2$ extractable Al in August were significantly greater, and Ca and Mg significantly lower compared to the control, for both horizons. In 1993, $SrCl_2$ extractable soil Al and Mn were significantly greater in the treated soil compared to the control, for both horizons, and Ca, Mg, and pH were significantly greater in the control plots compared to treated plots, for both horizons (Table 3-4).

In 1994, significant differences between soil from the treated plots and the control plots were found (Table 3-4), and these changes were also evident in the soils sampled from other areas on the watershed (data not shown). The soil pH was significantly greater in the control compared to the treated soil, except for the July A horizon data. Soil Al concentrations were significantly greater in all treated soil samples collected in 1994 compared to controls. Calcium and Mg concentrations were greater in the control plots compared to treated plots (Table 3-4) while soil Mn concentrations were greater in the treated plots (Fig. 3-14). Most differences were significantly different.

Table 3-4. Soil chemistry (0.01 M $SrCl_2$ extractable) mean concentrations, from control and treated plots (Pickens 1995). Different letters within columns by months indicate statistically significant difference at $p \leq 0.05$; $n = 6$.

	O Horizon			A Horizon		
Date and plot	Al	Ca	Mg	Al	Ca	Mg
1992 July	meq $100g^{-1}$					
Control	0.018a	0.879a	0.119a	0.032a	0.522a	0.058a
Treated	0.033b	0.642b	0.084b	0.081b	0.487b	0.046b
1992 August						
Control	0.029a	0.876a	0.185a	0.022a	0.852a	0.101a
Treated	0.069b	0.519b	0.084b	0.191b	0.154b	0.033b
1993 July						
Control	0.047a	0.794a	0.144a	0.091a	0.555a	0.054a
Treated	0.212b	0.500b	0.096b	0.247b	0.296b	0.029b
1993 August						
Control	0.046a	0.802a	0.149a	0.017a	0.661a	0.069a
Treated	0.136b	0.782b	0.084b	0.188b	0.326b	0.030b
1994 July						
Control	0.010a	0.446a	0.155a	0.076a	0.430a	0.078a
Treated	0.205b	0.423b	0.066b	0.275b	0.303b	0.041b
1994 August						
Control	0.012a	0.539a	0.152a	0.015a	0.635a	0.066a
Treated	0.142b	0.443b	0.072b	0.255b	0.338b	0.028b

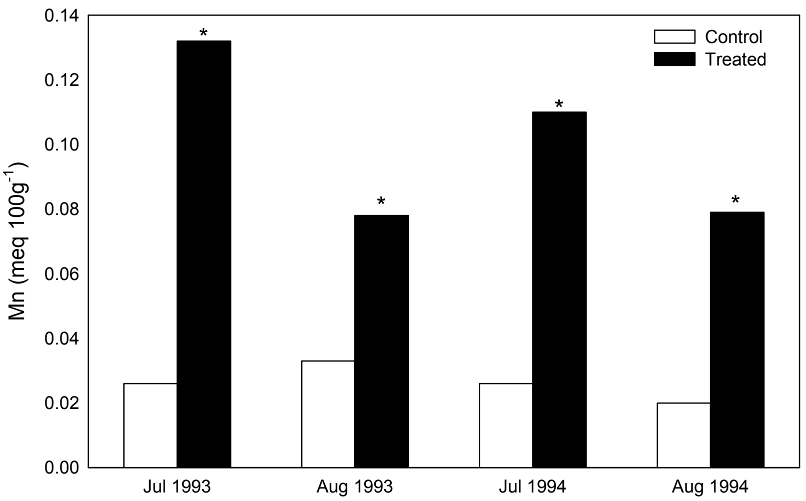

Figure 3-14. Mean $SrCl_2$ extractable Mn in the O horizon, WS9 (Pickens 1995). * indicates statistically significant differences between treatments at $\alpha < 0.05$; $n = 6$.

These results indicate significantly lower concentrations of Ca and Mg in the soil of the treatment plots relative to the control plots and also suggest that the availability of Al and Mn was increased significantly by the treatment. We hypothesize that base cation depletion of these soil horizons has occurred and Al and Mn availability have increased in response to the acidification treatment.

3.3.4 Soil N Cycling

A good deal of work has been dedicated to furthering our understanding of N cycling in the soil on these watersheds. When measuring nitrous oxide (N_2O) production from WS3 and WS4, Peterjohn et al. (1998) reported that mean monthly rates of N_2O production were consistent with measurements from other well-drained forest soils but much lower than those measured from N-rich sites with poorly drained soils. Chemoautotrophic nitrification accounted for 60% (WS3) and 40% (WS4) of total N_2O production. Production of N_2O on WS3 was constrained by low pH, while on WS4, it appeared that N_2O production was constrained by low NO_3 availability, as evidenced by extremely low N_2O production on south-facing slopes, where the lowest available NO_3 was found. The authors suggested this low NO_3 availability could be related to a distinct assemblage of woody vegetation (Christ et al. 2002). This low NO_3 availability on south-facing slopes of WS4 was also noted by Gilliam et al. (2001b) and is further evidence of high within-watershed spatial variability.

Venterea et al. (2004) measured nitric oxide (NO) emissions from plots on WS3 and WS7 in 2000-2001, and reported that on nearly every occasion that field measurements were made, mean NO emission rates were higher in plots within WS3, compared to those within WS7. Fluxes from the Fernow tended to be higher than those from Bear Brook Watersheds in Maine, but the differences were not significant. Field fluxes of NO were positively correlated with mineral soil NO_3 concentrations across all plots, suggesting that NO emissions may be a reliable indicator of NO_3 leaching potential. Decreased soil pH also provided evidence for the promotion of nitrification–derived NO production in Fernow soils.

Gilliam et al. (2001b) evaluated temporal and spatial variability in nitrogen transformations, particularly net mineralization and net nitrification on WS3 and WS4 and also on WS7. Net nitrification rates were high and were nearly 100% of net mineralization for all watersheds. Seasonal patterns of nitrification were related to soil moisture and ambient temperature in untreated watersheds. The spatial patterns in WS4 suggested that micro-environmental variability limits rates of N processing in some parts of this watershed. Spatial variability in soil N was lower in WS3, which the authors interpreted to mean that the N and S additions may have altered the responses of N-processing microbes to environmental factors, becoming less sensitive to seasonal changes in soil moisture and temperature. Additional analyses by Gilliam et al. (2001a) suggested that the nitrifying bacteria were present on these low N processing plots, but herbaceous layer vegetation, particularly ericaceous vegetation, may have inhibited the nitrifier populations.

Williard et al. (1997) also found that net nitrification rates accounted for 100% of net mineralization rates on WS4, an indication that this untreated watershed had the potential for high NO_3 leaching. In that study, WS4 had the highest net mineralization and nitrification rates and NO_3 export of nine untreated forested watersheds in the mid-Appalachians. Net mineralization and nitrification rates served as strong indicators of NO_3 export from the nine study watersheds. High soil N cycling rates were related to high exchangeable Ca concentrations (an index to soil fertility), low soil C:N ratios, and high soil moisture (Williard et al. 1997). Christ et al. (2002) reported that net nitrification potentials on WS4 and WS10 were correlated with many soil characteristics related to base cation supply, C:N ratio and water holding capacity.

4. DISCUSSION

The soil chemistry results from these watersheds provide interesting and apparently contradictory results. There are some indications of a direct soil response to the N and S additions on WS9 and WS3. For example, total N concentrations (WS3, WS9) and total S concentration (WS9) increased in the upper horizons of the soil, reflecting the elevated inputs of these two nutrients. There is also evidence that these changes have indirectly affected other processes including cycling of N, C and base cations. The increases in soil C may reflect a disruption of microbial activities. Tamm (1990) explained that the increase in N mineralization after application of high doses of acid in field experiments could depend on partial mortality of the microflora followed by mineralization of biomass N. Aber (1992, Aber et al. 1998) suggested that this was a short-term phenomenon, and that long-term increases in N mineralization were unlikely to occur, because a decrease in C mineralization following acidification should be accompanied by a corresponding decrease in net N mineralization. Persson et al. (1989) reported that, following acidification, a decrease in carbon dioxide (CO_2) evolution was caused by lesser availability of C sources rather than a direct detrimental effect on the microorganisms. An 8% decrease in CO_2 evolution from WS3 relative to WS7 observed by Mattson and Adams (unpublished data, 1992) suggests some effect on C cycling. Increases in the organic matter in the O horizon during the study also support this hypothesis. Changes in mineralization of N are often paralleled by changes in rates of net nitrification (Aber et al. 1998, Jefts et al. 2004). In this study, although we have seen no change in net N mineralization or nitrification rates, the continual additions of N may have led to an decoupling of the cycling of C and N. The acidification treatment also may have contributed to reduced decomposition rates; Adams and Angradi (1996) reported slower decomposition (mass loss) rates for leaf litter of some tree species from WS3 after 3 years of treatment, but without significant differences in nutrient loss rates.

There is some evidence to support the hypothesis that the treatment of WS3 and WS9 has accelerated base cation leaching and resulted in elevated concentrations of Al and Mn in the soil. The observed differences in mean soil properties between WS3 and WS7, for instance, are generally consistent with expectations of effects of acidification on soil properties. Exchangeable base cation concentrations, such as Ca and Mg, were lower on WS3 when compared to soil from WS7, as might be expected when excess acid anions are leached through the soil and carry base cations with them. The observed elevated Al concentrations in soil can also be expected as base cation concentrations and soil pH are reduced. On WS9, soil exchangeable Ca concentrations consistently were 1 to 2 times greater on the control plots than on the treatment plots. WS9 showed consistent differences in Ca concentrations between treated and control plots in 1993, 1994 and 1995. Mean A horizon pH on WS3 decreased slightly (from 4.48 in 1988 to 4.34 in 1994 and to 4.20 in 2002), providing further support for the hypothesis that the fertilizer treatment may be leading to soil acidification. Although we are unable to unequivocally attribute the changes that we detected to the acidification treatment, observations from various watersheds sampled at different points in time suggest common, perhaps expected, patterns of acidification effects.

However, effects were not always what we expected, nor did all data provide immediate support for our hypotheses. Although mean WS3 A horizon soil pH decreased between 1988 and 1994, mean A horizon soil pH on WS4 increased during this time period. We hypothesized decreases in soil base cation concentrations, particularly Ca and Mg, over time, although the time frame was uncertain. Such declines in mineral soil Ca and Mg levels have been documented in response to acidification elsewhere (Currie et al. 1999, Fernandez et al. 2003). However, mean mineral soil concentrations of Ca and Mg on WS3 were generally greater than on WS4, and where significant differences were detected, between 1994 and 2002 on WS3, they were *increases* in concentrations. Exchangeable Ca concentrations on WS3 in 2002 were nearly triple those observed in 1994, although a similar increase was also recorded for WS4 for the same time period. It is not likely to be a sampling artifact, e.g., due to mixing of more organic matter into the A horizon, as similar patterns were observed for the O horizon. Some of these unexpected changes may be due in part to high spatial and temporal variability within the watershed–coefficients of variation for Ca concentration within a sampling horizon and year ranged from 50% to almost 200%. This apparent contradiction may also be a function of timing of sampling. Soil water Ca concentrations collected below the A horizon peaked in 1991 (see Chapter 4), decreased through 1996, then leveled off. Thus we might hypothesize that the levels of Ca in the A horizon in 1994 could represent an already depleted state, in which case, further change would not be expected. The increases between 1994 and 2002 do not fit well with this hypothesis, however. Finally, we may believe that the observed changes in organic matter are driving the chemistry of these upper horizons, and that the acidification treatment may have altered C and N relationships significantly.

Another unexpected observation was reported by Tepp (1995) for WS3 and WS7: soil Mn levels were lower on WS3 after 7 years of fertilizer treatment than on WS7. It was hypothesized that soil Mn would increase with acidification, as was observed for WS9. One explanation for the decrease on WS3 may be that exchangeable or plant available Mn levels in soil in the early stages of treatment may have been affected by two processes: cation mobilization and soil acidification. Manganese that occurred primarily as Mn^{2+} on soil exchange sites at the initiation of treatment could have been mobilized and leached, like base cations, causing exchangeable Mn^{2+} levels to initially diminish in the solid soil phase as observed in Tepp's soil samples. This could have produced a reduction in bolewood Mn as well. As base cations were depleted and soil began to acidify, Mn also could have been gradually mobilized, similar to soil Al, and then accumulated in bolewood tissue. Tepp's (1995) sampling could have occurred during the transition from Mn depletion due to cation leaching and Mn mobilization due to soil acidification. That some tree species showed such a transition from Mn depletion to Mn increase due to acidification between 4 and 8 years of treatment, provides some support for this explanation (see Chapter 5).

5. CONCLUSION

Analyses of soil samples from WS3, WS4, WS7, and WS9 provided some support for hypotheses of soil acidification as a result of the acidification treatment, and provided some results which do not appear to support our hypotheses. Generally, the greatest differences in soil chemistry of the treated and control watersheds were observed for the O horizon, suggesting that it is the most responsive to acidification treatment. However, there was considerable variability in response among watersheds, some of which may be due to spatial and temporal variability, and not all of the results support our hypotheses of base cation depletion. Further examination of patterns of organic matter production and accumulation should be made. Changes in base cation cycling among the watersheds also may be difficult to detect, requiring more information than is available from soil sampling alone.

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Chapter 4

SOIL WATER AND STREAM WATER CHEMICAL RESPONSES

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1. INTRODUCTION

Acidification of forested watersheds by anthropogenic inputs of nitrogen (N) and sulfur (S) compounds has been a concern for many decades in North America. While it has been difficult to show changes to vegetative health or species diversity (Hendershot and Belanger 1999, Hendershot and Jones 1989), changes to stream water and soil water chemistry and acid/base status have been easier to document (DeWalle et al. 1988, Wigington et al. 1996, Herlihy et al. 1993). Many of the first studies in which both chemical and biological effects of acidification were observed were in surface waters (Corbett and Lynch 1982, Schofield 1976, Haines 1981). Changes to or complete elimination of fish and other aquatic populations due to changes in lake and stream chemistries drove much of the research and political interest in acidic deposition in the United States during the 1970s-80s (Cowling 1982). Since that time, interest in stream water and soil water chemistry has shifted to trying to make connections between solution chemistry and the buffering capacity of watershed soils and forest health (Sverdrup and Warfvinge 1993, Cronan and Grigal 1995), and defining critical loads to predict future forest condition (Arp et al. 1996, Ouimet et al. 2001, Holmberg et al. 2001).

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2. METHODS

2.1 Soil Water Sampling

Soil leachate was collected from WS3, WS4, and WS9 (Fig. 4-1) with zero-tension pan lysimeters (see DeWalle et al. 1988 for lysimeter construction details). Lysimeters were installed at the base of the A and B horizons, and when possible, the C horizon at 15 locations on WS3 and WS4 (Fig. 4-2). Average depth of the A, B, and C horizon lysimeters was 13, 79, and 119 cm, respectively. On WS9, lysimeters were installed in 12 plots (Fig. 4-3) at 45.7-cm depth, which approximates the lowest rooting depth in the catchment. Six of the lysimeter plots on WS9 were untreated controls and six served as adjacent treated pairs (Fig. 4-3).

Soil water samples were collected approximately monthly from the lysimeters. Overflow that exceeded sample bottle capacity was collected in a bucket and its volume and the volume in the bottle were determined gravimetrically, but chemical analyses were determined only on the sample collected in the bottles. On WS3, the soil was allowed to equilibrate for approximately 5 months before the first sample was collected. On WS9, 2 months of equilibration were allowed after lysimeter installation. The first gravity-drained samples were collected 1 October 1986 on WS9 and in January 1989 on WS3 and WS4. Sample collection continued until October 2002 on WS9, and it continues today on WS3 and WS4. Lysimeter samples were not collected from October 1994 through January 1996 on WS9 and from June 1993 through December 1995 on WS3 and WS4 due to budget constraints.

2.2 Stream Water Sampling

Stream water was grab-sampled from WS3, WS4, and WS9 weekly from a fixed location near the mouth of each watershed (Figs. 4-2 and 4-3). This set of routinely collected samples (i.e., routines) includes chemistries influenced by baseflow as well as various stages of stormflow. From the routine data set from each watershed, the chemistries of all of the samples that were not from any portion of a storm hydrograph were placed into a separate data set for analysis (i.e., baseflow).

Stormflow samples from discrete runoff events also were collected from 1988-1995 for WS3 and from 1987-1997 in WS4 and WS9 using automatic pumping samplers on pre-set time intervals; however, there were no storms sampled in 1996 and only one in 1997. Storms that were sampled tended to be moderate to large in size, with a few smaller ones included when possible.

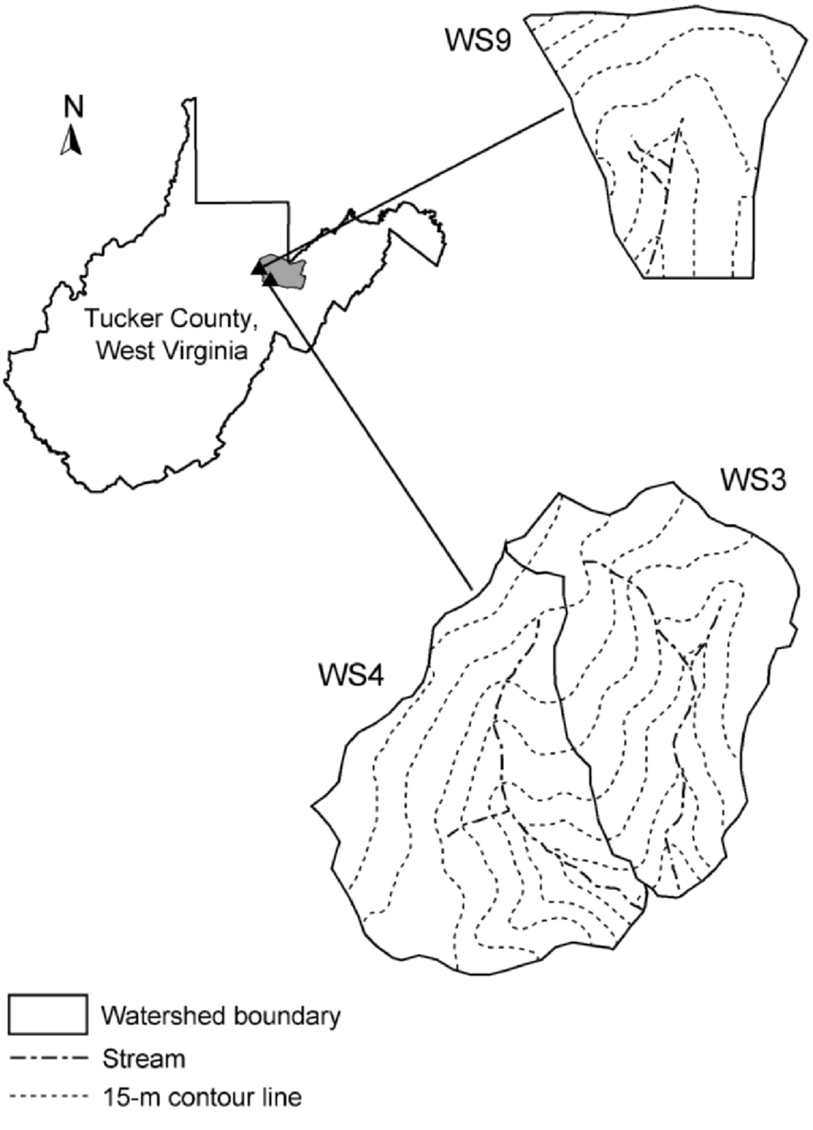

Figure 4-1. Locations and topographic conditions of WS3, WS4, and WS9.

Larger storms were focused on because smaller events often did not result in measurable flow or chemical changes. The overall average peakflows for the sampled events for each watershed were in the largest 10 percent of the storms for the years sampled, but the minimum peakflows sampled were as low as the 1 percent quantile for those years (Edwards et al. 2002).

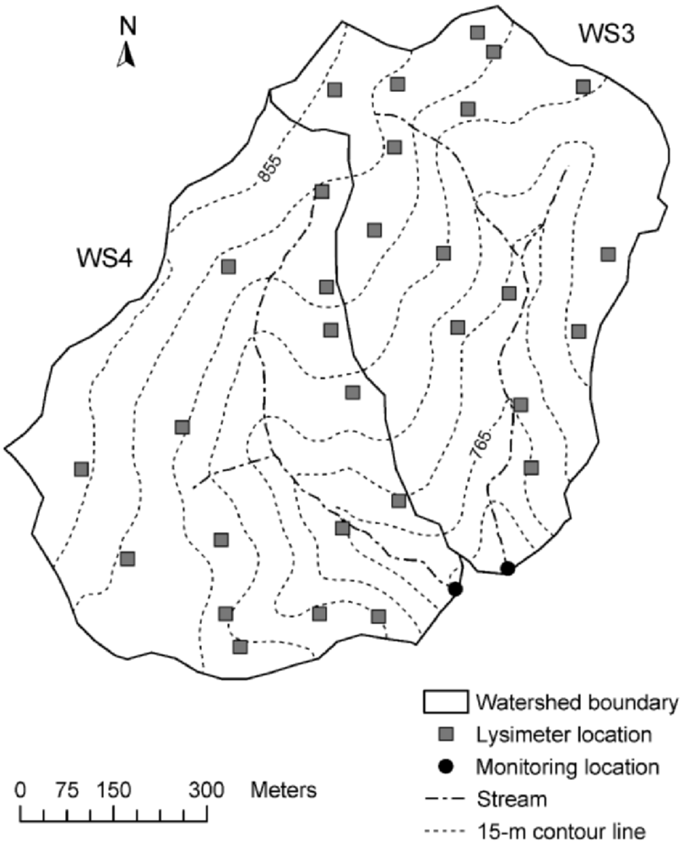

Figure 4-2. Lysimeter locations on WS3 (treatment) and WS4 (control).

Samplers typically were actuated manually because manual actuation provides more reliable sampling along the entire hydrograph than stage actuation in these flashy headwater streams. Growing season samples (May-October) were collected at approximately 15-minute intervals on the rising limb of the hydrograph and for at least several samples after peakflow. Dormant season samples were collected on 30- or 60-minute intervals on the hydrograph rising limb and for several samples after peakflow. Longer time intervals were used in the dormant season because the hydrologic responses are longer because soil moisture deficits are negligible or absent.

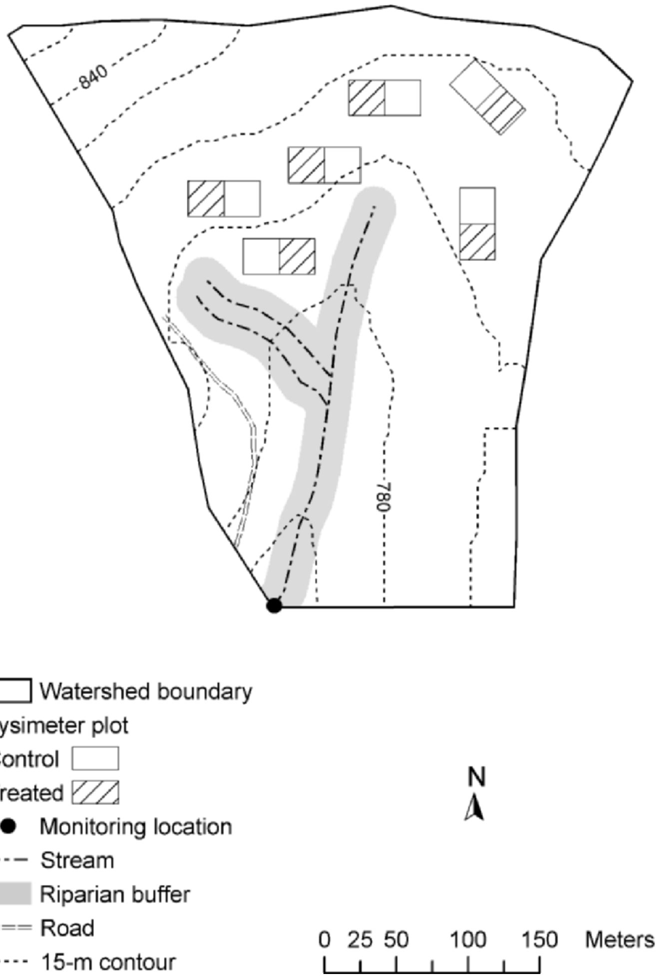

Figure 4-3. Treatment and control plot lysimeter locations in WS9.

From the stormflow data set, the chemistries of the sample collected nearest to the peakflow for each storm in each watershed was extracted and placed in a third data set (i.e., peakflow). These data represent samples that are generally the most chemically different from baseflow, as observation and analysis by Edwards et al. (2001) show. The greatest concentrations of all analytes except nitrate (NO_3) and pH occur near the time of peakflow. Nitrate is less consistent and can occur slightly before peakflow, but usually tends to occur several hours after peakflow, presumably because, to some degree, its behavior is controlled by biological reactions (Edwards et al. 2001). However, the differences in NO_3 concentrations between the actual maximum of NO_3 and those at peakflow are small. By contrast, pH reaches its minimum in-storm value near peakflow.

2.3 Chemical Analyses

Chemistry for the routine, baseflow, and peakflow stream water samples, and soil leachate samples was determined at the USDA Forest Service, Northeastern Research Station's Timber and Watershed Laboratory in Parsons, West Virginia using EPA-approved protocols. Samples were analyzed for calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), sulfate (SO_4), NO_3, chloride (Cl), and pH. Sample handling, processing, and analytical techniques are detailed in Edwards and Wood (1993). Due to budget constraints, analyses for total dissolved aluminum (Al) were performed only rarely for soil water samples collected from WS9; Al was not analyzed for any water samples collected from WS3 or WS4. Pretreatment samples were collected on 30 October, 14 November, and 10 December 1986 from the zero-tension pan lysimeters and analyzed at a water quality laboratory formerly operated by the USDA Forest Service, Northeastern Forest Experiment Station in Berea, Kentucky. Samples also were collected from the pan lysimeters on 13 August 1992, 4 January 1993, and 18 February 1993 to examine Al responses after a number of years of treatment. These samples were analyzed at The Pennsylvania State University's Environmental Resources Research Institute water quality laboratory. As part of another small study done in conjunction with the acidification study on WS9, a limited number of Al analyses were made for soil water samples collected in tension lysimeters located at 10-cm depth during 1992-1994. Foliar samples also were collected from WS9 as part of that smaller study and analyzed for total Al (Pickens 1995). These samples were analyzed at The Pennsylvania State University Agricultural Analytical Services Laboratory (Dahlquist and Knoll 1978).

Acid neutralizing capacity (ANC) was calculated as the difference in concentrations (μeq L^{-1}) between the sum of the mineral bases (Ca, Mg, Na, and K) and the sum of the mineral acids (SO_4, NO_3, and Cl). If ANC is negative the solution has a strong acid acidity (Reuss and Johnson 1986) and these mineral acids are supporting or counterbalancing hydrogen (H^+) ions or Al species (Baker et al. 1990). If the ANC is positive, the solution has net mineral base or alkalinity, and all or some of the H^+ ions are being countered by other anions, such as bicarbonate and organic anions (Rustad et al. 1993).

2.4 Data Analyses

To account for differences in dilution or concentration of soil water chemistry that could be caused simply by different catch volumes, volume-weighted mean concentrations by horizon were determined for WS3 and WS4, and for the control plot lysimeters and treatment plot lysimeters on WS9. These were calculated by multiplying the concentration for each sample by its corresponding volume. The volume was the sum of the lysimeter sample plus any overflow, if overflow existed in the bucket. Overflow was recorded as 16,148 ml if the bucket volume was overflowing, which was the maximum volume the buckets could hold with bottle displacement. Then for each date and by horizon, the concentration x volume results were summed and divided by the sum of the volumes, which yielded volume-weighted mean concentrations. Because pH is logarithmic and averages should not be calculated directly, H^+ concentration was determined from each pH, and mean volume-weighted concentrations were determined from the H^+ values. These values then were converted back to average pH values.

No flow-adjusting (i.e., to account for concentration or dilution effects) was performed for stream water samples collected. There were several reasons for not flow-adjusting. The typical way to adjust for flows for stream water is to do volume-weighted averaging. However, because only one sample was available per watershed per sampling date (vs. 15 per horizon per watershed for soil leachate) determining volume-weighted averages would result in reducing display of the data and the sample sizes for statistical analyses by at least 75 percent (e.g., four samples per week for routines reduced to one volume-weighted average per month). Furthermore, there was no real way to determine volume-weighted averages on just the peakflow chemistries; volume-weighted averages would have required considering every point collected during the storm and the result would not have been representative of the most episodic response during each storm. Flow-adjusting for stream water samples could have been done by plotting the concentrations against streamflow at the time the sample was collected and then using the time series of the residuals to display treatment responses (Helsel and Hirsch 2000, Hipel and McLeod 1994). However, by this method, there is no way to ascertain quantitatively how much the chemistry changed over time because the units of the residuals are not meaningful. But analysis of the relationships between the concentrations and flows indicated that no or only very weak relationships existed for most analytes. And even for the analytes that had the strongest relationships, predominantly pH, as well as SO_4 and NO_3 to a much lesser extent, there was little need to flow-adjust because the trend lines applied to flow-adjusted and unadjusted data showed essentially the same patterns and timing of responses. Consequently, to preserve the ability to consider the responses in concentration units we are using the original data without adjusting for streamflow.

The volume-weighted mean soil water concentrations and the stream water (routines, baseflow, and peakflow) concentrations of each ion were graphed against time, and a locally weighted regression line (Cleveland and Devlin 1988) was fitted through the data using Locfit software (Loader 1998) to aid in showing trends (Hipel and McLeod 1994). Locally weighted regression does not provide regression coefficients, but it does display data trends (especially non-monotonic trends) very effectively without the assumptions or limitations of predefined equation forms (i.e., linear, quadratic, cubic, etc.) that accompany least squares regression. Locally weighted regression also is appropriate for irregularly spaced nonparametric time-series data, which describe many of the data in this study.

To avoid oversmoothing the trend lines, various combinations of fitting degrees and smoothing values were applied to each ion vs. time data set. Then residuals were determined for each data point and were plotted against time. A locally weighted regression line developed using the same fitted degrees and smoothing values as for the original data was overlaid on the plotted residuals data. The degree of fit and smoothing values were considered appropriate when the latter locally weighted regression line was essentially flat using the lowest possible smoothing value (Cleveland 1994).

Mann-Kendall tests (Mann 1945) were used to determine whether the volume-weighted mean soil water concentrations or the stream water concentrations increased or decreased significantly over time (probability ≤ 0.05). These tests were performed on the concentrations and not the trend lines since locally weighted regression does not provide estimates of regression coefficients to test for significance. Because Mann-Kendall tests can determine the significance of only monotonic data trends, where the trend lines changed direction (indicating a change in the direction of the concentrations) a separate Mann-Kendall test statistic was calculated for the data on both sides of that change as recommended by Hipel and McLeod (1994). Sen-slope estimates (Sen 1968) were calculated to identify the direction (i.e., positive or negative) of the data trends, since these were not always obvious where the data were quite variable or where the change was small.

3. SOIL WATER

3.1 WS4 and WS3 Responses

The concentrations of many ions in soil water on WS4 changed significantly during at least some portion of the period of record, and the concentration of most ions decreased over the entire 15 year period (Table 4-1). Nitrate and the major base cations, Ca, Mg, and K, experienced the most consistent decreases in soil water concentrations in terms of both time and horizon (Fig. 4-4a and 4-4b). Sodium decreased during the initial half of the period of record and then increased resulting in little net change in concentrations over time. Sulfate decreased significantly in the A horizon, did not change in the B horizon and increased significantly through 1996 in the C horizon then did not change through 2003. The only constituent to increase significantly throughout the entire 15 years was pH in the A horizon (Table 4-1, Fig. 4-4b). ANC on WS4 was negative at the start of the study (Fig. 4-5), but it remained fairly constant in all horizons throughout the study, though in the C horizon there was a borderline, but significant decrease in ANC ($\alpha = 0.05$), probably resulting from the combination of increasing SO_4 and decreasing base cations.

While WS4 was not treated with ammonium sulfate fertilizer, it has received high levels of ambient acidic deposition over at least the last several decades (Council on Environmental Quality 1989, National Atmospheric Deposition Program 2000). But, because of implementation of the Clean Air Act Amendments, emissions and resulting deposition of NO_3, SO_4, and base cations have decreased slightly (Hedin et al. 1994, and see Chapter 7). Some of the decrease in NO_3 observed in soil water on WS4 is believed to be attributable to the NO_3 decreases in deposition. The base cation decreases could be from decreases in base cations in atmospheric deposition from new scrubber technologies (Hedin et al. 1994), or they could indicate base cation depletion over the long-term in ambient acidic deposition. The different responses to SO_4 with depth may have occurred simply because there was a lag in the time required for it to move deep into the soil; initially decreased deposition is showing only in A horizon soil water and will not occur for sometime in the lower soil horizons. The increasing concentrations in the C horizon reflect the accumulation of SO_4 ions leached from above under periods of higher deposition.

The ammonium sulfate treatments on WS3 had significant effects on many of the soil water ions (Table 4-1). Of the four base cations, Ca was affected the most. Calcium concentrations in A horizon soil water of WS3 increased steadily and significantly (Table 4-1) for approximately 3.5 years after the initiation of acidification (Fig. 4-4a) in response to increasing anion

Table 4-1. Mann-Kendall and Sen slope results for soil water from WS4 and WS3, by horizon.

		WS4			WS3		
Ion	Horizon	Period	Mann-Kendall probability	Sen slope	Period	Mann-Kendall probability	Sen slope
Ca	A	1989-2003	0.000	-2.88	1989-10/1992	0.032	29.98
					11/1992-5/1998	0.006	-20.71
					6/1998-2003	0.252	-4.78
	B	1989-2003	0.000	-7.57	1989-10/1992	0.039	17.63
					11/1992-2003	0.032	-5.41
	C	1989-2003	0.000	-5.23	1989-7/1996	0.000	22.30
					8/1996-2003	0.000	-17.46
Mg	A	1989-2003	0.000	-1.28	1989-2003	0.000	-1.28
	B	1989-2003	0.000	-2.30	1989-10/1992	0.234	1.90
					11/1992-2003	0.061	-1.23
	C	1989-2003	0.000	-2.74	1989-7/1996	0.000	8.17
					8/1996-2003	0.003	-6.86
Na	A	1989-7/1996	0.909	-0.01	1989-2003	0.500	-0.03
		8/1996-2003	0.000	0.38			
	B	1989-7/1996	0.000	-0.50	1989-2003	0.002	0.13
		8/1996-2003	0.000	0.39			
	C	1989-7/1996	0.000	-0.34	1989-2003	0.648	-0.03
		8/1996-2003	0.000	0.42			
K	A	1989-2003	0.000	-1.10	1989-8/1994	0.472	-1.59
					9/1994-3/2000	0.002	7.66
					4/2000-2003	0.023	-12.12
	B	1989-2003	0.000	-0.33	1989-5/1998	0.005	-0.76
					6/1998-2003	0.086	-1.12
	C	1989-8/1994	0.042	-3.47	1989-7/1996	0.650	-0.20
		9/1994-2003	0.756	-0.17	8/1996-2003	0.001	-2.58
SO_4	A	1989-2003	0.000	-4.65	1989-10/1992	0.000	88.39
					11/1992-2003	0.599	-2.78
	B	1989-2003	0.077	-0.96	1989-7/1996	0.000	31.65
					8/1996-2003	0.685	-2.08
	C	1989-7/1996	0.001	8.33	1989-7/1996	0.000	35.83
		8/1996-2003	0.077	-8.29	8/1996-2003	0.002	-8.82
NO_3	A	1989-2003	0.015	-2.96	1989-3/2000	0.000	17.50
					4/2000-2003	0.149	-33.34
	B	1989-2003	0.000	-7.77	1989-3/2000	0.000	28.47
					4/2000-2003	0.537	-21.76
	C	1989-2003	0.000	-5.96	1989-3/2000	0.000	31.94
					4/2000-2003	0.115	18.73
Cl	A	1989-2003	0.063	-0.16	1989-2003	0.005	0.47
	B	1989-2003	0.001	-0.29	1989-7/1996	0.000	0.91
					8/1996-2003	0.001	-1.71
	C	1989-7/1996	0.058	-0.43	1989-7/1996	0.088	0.76
		8/1996-2003	0.120	-0.99	8/1996-2003	0.000	-1.28
pH	A	1989-2003	0.010	0.01	1989-2003	0.000	-0.01
	B	1989-2003	0.227	0.00	1989-2003	0.000	-0.01
	C	1989-12/1992	0.001	-0.08	1989-2003	0.000	-0.01
		1/1993-2003	0.054	0.01			
ANC	A	1989-2003	0.311	0.77	1989-1994	0.000	-74.78
					1995-2003	0.080	-13.21
	B	1989-2003	1.000	-0.00	1989-1997	0.000	-48.14
					1998-2003	0.455	10.19
	C	1989-2003	0.043	-1.63	1989-1997	0.000	-30.51
					1998-2003	0.037	20.16

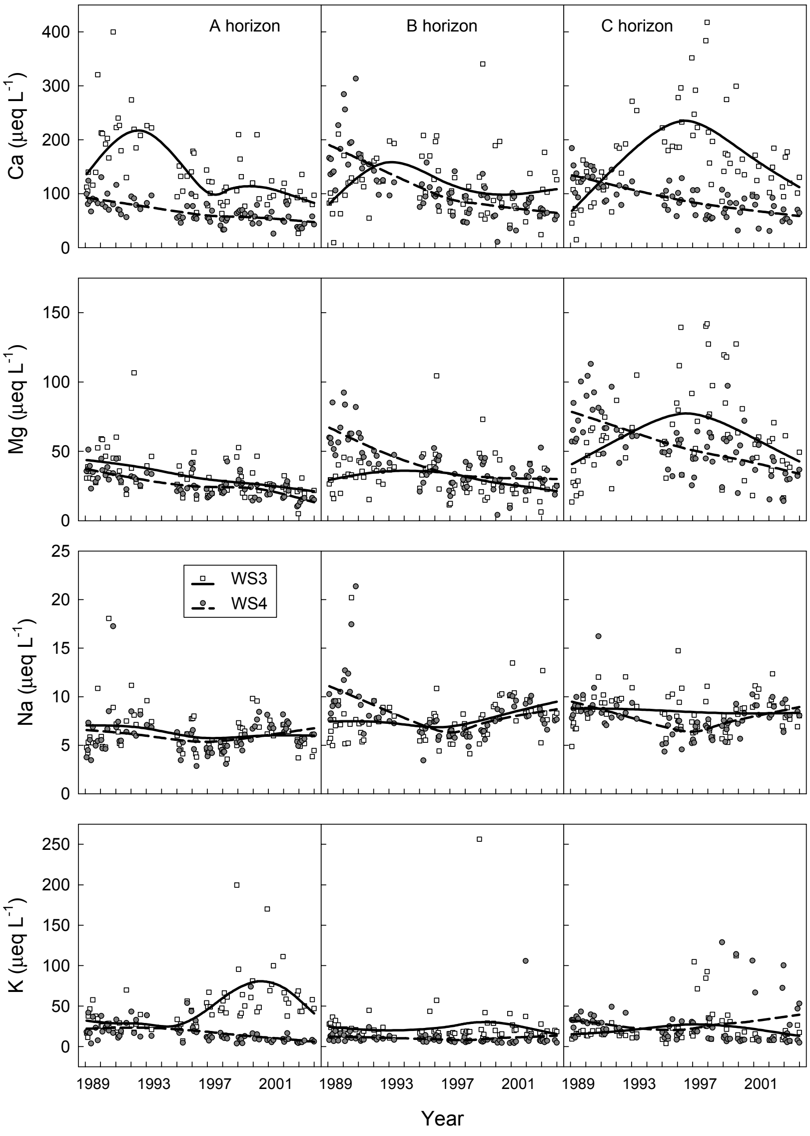

Figure 4-4a. Volume-weighted average chemical concentrations for soil water from WS3 and WS4 with trend lines overlaid, by horizon.

concentrations (Fig. 4-4b). The trend line for the A horizon peaked in approximately 1992, at a concentration slightly greater than 200 μeq L^{-1}, though a few individual concentrations increased to much greater

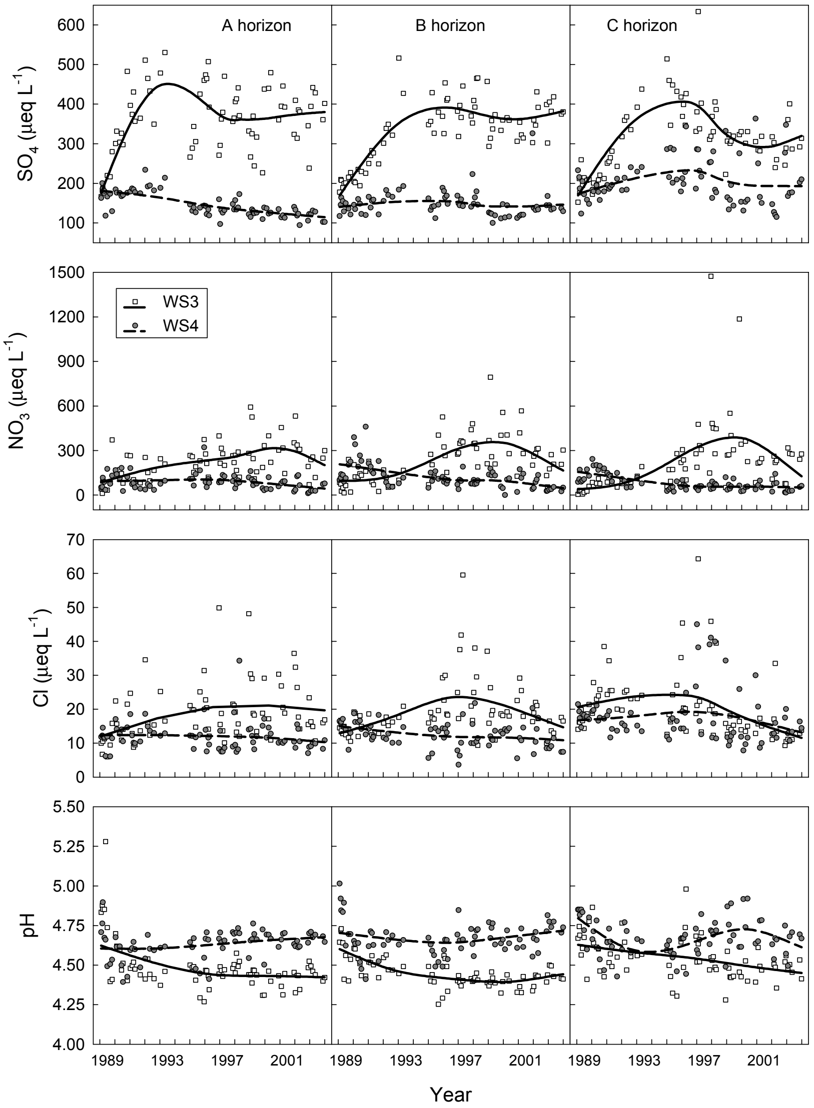

Figure 4-4b. Volume-weighted average chemical concentrations for soil water from WS3 and WS4 with trend lines overlaid, by horizon.

concentrations than 200 µeq L^{-1}. The trend line then decreased significantly through about 1996 and then leveled off (Table 4-1, Fig. 4-4a) and concentrations have returned to approximately those observed just at the initiation of treatment (~100 µeq L^{-1}) in 1989 (Fig. 4-4a).

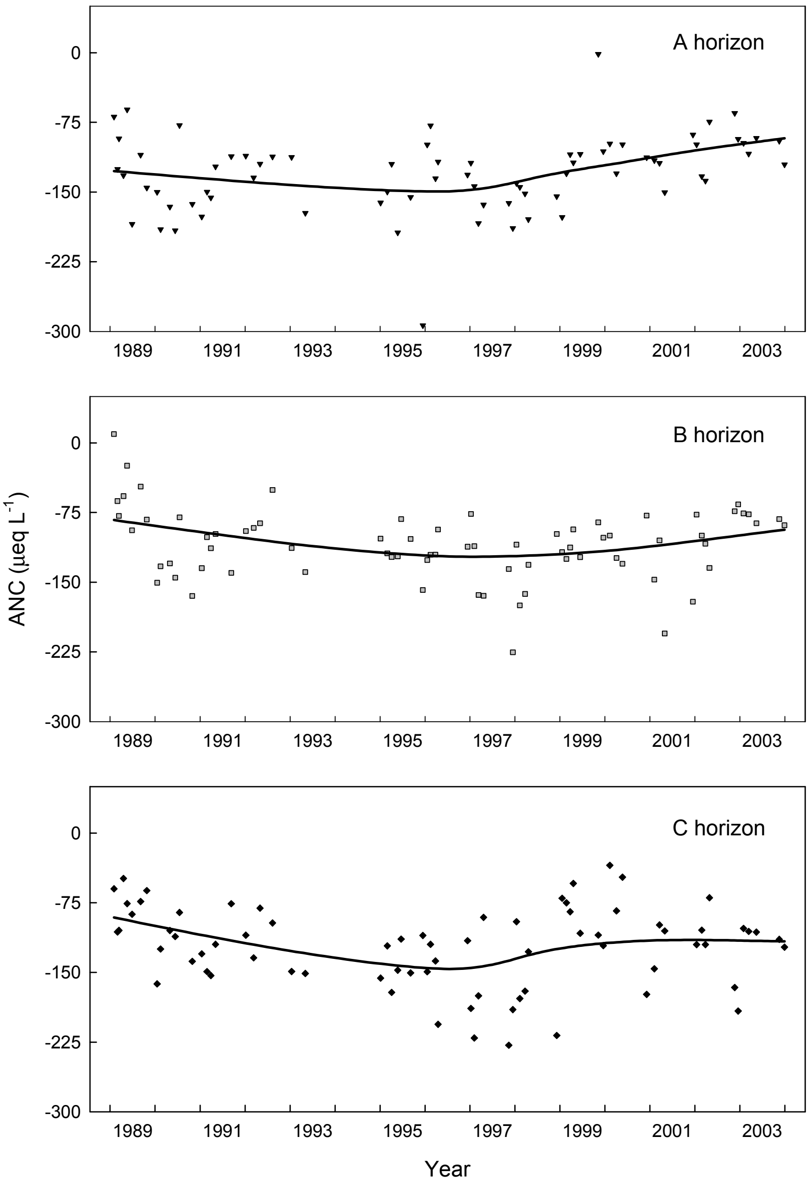

Figure 4-5. ANC for soil water by horizon for WS4.

Calcium concentrations in soil water from the B and C horizons of WS3 increased significantly in response to treatment (Table 4-1, Fig. 4-4a). In the

B horizon the increases lasted only about 3.5 years – the same duration as in the A horizon – compared to 7 years in the C horizon. Calcium concentrations in B horizon soil water essentially returned to pretreatment levels by 1996-97, whereas in the C horizon by 2003 they still were above the 1989 Ca concentrations (Fig. 4-4a).

Magnesium concentrations in A horizon soil water were only about 50 µeq L^{-1} at the beginning of the study (Fig. 4-4a), and they decreased steadily and significantly (Table 4-1) throughout the entire study period, ending at approximately 25 µeq L^{-1}. Throughout the 15 years of record, Mg concentrations in WS3 soil water were very similar to those in untreated WS4 (Fig. 4-4a). The inability of Mg to increase with increasing anion concentrations (Fig. 4-4b) indicates that reserves of exchangeable Mg were not present in WS3, even before the acidification treatments were initiated. Soil chemistry data from WS3 indicate substantially lower Mg concentrations than Ca or K from 0-10 cm depth (Adams and Kochenderfer 1999).

The trend line for Mg soil water concentrations in the B horizon suggests a slight increase in concentrations through 1992 followed by a slight decrease after 1992 (Fig. 4-4a). However, statistical analyses do not indicate a significant change during either of these two periods (Table 4-1).

Changes to Mg in the C horizon were much greater than in the A or B horizons (Fig. 4-4a), and there was a significant increase from 1989-1996 (Table 4-1) in response to the increasing availability of acid anions in soil solution during that time period (Fig. 4-4b). From 1996-2003 there was a significant decrease in Mg concentrations (Table 4-1, Fig. 4-4a), but concentrations did not return to pretreatment levels by 2003. The trend line indicates that Mg concentrations generally increased about 80 µeq L^{-1} above 1989 levels. However, several of the volume-weighted means increased much more than that and had values between 100 and 150 µeq L^{-1} (Fig. 4-4a).

Sodium concentrations in A horizon soil solution did not respond to the treatment (Table 4-1). Sodium concentrations were quite low compared to any of the other base cations, with most of the sample concentrations below 10 µeq L^{-1} (Fig. 4-4a). The lack of or very small responses by Na in any of the lysimeters on WS3 is not surprising given that it is present in low concentrations in these soils (Chapter 3). The area receives negligible inputs of Na from sea salt because of its distance from the Atlantic Ocean and the predominant westerly and northwesterly wind current, and it receives only low concentrations and small loads annually from atmospheric sources (National Atmospheric Deposition Program 2000).

There was no significant response in K concentrations in A horizon soil water for approximately 6 years (Table 4-1), but by the end of 1994, the trend line increased in response to treatment (Fig. 4-4a) and K concentrations increased significantly through 2000 (Table 4-1). The trend line shows concentrations generally increased from approximately 30 μeq L^{-1} to 80 μeq L^{-1}. From the end of 2000 through the period of record, K concentrations again declined significantly (Table 4-1) to levels approximately equal to those at the beginning of the study (Fig. 4-4a).

Normally, monovalent cations, such as K, are exchanged into soil solution more easily than divalent cations, such as Ca, which would suggest that K should have become mobilized in A horizon soil solution at least as early as Ca. While K exchange can be delayed by strong adsorption on certain types of 2:1 layer silicates (Bohn et al. 1985), the soils on all of the study watersheds contain 1:1 not 2:1 layer silicates. Thus, the cause of the 6-year delay in exchange of K in the A horizon is not known.

Potassium concentrations changed much less over time in B and C horizon soil water than in A horizon soil water (Fig. 4-4a). Even though the trend line from 1989-1998 suggests a slight increase in B horizon soil water concentrations (Fig. 4-4a), the Mann-Kendall results indicate that the concentrations actually decreased significantly during that period (Table 4-1). This discrepancy is primarily due to the large number of clustered concentrations that were just slightly greater than other subsequent values at the very beginning of data collection. Because these values were clustered over such a short period of time, the number of observations had a much greater effect on the Mann-Kendall results than they had on the locally weighted regression line. There were no significant changes after 1998 (Table 4-1). In the C horizon, K concentrations did not change significantly from 1989-1996, but they decreased after 1996 (Table 4-1, Fig. 4-4a). However, the net change in K concentrations in soil water in the B and C horizons between 1989 and 2003 was very small (Fig. 4-4a).

The base cation concentrations observed for WS3 can be interpreted in terms of a conceptual model described by Fernandez et al. (2003) for soil water and stream water. In this model, seven states of base cation availability or depletion are described in terms of elevated or declining levels of N and S inputs to soils. Stage I describes concentrations of base cations in equilibrium with existing conditions, so concentrations are essentially constant over time. During Stage II, N and S inputs increase and are accompanied by increases in exchangeable base cations in solution to counterbalance the negative charges of increasing acid anion concentrations (i.e., NO_3 and SO_4). Base cation concentrations continue to increase until soil exchangeable base cations begin to become depleted, and they can no longer counterbalance the levels of acid anions they once could. At that point Stage III is entered, and base cation concentrations begin declining until they return to approximately the same concentrations that were present before N and S loads were elevated (i.e., in Stage I). In Stage IV, base cation concentrations remain approximately constant at that initial equilibrium concentration, during which base cation exchange to soil solution is in equilibrium with mineral weathering. Because base cations no longer provide the dominant source of buffering, in Stage IV, Al predominantly replaces base cations in counterbalancing the negative charges of mobile acid anions. Stage V is entered at the time where excess N and S loadings decline or cease, and is marked by decreasing concentrations of base cations below levels that were observed in Stage I. During this time, soil exchangeable pools of base cations are recovering, which causes the concentrations to decrease. In Stage VI cation soil exchange pools become replenished to the level at which base cations can now be exchanged and enter soil solution at an increasing level; thus, base cation concentrations in soil water increase in Stage VI. Eventually, concentrations return to equilibrium, where mineralization inputs control exchange of base cations. At this point, the system is in Stage VII until another alteration to acid inputs occurs. It is clear from the different responses and timing of responses of base cations in Figure 4-4a that the base cations were in different states of cation availability or deficiency through time as well as across horizons.

The inputs of N and S at known elevated levels on WS3 make the evaluation of the base cation responses fairly easy to interpret in terms of the base cation model. Available Ca was present on exchange sites in all horizons so Stage II was entered immediately in response to the acidification treatments in all three soil horizons (Fig. 4-4a). Initial signs of increasing depletion of Ca, or the start of Stage III occurred in the A and B horizons about 4 years after the start of increased N and S inputs. In the C horizon, Stage II lasted about 8 years for Ca. In the A and B horizons, Stage III lasted about 4-5 years. Mineralization has controlled exchangeable Ca (Stage IV) since about 1997 in the A horizon and since about 1998 in the B horizon. The C horizon is still in Stage III, but concentrations in soil solution are approaching those prior to treatment. At its current rate of decline (Fig. 4-4a), Stage IV will be reached in approximately 2007.

Since Mg concentrations in soil water from the A horizon decreased significantly through the entire period of N and S applications, the supply of exchangeable Mg already was largely depleted before the study began meaning the A horizon was in Stage III at the beginning of the study (Fig. 4-4a). Given that A horizon concentrations of Mg have continued to decrease, it appears that the A horizon remained in Stage III through 2003. This region has received some of the highest levels of pollutant inputs of N and S for decades (Council on Environmental Quality 1989, National Atmospheric Deposition Program 2000), which accelerated depletion of Mg reserves on soil exchange sites, particularly since Mg concentrations in these soils are very low compared to Ca (Chapter 3) and Mg is removed more easily than Ca from soil colloids (Bohn et al. 1985). The general lack of change in WS3 Mg concentrations in the B horizon (Table 4-1), suggests that Mg depletion already had occurred, and the B horizon was in Stage IV, where mineralization is controlling exchangeable Mg concentrations.

The greatest Mg response to the acidification occurred in the C horizon (Fig. 4-4a). Mg was not deficient at the beginning of the study in the C horizon presumably because the C horizon acted as a receptor for some of the Mg ions that had been leached from the overlaying A and B horizons. The fertilizer applications induced an increase in Mg exchange and charge pairing (Stage II) through approximately the end of 1995, at which time Stage III was entered and continued through 2003.

The base cation depletion model includes a lag in base cation exchange (Stage II) in relation to the timing of elevated N and S loadings; thus, K follows the graphical depiction of the model as it is presented in Fernandez et al. (2003). Average K concentrations in the 0-10 cm soil depth, which corresponds approximately to the A horizon, were about double the Mg concentrations in 1994 (Adams and Kochenderfer 1999), which explains the substantial differences in responses over time between K and Mg (Fig. 4-4a). By 2003, the A horizon was in Stage III with respect to K concentrations. In the B and C horizons, the very small changes in K trend lines in WS3 (Fig. 4-4a) and the very small Sen slopes that were present even when the concentration changes were significant (Table 4-1), make it difficult to determine whether these horizons are nearing the very end of Stage III or have entered Stage IV. Either way, the level of neutralization of acid anions by K in either the B or the C horizon was small throughout the study.

In all three horizons, SO_4 concentrations increased immediately and significantly in response to treatment on WS3 (Table 4-1, Fig. 4-4b). The increase was expected since SO_4 is the principal ion in the applied fertilizer, and SO_4 is not normally limiting in forest soils (Reuss and Johnson 1986). However, within 5 to 7 years after the initiation of ammonium sulfate applications (depending on the horizon), SO_4 concentrations essentially leveled off (Table 4-1, Fig. 4-4b), indicating that SO_4 was being retained in all of the soil horizons. Interestingly, the change in SO_4 responses occurred when the concentrations reached similar values in all three horizons and when the absolute maximum concentration reached approximately 500 μeq L^{-1} (Fig. 4-4b).

It is unlikely that increased biotic assimilation of SO_4 was important in controlling SO_4 mobilization, as S rarely is limiting to plant growth, particularly in this region that receives high levels of atmospheric S deposition (National Atmospheric Deposition Program 2000). More likely, adsorption and/or precipitation of SO_4 minerals would explain the retention of SO_4. Adsorption would be enhanced if soils in WS3 had pH-dependent charge. Anion adsorption on pH-dependent exchange sites increases as pH decreases and occurs predominantly in kaolinitic (1:1) soils (Bohn et al. 1985). The pH in WS3 soil solution decreased significantly over time in all the soil horizons, reaching between 4.25 and 4.5 during the time that SO_4 retention occurred (Fig. 4-4b), and the soils are kaolinitic, making it highly likely that some pH-dependent adsorption occurred. Whether precipitation of SO_4 minerals was a factor in SO_4 retention is unknown, as there is disagreement as to how low soil pH has to be before precipitation becomes important (e.g., Neary et al. 1987, Plumlee et al. 1995, Reuss and Johnson 1986).

The very similar shapes and timing of upturns and downturns of the trend lines for Ca and SO_4 (Fig. 4-4a and 4-4b) suggest that the mobility of Ca was controlled by SO_4 mobility. And indeed, cooperative adsorption or co-adsorption of SO_4 and base cations has been reported in the literature (Marcano-Martinez and McBride 1989, Mitchell et al. 1992, Sumner 1990). However, an analysis of the relationship between concentrations of Ca and SO_4 show little stoichiometric dependency of Ca on SO_4 (Fig. 4-6), with the exception of the C horizon. Thus, the similarities between the two are mostly coincidental, and Ca is controlled predominantly by the exchange processes described earlier. These processes obviously involve SO_4 since it is an acid anion, but Ca responses, particularly during Stages III and IV were clearly controlled by the availability of Ca on exchange sites and its progressive depletion, not by the cessation of increasing SO_4 concentrations.

The other major anion that increased in soil water from the acidification treatments was NO_3. Nitrogen inputs from the fertilizer were as ammonium (NH_4), but Gilliam et al. (1996) reported the vast majority of applied NH_4 on WS3 is nitrified rapidly to NO_3 so that soil water NH_4 concentrations were very small and typically below detection limits throughout most of the study in all soil horizons (Fig. 4-7).

Nitrate concentrations in soil water of all three horizons increased significantly for 11-12 years (Table 4-1). Following that period, the trend line suggests a decrease in NO_3 (Fig. 4-4b), but the Mann-Kendall tests indicate no statistical change from 2000-2003 (Table 4-1). The discontinuation of rising NO_3 concentrations was unexpected, particularly at this late point in the study, because ammonium sulfate was applied during every year of the study. As with SO_4, some type of NO_3 retention or conversion to another chemical species must have occurred.

Retention of NO_3 (though likely as some other form of N) may have occurred but none of the reported processes as currently understood can fully explain the retention of NO_3. An onset of nonspecific adsorption of NO_3 is improbable because SO_4 was readily available and would have been preferentially adsorbed over NO_3. Inducement of biotic NO_3 assimilation by vegetation or microorganisms would have been unlikely at this late time in the stand's age. Additionally, if the watershed soils were N deficient, NO_3 retention by tree assimilation or microorganisms would have occurred and been evident when the fertilizer applications were begun (Aber et al. 1998).

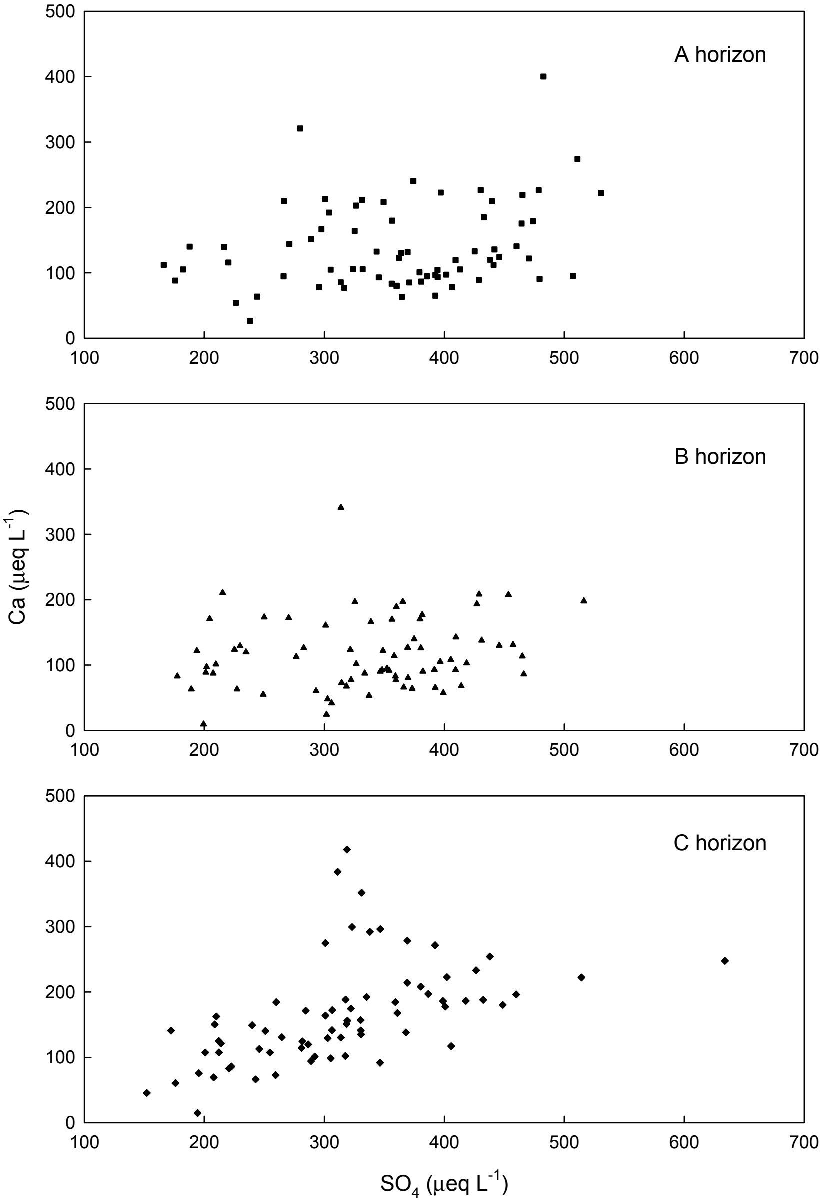

Figure 4-6. Relationships between Ca and SO$_4$ concentrations in soil water from WS3, by horizon.

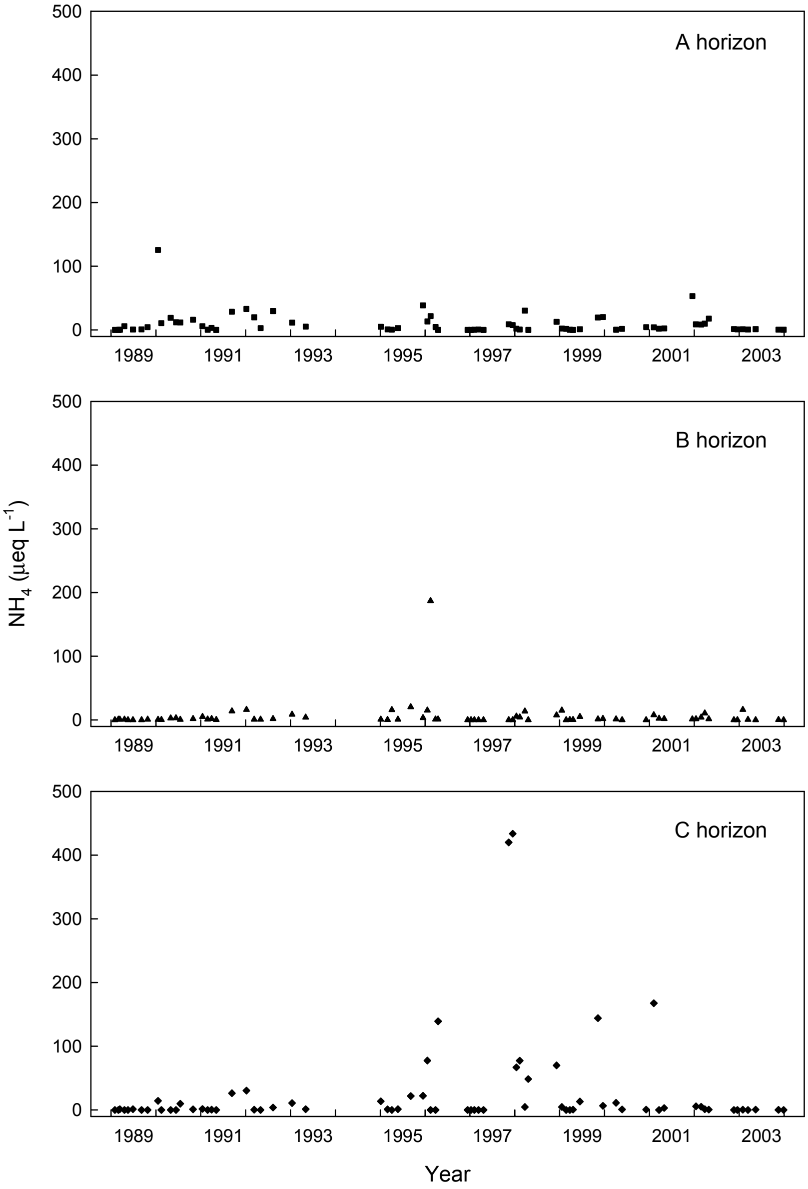

Figure 4-7. Volume-weighted average NH_4 concentrations in WS3 soil leachate, by horizon.

The delayed inducement of large levels of biotic immobilization simply by providing more NO_3 to the soil is contrary to current understanding of nutrient demands. Likewise, N retention through biotic immobilization by mycorrhizae (Aber 1998) also should have been demonstrated earlier rather than later in this study and not below the A horizon. Abiotic immobilization of NH_4 and nitrite (NO_2) in soil organic matter (Fitzhugh et al. 2003, Berntson and Aber 2000, Dail et al. 2001) would have been unlikely in the deeper B and C horizons where organic matter composed <6 percent of the soil (see Chapter 3). Soil conditions, such as high concentrations of organic matter, reducing conditions, or basic soil pH to support some of the more contemporary proposals or theories of abiotic NO_3 retention as green rusts (Hansen et al. 1996, 2001), or by iron (Fe) and possibly manganese (Mn) catalysts (Davidson et al. 2003, Kaiser et al. 1996, Currie et al. 1996) also are not believed to be present broadly or with depth across WS3. It also is possible that abiotic transformations of NO_3 to dissolved organic nitrogen (DON) occurred, but DON was not measured in this study. However, because a large percentage of available DON tends to be retained rather than exported from forested watersheds on an annual basis (Davidson et al. 2003), DON retention may have been an important N-controlling mechanism on WS3. Clearly, the N-retention mechanisms that developed over time on WS3 are not understood, and they do not fit into the current understanding of N saturation theory as presented by Aber et al. (1998).

Chloride is an acid anion, but was present in soil water in significantly lower concentrations than NO_3 or SO_4. Like Na, atmospheric inputs of Cl by sea salts are not high in this region. However, the dissimilar Cl responses on WS3 and WS4 suggest that the Cl increases in the A horizon and in the B horizon through 1996 in WS3 (Table 4-1) were attributable to treatment. It is possible that some of the Cl response was due to contamination in the fertilizer, but Cl was not one of the constituents analyzed during fertilizer assays. The changes to Cl concentrations were not large (Fig. 4-4b) and Cl represents on average only 3.7 percent of the acid anion concentration in soil water.

Through the additions of excess NO_3 and SO_4 and the corresponding movement toward base cation depletion in all horizons, soil water in WS3 became significantly more acidic. At the start of the study, the total concentration of acid anions in WS3 always exceeded the total concentrations of the base cations (Fig. 4-8), resulting in soil solution with a net acidity, or negative ANC, in all soil horizons (Fig. 4-8). At that time, the base cations could counterbalance about 80 percent of the negative charge of the soil water in the A horizon of WS3, and about 60 percent in the B horizon. While there was more sample to sample variation in the C horizon, on average about 60 percent of the acidity could be neutralized in 1989 (Fig. 4-9). The ratio of base cations to acid anions leveled off by about 1996 in all horizons and has stayed approximately level since then. Thus, whether a horizon is nearing the end of Stage III or already within Stage IV of base cation depletion, under current N and S input rates and levels of S and N mobilization in the soil, weathering is able to fulfill only about 20-30 percent of the buffering capacities in WS3 soil water (Fig. 4-9).

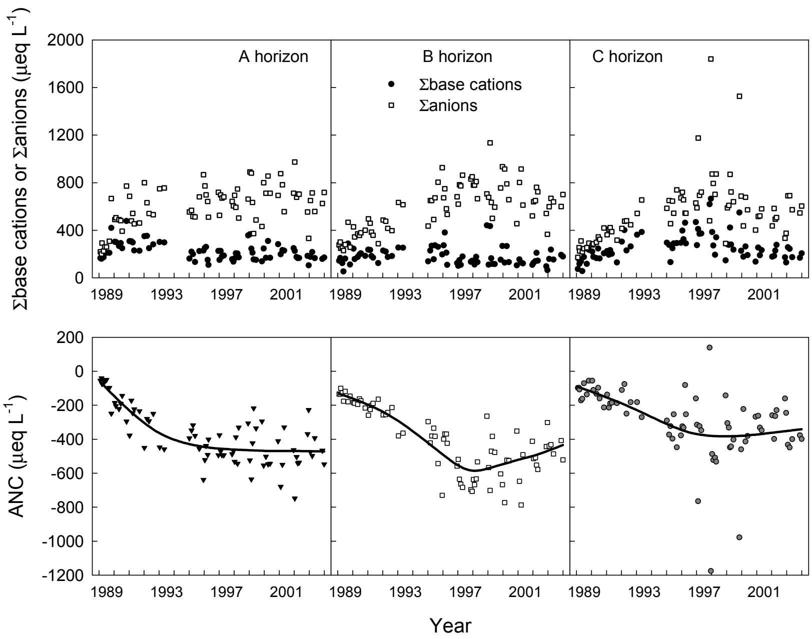

Figure 4-8. The sums of the base cations and acid anions in soil water for WS3 by horizon (top), and ANC for soil water by horizon for WS3 (bottom).

The deficits in charge neutralization throughout the study presumably have been filled by Al since the pH values of soil water were generally <4.75, soil water pH declined significantly through 2003 in all soil horizons (Table 4-1, Fig. 4-4b), and soil pH values throughout the mineral soil were below 4.55 in 1994 and 1997 (Adams and Kochenderfer 1999). Aluminum solubility increases substantially below pH 5.0, with Al^{3+} being the dominant form in acidic forest soils. Thus, Al fulfilled approximately 20 or 40 percent (depending on horizon) of the positive charge in soil solution in 1989, but by 1996 the contribution of Al had risen to approximately 70 percent in the A horizon, approximately 80 percent in the B horizon, and about 60-65 percent in the C horizon. The lower percentage of charge counterbalancing by Al in the C horizon reflects the fact that the C horizon is in Stage III with respect to Ca, Mg, and perhaps K.

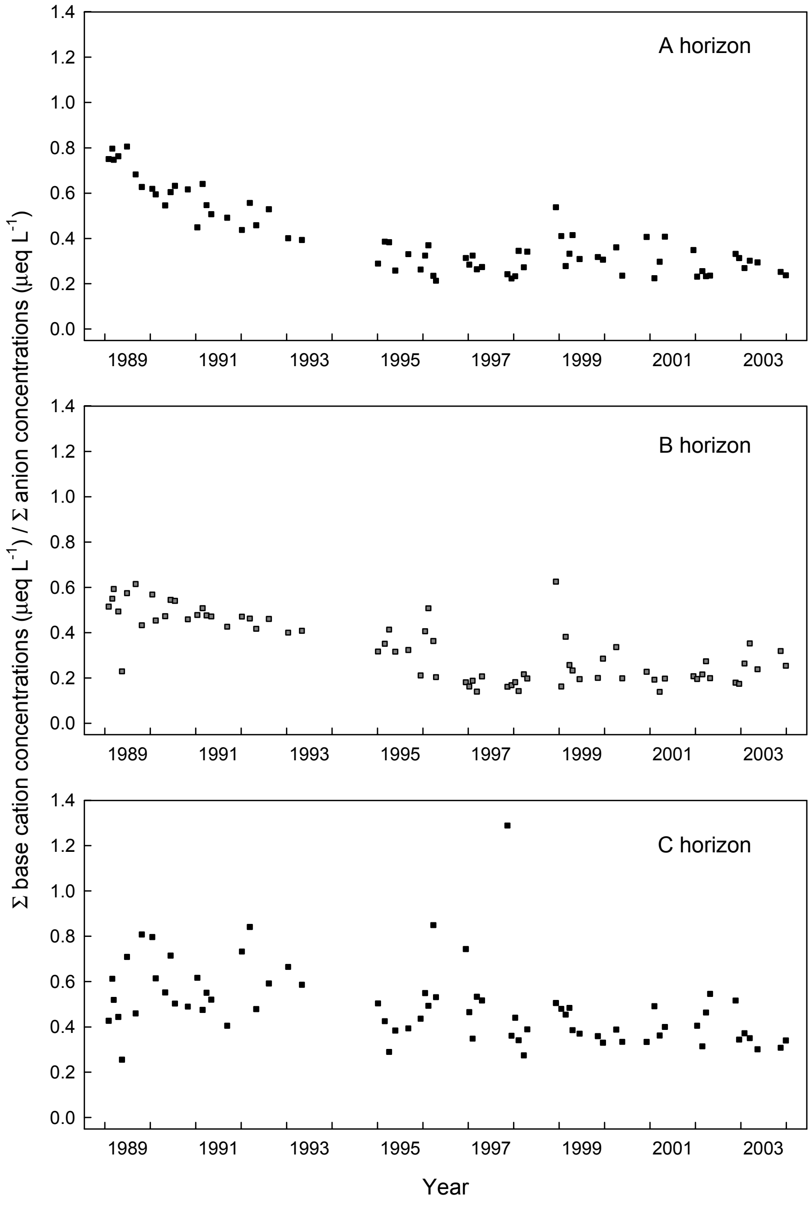

Figure 4-9. The proportion of acid anion charge counterbalanced by base cations in soil water from WS3, by horizon.

There was a noticeable shift over time in the relationships between SO_4 and NO_3, and ANC levels in all three horizons (Figs. 4-10 and 4-11, respectively) During the time that ANC was declining, ANC responses were strongly correlated stoichiometrically to SO_4 but not to NO_3. After ANC leveled off, which also corresponded to the periods that SO_4 retention was

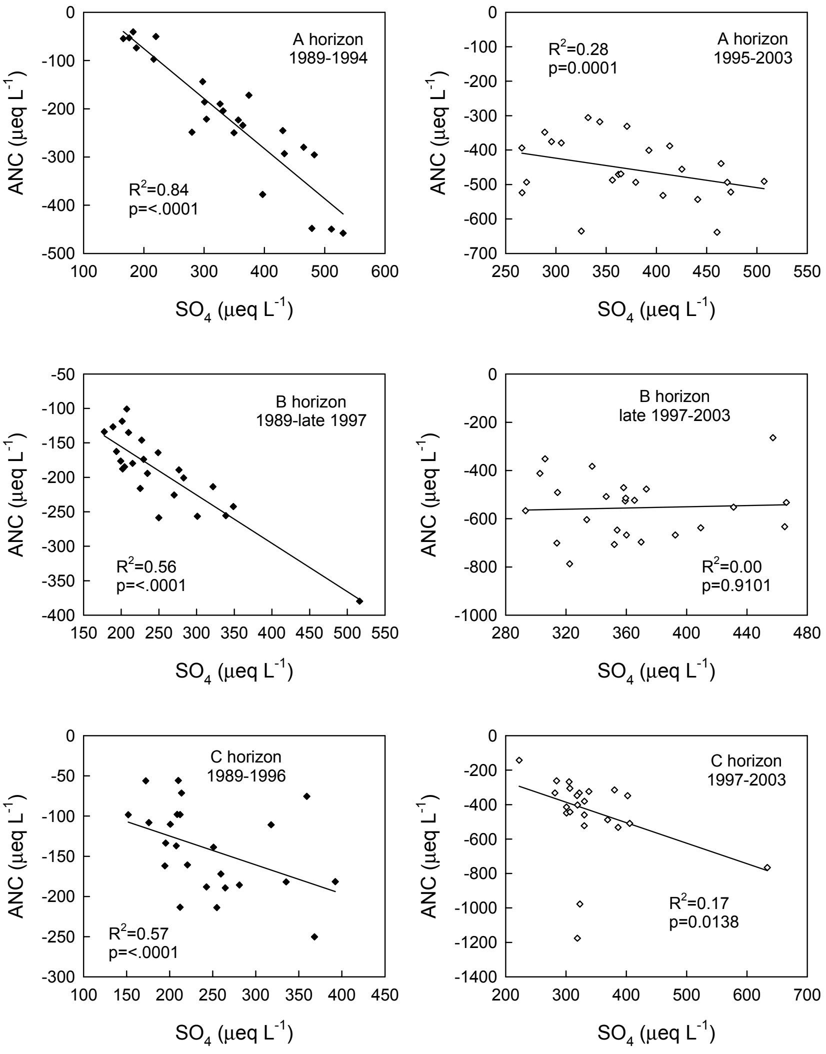

Figure 4-10. Stoichiometric relationships between SO_4 and ANC for WS3 soil leachate before and after the ANC trend lines stopped decreasing (refer to Figure 4-8).

occurring, there was no strong relationship between ANC and SO_4; NO_3 then became correlated strongly with ANC. This relationship shows how the importance of SO_4 and NO_3 in affecting ANC could change in the future under predicted conditions of decreasing SO_4 and increasing NO_3 deposition.

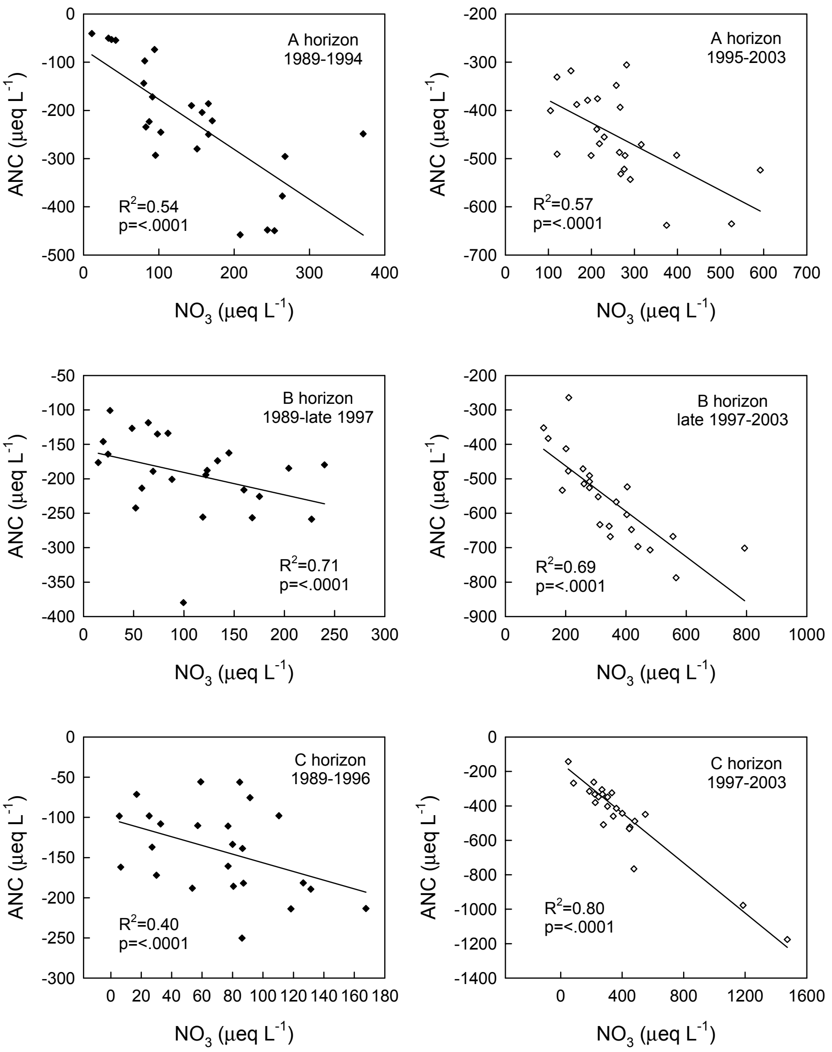

Figure 4-11. Stoichiometric relationships between NO_3 and ANC for WS3 soil water before and after the ANC trend lines stopped decreasing (refer to Figure 4-8).

3.2 WS9 Responses

Calcium and Mg concentrations collected from the control lysimeters in WS9 declined significantly throughout the entire 16 years of record (Table 4-2), suggesting that the unfertilized plots are in Stage III with respect to Ca and Mg levels. However, these trends are difficult to see from the data and the trend lines (Fig. 4-12). Thus, it is difficult to say with great certainty that the watershed soils were in Stage III. Sodium and K concentrations decreased through 1994, but then increased from 1996 through 2002 (Fig. 4-12, Table 4-2). Nitrate and Cl concentration trend lines for the control lysimeters followed the K and Na concentration patterns (Fig. 4-12). However, there was no meaningful correlative relationship between these anion:cation pairs. Thus, rather than either NO_3 or Cl driving the K and Na responses, all four ions simply responded similarly (i.e., the trend lines) to some event that apparently has affected availability/exchange of these ions. Whatever the process that resulted in the K and Na increases since 1995, the data suggest that there is still some K and Na on the exchange sites to provide enhanced levels of buffering, or Stage II, as the concentrations of Ca and Mg decrease. But because the K and Na concentrations are both very low (Fig. 4-12), the actual amount of buffering that they provide is small.

Table 4-2. Mann-Kendall and Sen slope results for soil water from WS9 control and treated lysimeters.

	Control			Treated		
Ion	Period	Mann-Kendall probability	Sen slope	Period	Mann-Kendall probability	Sen slope
Ca	1986-2002	0.005	-1.58	1986-10/1990	0.000	29.33
				11/1990-1998	0.000	-15.25
				1999-2002	0.778	-0.97
Mg	1986-2002	0.000	-0.25	1986-10/1990	0.000	5.87
				11/1990-1998	0.000	-3.30
				1999-2002	0.310	-0.87
Na	1986-2002	0.078	-0.06	1986-10/1990	0.002	1.17
	1986-1994	0.041	-0.17	11/1990-1994	0.029	-0.55
	1995-2002	0.001	0.52	1995-2002	0.000	0.89
K	1986-12/1995	0.000	-0.44	1986-1994	0.000	0.78
	1/1996-2002	0.000	1.95	1995-2002	0.105	0.94
SO_4	1986-2002	0.000	-2.51	1986-10/1992	0.000	32.27
	1986-1994	0.000	2.11	11/1992-2002	0.000	-17.56
	1995-2002	0.000	-6.21			
NO_3	1986-2002	0.000	2.61	1986-10/1990	0.000	12.44
				11/1990-1994	0.005	-7.01
				1995-2002	0.524	0.35
Cl	1986-12/1995	0.018	-0.12	1986-2002	0.000	-0.35
	1/1996-2002	0.012	1.25			
pH	1986-2002	0.000	-0.01	1986-2002	0.000	-0.01

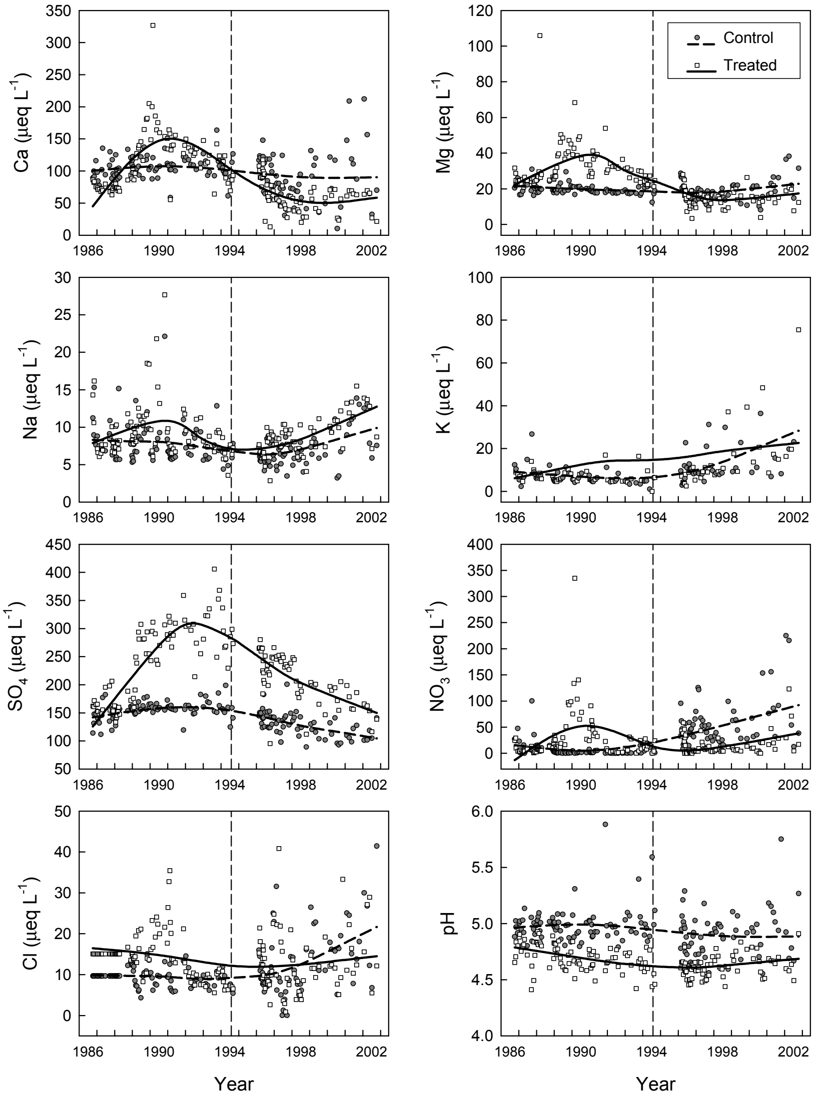

Figure 4-12. Volume-weighted average chemical concentrations for soil water from WS9 control and treatment lysimeters with trend lines overlaid. Dashed vertical line marks end of treatment.

Sulfate concentrations in the control lysimeters declined significantly over time (Table 4-2), but the majority of that decline occurred after 1995 (Fig. 4-12). If the data set is analyzed in two parts (pre and post 1995), SO_4

concentrations decreased only after 1995, and the slope of that change was larger than the slope for the single analysis of the entire period of record (Table 4-2). Sulfate concentrations and loadings in atmospheric deposition have been declining significantly in this area since 1978 (see Chapter 7) and the declining SO_4 concentrations in soil water from control plots may be reflecting lower atmospheric inputs.

The pH of soil water collected from the control lysimeters in WS9 has declined slightly but significantly over time (Table 4-2). The pH of soil water in the WS9 control lysimeters is and has been much higher than WS4 since 1989 (Figs. 4-12 and 4-4b, respectively). The greater pH of soil water from the control lysimeters on WS9 is surprising; this watershed has been reported to have undergone abusive farming in the past and was abandoned because of poor soil productivity, and it was thought to have had low nutrient supplies at the start of this study. Furthermore, the planting of Japanese larch on the watershed was expected to reduce soil pH as this tree is a deciduous conifer, so a large supply of acidic needles is dropped onto the soil annually. However, Japanese larch has low rates of Ca uptake and high rates of Ca leaching (Eriksson and Jönsson 1994), thus contributing to the relatively high pH levels in soil water on WS9. In 1983 when the previously existing low-quality hardwood stand was harvested, a substantial amount of tops and woody debris were left on the site. So while there was a net loss of base cations, especially Ca, to the site from bole removal, there was a sustained elevated return of Ca and other cations to the soils during the time those materials mineralized. This also potentially could explain some of the high pH and base cation concentrations, at least why they were greater than those expected from earlier reports. However, the logging slash was windrowed after harvesting (Kochenderfer and Helvey 1989), which would have tended to concentrate those base cations along the contoured areas but not across the whole watershed, so harvesting may not be a factor in the explanation.

Soil water from the treated lysimeters clearly showed responses to the acidification treatment (Fig. 4-12). In many respects, during the applications of ammonium sulfate (1987-1994), the responses from WS9 were similar to those from WS3. But examination of WS9 also provides the opportunity to examine the recovery phase of base cations in response to the termination of the artificially elevated loadings of S and N.

Calcium and Mg concentrations in soil water became mobilized immediately (Stage II) and increased significantly (Table 4-2) with the initiation of fertilization. Stage II lasted about 3 years for both cations (Fig. 4-12). Progressive depletion of Ca and Mg (Stage III) began sometime just before or during 1990 and for Ca it continued until perhaps 1996, though the timing is impossible to define well with no data from the second half of 1994-1995. However, the high initial Ca concentrations present in 1996 (Fig. 4-12), suggest that Stage III still existed in 1996. The very rapid decline in concentrations in 1996 indicates a short period of equilibrium with weathering (Stage IV) with respect to Ca concentrations. Magnesium appears to have experienced Stage IV from 1994 to 1996, as the final concentrations in 1994 and the initial concentrations in 1996 were approximately equal to those in 1986 and early 1987 before treatment began (Fig. 4-12). Recovery of Ca and Mg and replacement on soil exchange sites (Stage V) appears to have begun in about 1996.

Calcium recovery was more obvious; the data visibly illustrate (Fig. 4-12) a significant decrease in soil water concentrations (Table 4-2) through 1998 (Stage V), followed by increased exchange into soil water (Stage VI) through 2002. The number of data points available from 2002 are insufficient to determine if Ca had returned to equilibrium, or Stage VII by that time; the majority of the Ca concentration values in 2002 are above the trend line and approximate the lowest concentrations in 1986, but there are two points below the trend line that suggest recovery was still occurring. Either way, it is likely that by now equilibrium (Stage VII) has been reached since two additional years have passed since the last sample shown was collected.

Magnesium concentrations did not drop as much as Ca concentrations, resulting in a more muted recovery period and greater difficulty in distinguishing between Stages V and VI. However, since 2000 the concentrations in soil water do appear to have increased slightly (Stage VI) but not signifycantly (Table 4-2). Magnesium concentrations had not returned to Stage VII by 2002, and the slow rate of increase shown for Mg concentrations (Fig. 4-12, Table 4-2), makes it difficult to estimate whether equilibrium has been reached in the subsequent two years.

The behavior of K was very unusual compared to any of the other base cations on either watershed. The trend line and Mann-Kendall tests show increasing concentrations throughout the entire period of record (Fig. 4-12, Table 4-2), though the actual concentrations are small. This pattern suggests an immediate increase of K in response to the acidification treatment (Stage II), but at a very slow rate. The slow rate of exchange may reflect the unknown soil conditions that also were responsible for the slow release of K in the A horizon of WS3. Potassium concentrations became more variable beginning in about 1999, which coincided with the timing of some substantially higher values from 1999-2002 (Fig. 4-12). By 1999, the pH values of soil water had dropped about 0.2 pH units and were just above pH 4.5 (Fig. 4-12), so that the progression of soil acidification may have spurred the elevated exchange of K. Thus, with respect to K the soil was in Stage II throughout the entire treatment and post-treatment period.

Nitrate concentrations increased significantly (Table 4-2) through 1990 (for about 2.5 to 3 years after the initiation of fertilization) and then decreased significantly until the end of 1995 (Fig. 4-12, Table 4-2) in a manner similar to but more distinct than what occurred on WS3 (Fig. 4-4b). Consequently, the NO_3 retention phenomenon observed on WS3 was not an isolated anomaly. The concentrations present during the period of retention were generally quite low, almost always <40 μeq L^{-1} and typically ≤25 μeq L^{-1} (Fig. 4-12). After 1995, NO_3 concentration responses did not change significantly (Table 4-2), even though the watershed transitioned from a period of treatment to non-treatment.

Edwards et al. (1999) originally reported this decline in NO_3 concentrations for WS9 soil water but attributed it to a vegetative uptake by the Japanese larch planted on the site. They suggested that the planted larch did not fully utilize the N applied to the site because the tree roots had not become established sufficiently during the first years of the study to fully occupy the soil and exploit available nutrients. However, there are several pieces of evidence and reasoning that indicate this original interpretation was incorrect: the similar response in WS3, the fact that Japanese larch do not require or even thrive in high N-available environments (VanGoor 1953), the lack of other, more gradual changes in concentrations that would be expected as N uptake increased with root establishment, and that biotic assimilation cannot be induced simply by adding N if the site is not initially N deficient. These factors all indicate that the NO_3 decline on WS9 was due to something other than biotic immobilization.

DeWalle et al. (1985) reported that WS9 had lower soil nutrient pools than WS3 and suggested that WS9's past farming history created N-limited conditions in the soil, but in such an environment, immobilization of NO_3 by microorganisms and vegetation would have been expected to occur immediately upon fertilization, not several years after treatment began. Sudden and substantial increases in ammonification rates at the expense of nitrification processes also are not suggested by the NH_4 concentrations in soil water on WS9 (Fig. 4-13). Thus, as on WS3, some type of abiotic immobilization again seems to be a reasonable explanation for the decreases in mobile NO_3.

Soil water concentrations of SO_4 increased significantly at a rate of about 32 μeq L^{-1} yr^{-1} until 1992 (Fig. 4-12, Table 4-2). Concentrations leveled off until treatment stopped in 1994, presumably due to adsorption. Once the ammonium sulfate applications were terminated, SO_4 concentrations in soil water decreased at a fairly constant rate annually (11 μeq L^{-1} yr^{-1}) indicating the adsorption was at least partially reversible (Reuss and Johnson 1986).

Soil water from the control lysimeters in WS9 had nearly equivalent amounts of base cations and acid anions until 1996 so that the ANC values remained just below 0 μeq L^{-1} (Fig. 4-14). But beginning in 1996, the ANC trend line dropped slightly and then stayed constant at that lower level through the end of the data collection period. The variability in the base cations and acid anions also increased after 1995. This may signal a slight degree of contamination from fertilizer leaching into the control plots from the surrounding treated area. The individual ion concentrations do not suggest this to have been a problem, but because ANC involves summing the base cations and acid anions, the accumulation of small undetectable leaching of individual constituents may become more visible or measurable. It is doubtful that the change in 1996 was due to ambient deposition changes of acid anions and base cations because these latter changes occurred over time. ANC changes from decreasing ambient deposition would have occurred gradually over time rather than during one year.

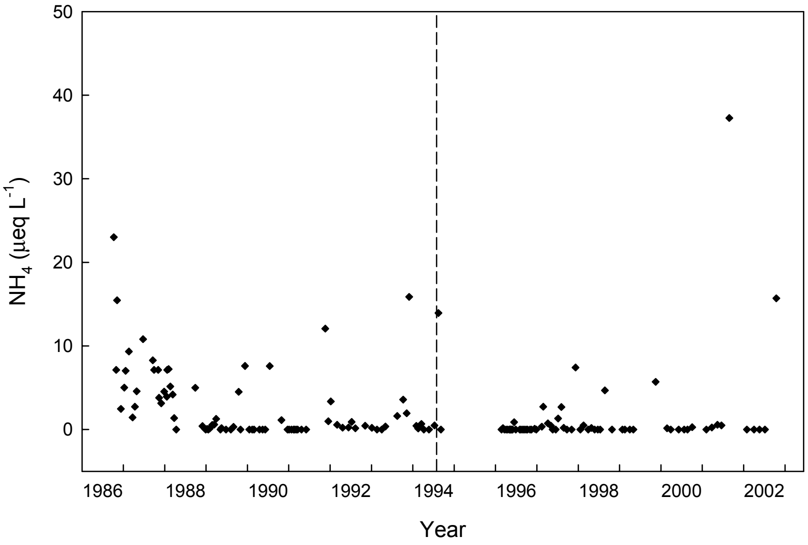

Figure 4-13. Volume-weighted average NH_4 concentrations in soil water for WS9 (treatment lysimeters). Dashed vertical line marks end of treatment.

Average Al concentrations in soil water samples collected monthly from October through December 1986 from the control and treatment zero-tension lysimeters were similar prior to treatment (control = 0.24 mg L^{-1}, treatment = 0.31 mg L^{-1}). Samples from three dates in late 1992 to early 1993 showed the concentrations from the control lysimeters remained at similar levels (Table 4-3) with an overall mean of 0.33 mg L^{-1}. By contrast, Al concentrations in the treatment lysimeters increased significantly to an overall mean of 1.13 mg L^{-1}. Sample results from the shallower 10-cm tension lysimeters (Pickens 1995) suggest the Al concentrations were not altered by the acidification as much near the soil surface, as mean Al values at 10 cm were substantially less than those from the deeper pan lysimeters.

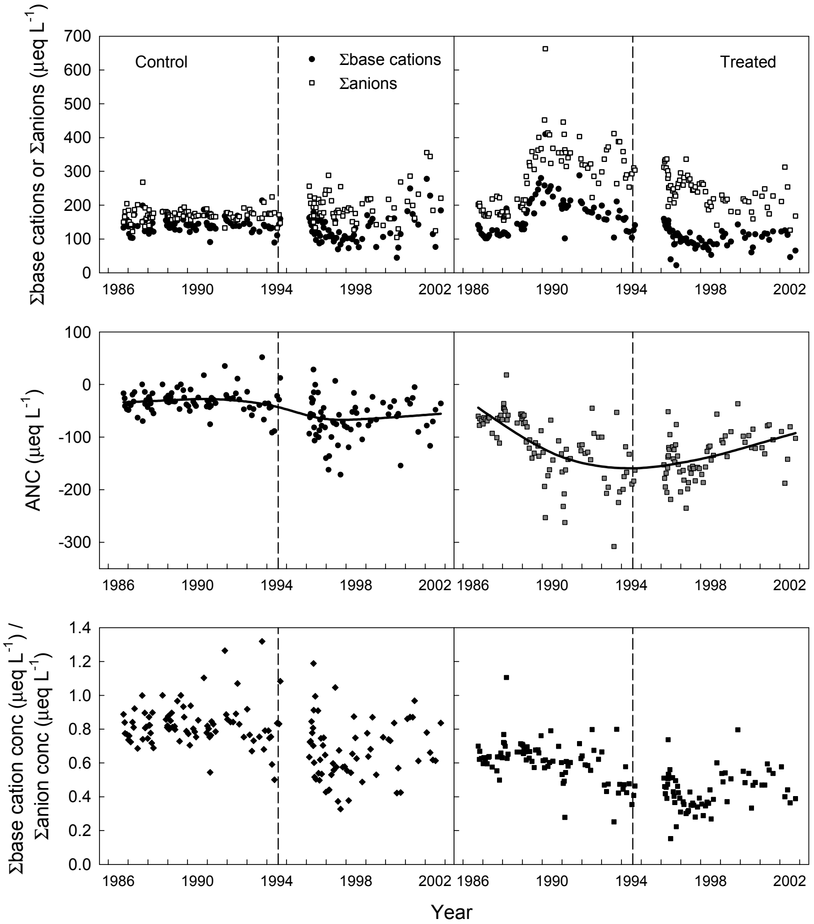

Figure 4-14. Sum of base cations or sum of acid anions in soil water from control and treated lysimeters in WS9 (top), ANC of soil water from control and treated lysimeters in WS9 (middle), and the proportion of acid anion charge counterbalanced by base cations in soil water from control and treated lysimeters in WS9 (bottom). Dashed vertical lines mark end of treatment.

Table 4-3. Al concentrations for pan lysimeters on WS9.

	13 August 1992		4 January 1993		18 February 1993	
Pair	Treated	Control	Treated	Control	Treated	Control
			mg L^{-1}			
1	0.914	0.100	0.393	0.020	0.776	0.013
2	2.450	0.826	2.578	0.780	2.608	0.743
3	2.154	0.498	2.177	0.314	2.618	0.305
4	0.176	0.769	0.079	0.576	0.122	0.726
5	0.114	0.044	0.067	0.018	0.052	0.013
6	1.095	0.082	0.915	0.041	1.059	0.031

The Al concentrations increased significantly over time in the treated lysimeters and were significantly ($p = 0.0003$) greater than the control concentrations (Fig. 4-15). The mean Al concentration in the tension lysimeters in treated areas was 0.25 mg L^{-1} for samples collected between October 1992 and July 1994, compared to 0.11 mg L^{-1} for tension lysimeters in the control plots. Foliage of blackberry, red maple, and Japanese larch growing in the treatment plots also had significantly greater Al concentrations than that growing in the control plots (Pickens 1995). Thus, these data support the assumption that Al became an increasingly more important component of soil water and increasingly important to charge pairing with acid anions.

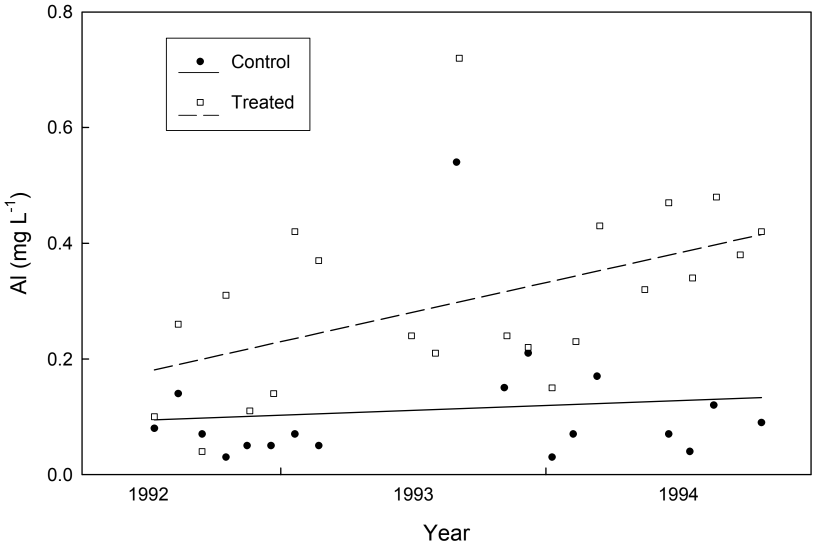

Figure 4-15. Al concentrations from control and treated 10-cm-deep tension lysimeters on WS9 (adapted from Pickens 1995).

4. STREAM WATER

As described in section 2.2, the baseflow data sets were extracted from the routine data set. Baseflow periods dominate annual streamflow in these small Appalachian watersheds; storm discharges generally constitute only about 30 percent of the annual streamflow (unpublished data). Storm runoff in this area responds very quickly to rain or snowmelt events when soil moisture is not highly depleted. More than 50 percent of precipitation events in this area typically begin between midnight and 7:00 AM and are less than

7 hours in duration (Patric and Studenmund 1975), so that by the time the weekly routine samples from WS3, WS4, and WS9 are taken during the workday the influence of many storms has passed. Even when a storm runoff event is in progress at the time routine samples are taken, there is only a small probability that the associated streamflow will be at or near peakflow. As a result, the chemistry data sets for routine and baseflow stream chemistry are almost identical for all three watersheds (Fig. 4-16). This information is important in understanding that nutrient exports calculated using

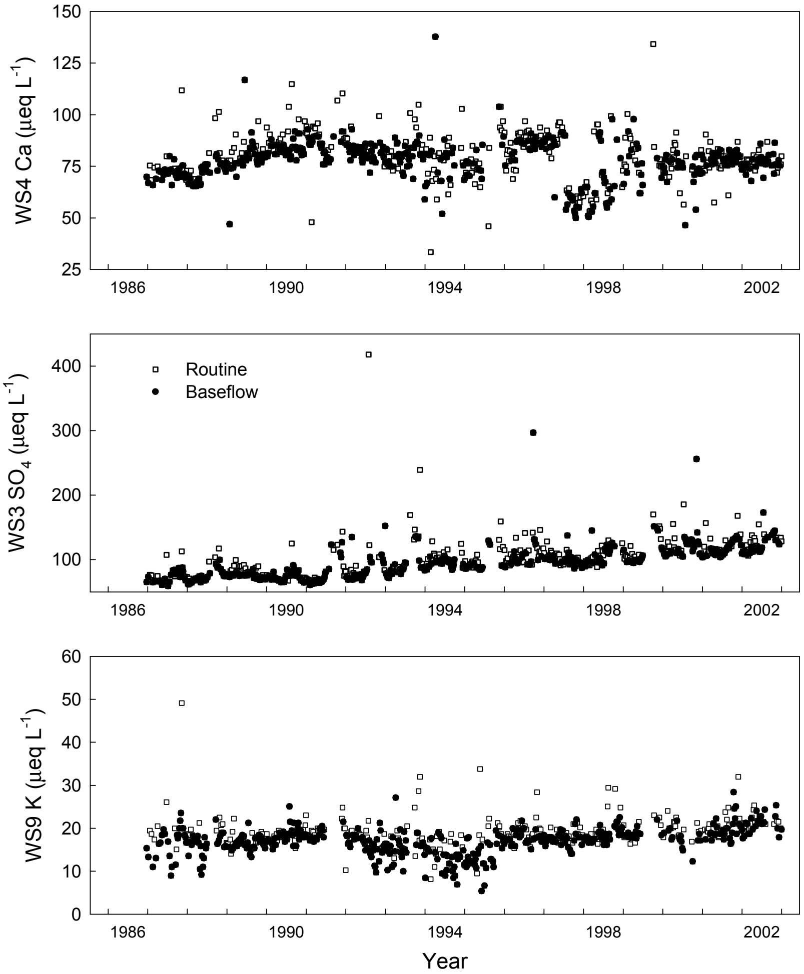

Figure 4-16. Representative examples showing the similarity between ionic concentrations in baseflow samples and weekly routine grab samples. The data for all of the ions for all three watersheds were almost identical.

concentrations from routine weekly samples (e.g., Chapter 7) will underestimate actual annual exports at least slightly since most chemical concentrations on WS3, WS4, and WS9 exhibit maximum concentrations near the period of peakflows (e.g., Edwards et al. 2001). The lack of chemical data along the hydrograph during stormflow may not result in highly significant differences in annual export estimates for some nutrients for watersheds that receive only ambient deposition (Edwards et al. 2004), but it may result in significant underestimates of nutrient exports on watersheds that are anthropogenically manipulated, since the manipulation may cause substantially elevated chemical responses during episodes.

Due to the similarities in the baseflow and routine concentrations (Fig. 4-16), their virtually identical fitted trend lines (not shown), and that conclusions drawn from both data sets are the same, only baseflow chemistries are described. However, the results approximate those of the routine sample chemistries. Baseflow was chosen so that concentrations from this flow regime could be contrasted to concentrations associated with peakflow.

4.1 Concentrations in Baseflow

4.1.1 WS4 Responses

Baseflow chemistry from WS4 showed significant changes over time for the major constituents (Table 4-4). However, most of the ions went through cycles of increases and decreases (Fig. 4-17), so that in most cases the actual net change in concentrations between the beginning and end of data collection were small – typically less than 10 μeq L^{-1} for any ion. It is

Table 4-4. Mann-Kendall and Sen slope results for baseflow from WS4.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-9/1991	0.000	4.07
	10/1991-6/1998	0.057	-0.99
	7/1998-2002	0.008	1.44
Mg	1986-9/1991	0.000	1.73
	10/1991-2002	0.000	-0.62
Na	1986-2002	0.275	0.00
	1986-11/1995	0.072	-0.14
	12/1995-2002	0.000	0.86
K	1986-1/1995	0.038	-0.13
	2/1995-2002	0.000	0.52
SO_4	1986-11/1995	0.000	1.77
	12/1995-2002	0.000	-1.35
NO_3	1986-2002	0.093	-0.14
Cl	1986-2002	0.000	-0.18
pH	1986-2002	0.005	0.004
ANC	1986-2002	0.092	-0.25

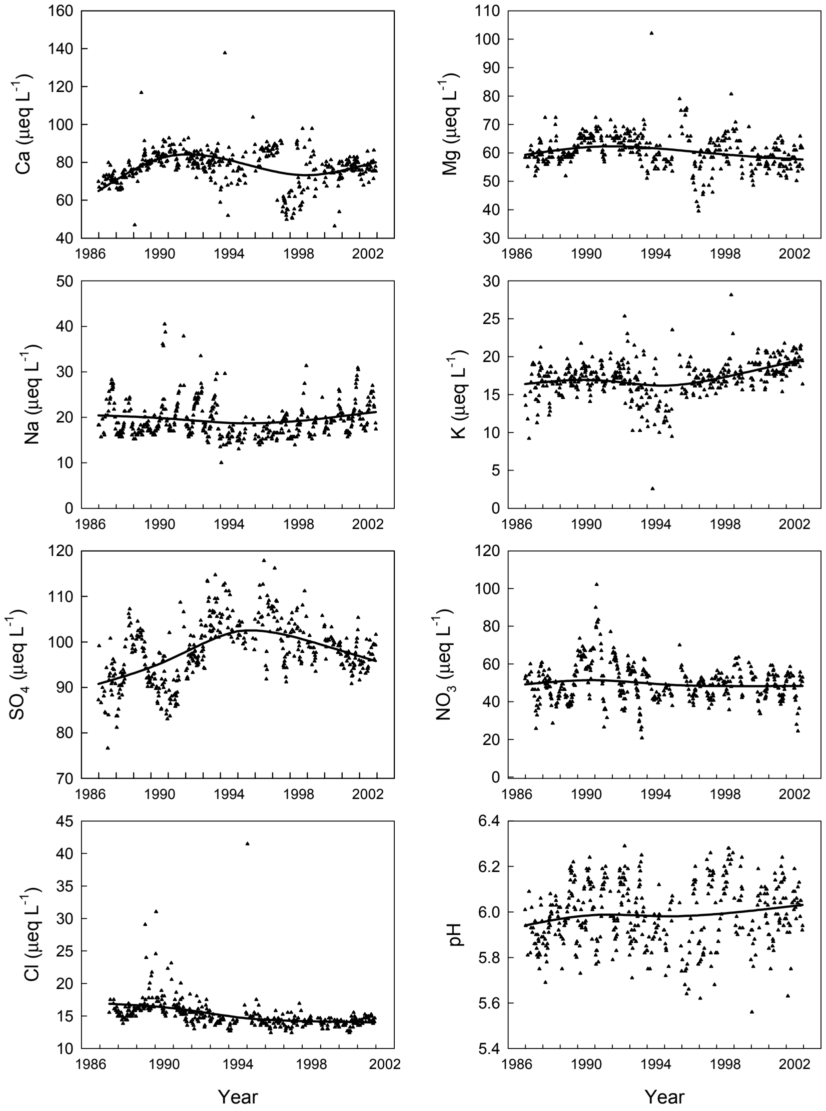

Figure 4-17. Chemical concentrations in baseflow from WS4 with trend lines overlaid.

impossible to know if these changes are simply fluctuations in the normal long-term variation of baseflow concentrations (i.e., Stage I), or if they occurred in response to changes in ambient deposition. We believe they are due to the latter, particularly based on SO_4 responses. The first phase of sulfur dioxide (SO_2) emissions reductions resulting from the Acid Rain Program (one of the 1990 Clean Air Act Amendments) began in 1995 and targeted power plants with the highest SO_2 emissions. Sulfur dioxide emissions at the Harrison power plant, which is upwind of the experimental watersheds, were reduced by 95-98 percent in 1996 compared to 1990. The downturn in SO_4 trend line for WS4 baseflow began in 1995 (Fig. 4-17), coincident with the first phase of SO_2 reductions (http://www.epa.gov/airmarkets/arp/overview.html). Improvements in visibility for nearby wildernesses also became evident in 1995-1996, further supporting the idea that lower acidic deposition caused a change in SO_4 in baseflow on WS4.

Thus, the initial mobilization of Ca and Mg would have been due to ambient inputs of acid anions from wet and dry deposition. Declines in Ca and Mg concentrations occurred before the 1995 improvements to scrubbers, suggesting the downturns signaled the onset of Ca and Mg depletion. Even though deposition of base cations would have decreased with the improved scrubber technology, the decrease in SO_4 deposition may have been so substantial that Ca concentrations could have shown some symptoms of recovery. The increase in K concentrations beginning in about 1995-1996 also may be from recovery following the large reduction in SO_4 emissions; however, the concentration patterns are not consistent with recovery in the base cation depletion model.

The pH concentrations of WS4 baseflow increased very slightly over time (Table 4-4). In 1987, the pH value at the trend line position was approximately 5.95; in 2002, it had risen to about 6.0 (Fig. 4-17). There was substantial variation in the pH values within years, which probably reflects the seasonality of pH.

The ANC of WS4 baseflow did not change significantly from 1987-2002 (Table 4-4) and typically was between 0 and 40 $\mu eq\ L^{-1}$, though several samples had negative ANC values (Fig. 4-18). The negative values primarily occurred in 1994, 1997, and 1998 though they were all $>-40\ \mu eq\ L^{-1}$. These years were associated with decreased levels of base cations (K in 1994, Mg in 1997, and Ca in 1997-1998) rather than increases in acid anions (Fig. 4-17). Similarly, the earlier increases in ANC (Fig. 4-18) corresponded to periods of increasing base cations. ANC did increase after 1996, which coincides with the decreases in SO_2 emissions and SO_4 concentrations in baseflow. The pH of baseflow on WS4 was always greater then 5.5 (Fig. 4-17), so when the ANC was <0 (Fig. 4-18), the amount of Al that would have been available to leach into the stream would have been present in fairly low concentrations and would have had trivalent Al as a minimal component.

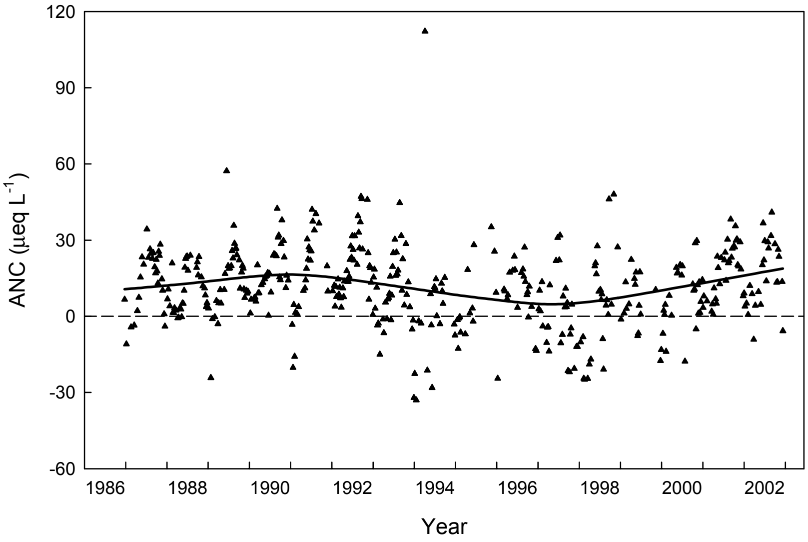

Figure 4-18. ANC concentrations of baseflow from WS4.

4.1.2 WS3 Responses

For the first 2 years of fertilizer treatments, concentrations in baseflow experienced some intra-year variation, but generally did not start showing consistent increases in concentrations for approximately 1.5-2 years (Fig. 4-19). This delay corresponds to the approximate 1.6-year mean transit time required for precipitation to become expressed as baseflow in WS3 (DeWalle et al. 1997).

Baseflow originates from two sources: groundwater in the water table that has percolated vertically through the soil column and the slow seepage of water through the soil to the stream (Hewlett and Nutter 1969). The latter is more important in mountainous terrain than in flatter landscapes. Thus, the chemistry of baseflow ultimately is controlled by the biogeochemical processes in the soil source areas that contribute soil water and bedrock through which groundwater is transmitted. The deep soil sources that contribute directly to baseflow can have different biogeochemical characteristics than deep upland soils because the source areas are near the stream and act as long-term receptors of chemical leachates from the uplands. Source-area soils typically have different chemical characteristics because they are colluvium and they are thicker because organic and mineral material accumulates at the base of slopes along stream channels.

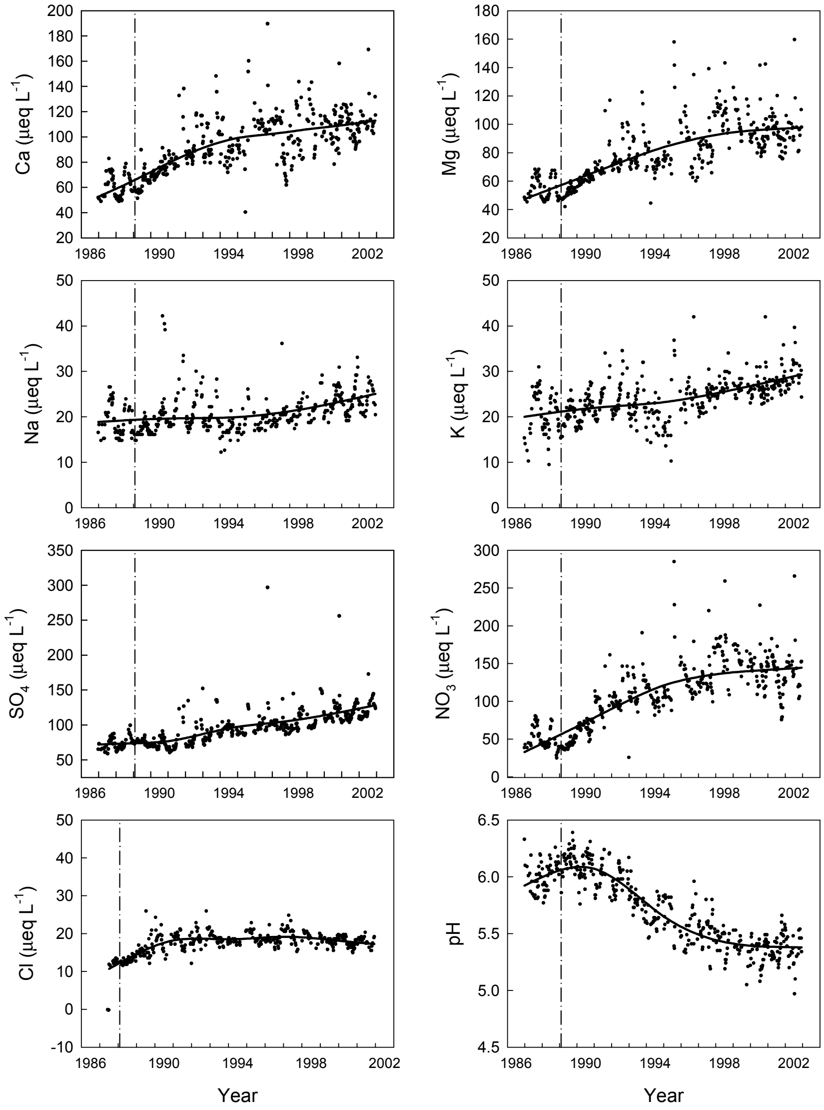

Figure 4-19. Chemical concentrations in baseflow from WS3 with trend lines overlaid. Dashed vertical line marks beginning of treatment.

Examination of the baseflow concentrations from WS3 compared to soil water (Figs. 4-19 and 4-4, respectively) show that the biogeochemistry of the uplands is very different from that which controls baseflow chemistry. Calcium, Mg, K, and Na cation concentrations on WS3 all increased in baseflow throughout the period of treatment in response to increasing acid anion concentrations (Fig. 4-19, Table 4-5). Therefore, the portion of the watershed controlling baseflow has at least some reserves of available base cations for neutralizing acidic inputs (Stage II). The influence of the source areas and bedrock on Mg was substantial, as Mg concentrations in baseflow were present in higher concentrations than Mg in soil (Chapter 3) and soil water (Fig. 4-4a). In fact, Mg concentrations in baseflow almost approximated those of Ca. A lag in K availability was not evident in baseflow (Fig. 4-19) compared to soil water (Fig. 4-4a), but the rate of increase in K concentrations in baseflow did become greater in about 1995 (Fig. 4-19), seemingly reflecting the lagged increases of K to stream water from soil water.

Table 4-5. Mann-Kendall and Sen slope results for baseflow from WS3.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-2002	0.000	3.73
Mg	1986-2002	0.000	3.27
Na	1986-2002	0.000	0.37
K	1986-2002	0.000	0.55
SO_4	1986-2002	0.000	3.52
NO_3	1986-2002	0.000	7.45
Cl	1986-1990	0.000	1.73
	1991-2002	0.014	-0.06
pH	1986-1/1989	0.017	0.08
	2/1989-2002	0.000	-0.07
ANC	1986-2002	0.000	-3.30

Chloride concentrations in baseflow increased a small amount during the first four years of treatment but then decreased slightly but significantly through 2002 (Fig. 4-19, Table 4-5). Overall, however, Cl concentrations only increased by approximately 10 µeq L^{-1}, which was only one-tenth or less of the increases in SO_4 or NO_3 over the 15 years of fertilization (Fig. 4-19).

Nitrate concentrations in baseflow increased throughout the study, but the rate of increase declined (based on the trend line) from about 11 µeq L^{-1} yr^{-1} through 1995 to 1.5 µeq L^{-1} yr^{-1} after 1995 (Fig. 4-19). The reduction in the rate of increase may suggest an increase in NO_3 retention, similar to that, but not as far advanced as in soil water on WS3 (Fig. 4-4b).

There was no evidence of SO_4 retention in the soil source areas or bedrock. Instead, SO_4 concentrations in baseflow increased at an almost constant rate through the study (Fig. 4-19, Table 4-5). If the deep soil source areas that contribute to baseflow have acted as receptors for SO_4 over the long-term, it would not be surprising to have essentially no capacity for anion adsorption remaining, assuming any ever existed.

The pH of baseflow has decreased significantly since the initiation of the acidification treatment (Fig. 4-19, Table 4-5). Before treatment began in 1987, pH of baseflow generally was about 5.9 (based on the trend line) and then it increased for the next 2 years of pretreatment to above pH 6.0, with some values as high as 6.3-6.4. pH responded almost immediately to fertilization and by 2002 the pH on the trend line was about 5.4, though there were pH values in 2001-2002 as high as ~5.6 and as low as ~5.0. The reduction from pH 6.0 to 5.4 is quite substantial and equivalent to an increase of 2.9 µeq H^+ L^{-1}.

ANC in baseflow on WS3 decreased significantly throughout the study (Fig. 4-20, Table 4-5). WS3 ANC transitioned from being predominantly positive, generally between 0-40 µeq L^{-1} (similar to WS4) to predominantly negative during the last half of 1992 and the first half of 1993. During the transition period, there were approximately as many positive as negative ANC values and they ranged from about 10 µeq L^{-1} to about -20 µeq L^{-1}. After mid 1993, 90 percent of the ANC values associated with baseflow samples were negative. Thus, even though the concentrations of base cations in baseflow increased through time, the deep soil source areas and bedrock, through which baseflow is transmitted, buffer increasingly smaller percenttages of acid anions (Fig. 4-21). As a consequence, baseflow has shifted from being only episodically acidic to being chronically acidic.

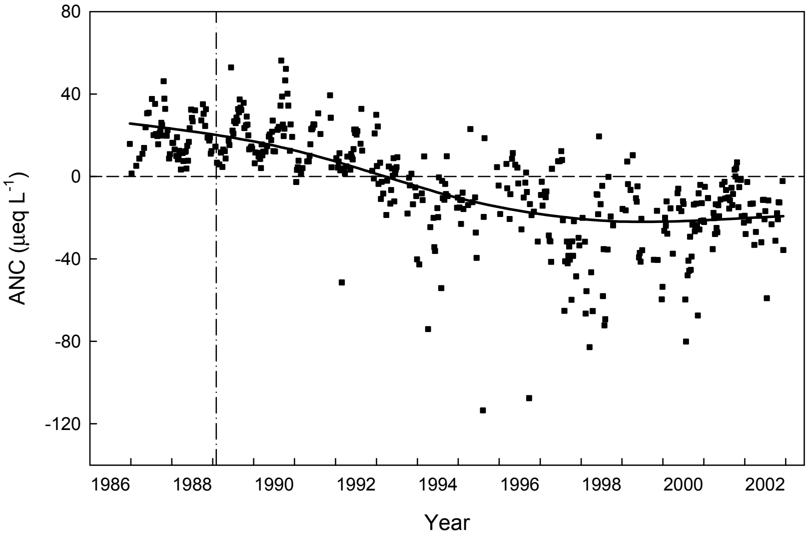

Figure 4-20. ANC concentrations of baseflow from WS3. Dashed vertical line marks beginning of treatment.

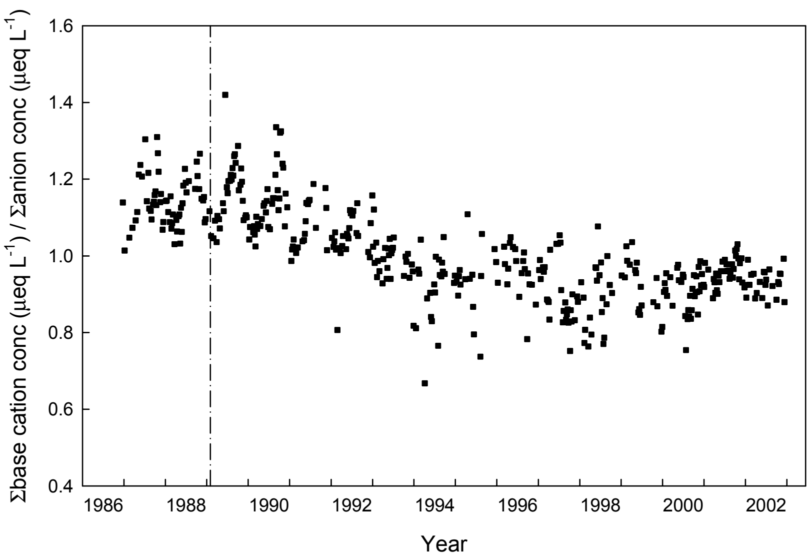

Figure 4-21. The proportion of acid anion charge counterbalanced by base cations in baseflow from WS3. Dashed vertical line marks beginning of treatment.

The acidification treatment clearly had a substantial effect on the buffering status of baseflow, but even the most negative ANC values in WS3 baseflow (Fig. 4-20) were greater than those present at the beginning of the study for upland soil water from WS3 (Fig. 4-8). As with soil water, Al probably has made up most of the deficit in positive charge as baseflow has become more acidic, but because the pH of baseflow is still above 5.0 (Fig. 4-19), the Al ions in baseflow are probably dominated by those of a +2 valence rather than trivalent aluminum since Al^{3+} is not common until the pH is ≤5.0.

4.1.3 WS9 Responses

While the chemical concentrations of WS3 and WS4 became widely divergent as the acidification treatment progressed, WS9 baseflow concentrations changed little. Indeed, WS9 and WS4 concentrations followed very similar patterns over time (Fig. 4-22), including during the treatment period from 1987-1994. There is a reasonably strong stoichiometric relationship for all constituents between the two watersheds, except Cl and pH (Fig. 4-23). Sulfate, NO_3, and K have nearly 1:1 slopes illustrating the nearly identical baseflow responses of the two watersheds for these ions. The two watersheds seemed to be responding very similarly to very dissimilar inputs of N and S.

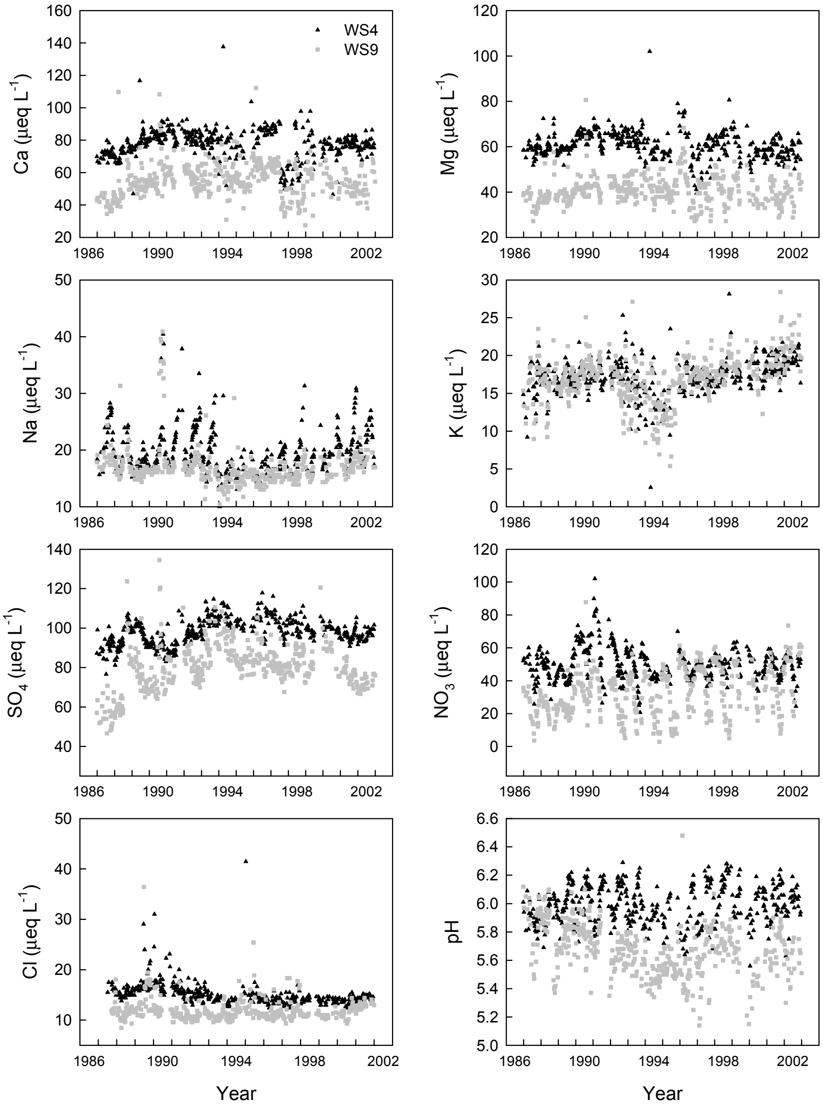

Figure 4-22. The chemical concentrations for baseflow in WS4 (reference) and WS9 (treated) displayed similar temporal patterns.

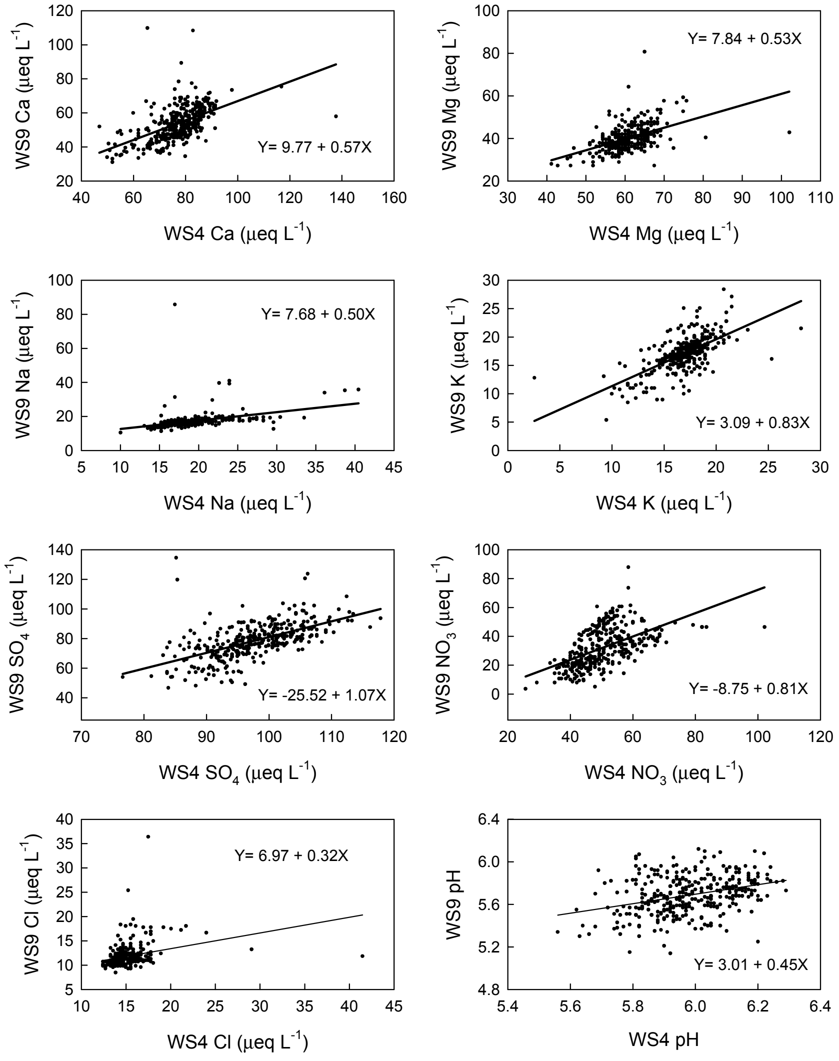

Figure 4-23. Stoichiometric relationships between WS9 and WS4 for baseflow.

Calcium and Mg concentrations in WS9 baseflow increased significantly through 1991 and then decreased through 2002 (Fig. 4-24, Table 4-6), indicating that the watershed sources affecting baseflow could provide additional buffering of some of the increased acid anions (Stage II) but those levels of available cations were small and short-lived. Calcium and Mg remained in a state of progressive depletion after 1991 (Stage III) even though the elevated additions of S and N were terminated in 1994. Baseflow concentrations of both ions were slightly less than the concentrations in soil water at the beginning of the study, but the overall changes in their concentrations were much more muted in stream water (Fig. 4-24) than in soil water (Fig. 4-12).

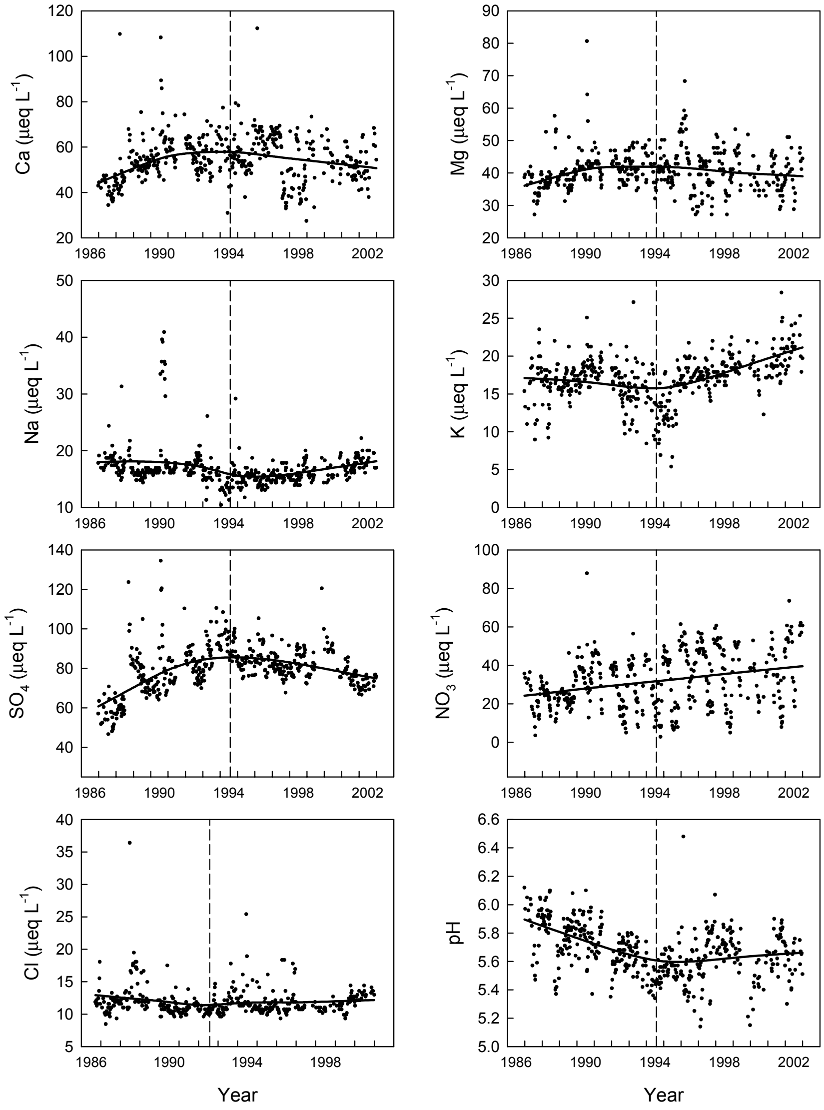

Figure 4-24. Chemical concentrations in baseflow for WS9 with trend lines overlaid. Vertical line marks end of treatment.

Table 4-6. Mann-Kendall and Sen slope results for baseflow from WS9.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-1991	0.000	4.89
	1992-2002	0.000	-0.60
Mg	1986-1991	0.000	1.76
	1992-2002	0.007	-0.27
Na	1986-2002	0.001	-0.06
	1986-1995	0.000	-0.28
	1996-2002	0.000	0.50
K	1986-9/1994	0.003	-0.26
	10/1994-2002	0.000	0.76
SO_4	1986-9/1993	0.000	4.18
	10/1993-2002	0.000	-1.79
NO_3	1986-2002	0.000	1.09
Cl	1986-2002	0.731	0.00
pH	1986-2002	0.000	-0.02
	1986-11/1994	0.000	-0.05
	12/1994-2002	0.005	0.01
ANC	1986-2002	0.000	-1.36
	1986-7/1994	0.000	-2.51
	8/1994-2002	0.384	0.30

Potassium concentrations decreased until 1994 (Fig. 4-24, Table 4-6), as they did for WS4 baseflow (Fig. 4-17), suggesting that K concentrations in baseflow were depleting (Stage III) even before the study began. The termination of the N and S additions to the watershed appear to have resulted in an increase in K concentrations; however, this pattern does not follow the expected recovery phase of the base cation depletion model.

The SO_4 concentrations in baseflow throughout the study and the magnitude of change in SO_4 concentrations (Fig. 4-24) were much less than those in soil water (Fig. 4-12). Sulfate concentrations increased significantly through 1994 and decreased thereafter (Fig. 4-24, Table 4-6). The decreases in SO_4 following the termination of treatment show that SO_4 adsorption was at least partially reversible (Reuss and Johnson 1986). Nitrate concentrations in WS9 baseflow continued to increase in stream water even after the termination of fertilization in 1994. This was the only instance for treated watersheds in which NO_3 retention was not evident. The continued release of NO_3 even after N inputs were reduced to much lower ambient levels shows that streamflow from some watersheds may exhibit continued acidification symptoms long after reductions in NO_3 emissions or deposition reductions.

The pattern of baseflow pH responses from WS9 (Fig. 4-24) was very similar to that for WS3 (Fig. 4-19), though the starting pH of the trend line was slightly less on WS9 (about pH 5.9) and the ending pH of the trend line was slightly greater (about pH 5.6). However, the spread of the actual pH values was nearly the same by the end of the period of record; a major difference was that the very low pH values (~5.2) were present on WS9 throughout a much larger period of the study and not just primarily at the end. Those pH values still remain above those at which high levels of Al become solubilized. There was a slight but significant increase in pH on WS9 after the fertilization ceased (Table 4-6), so that increases in Al in any form are not expected in the future, at least in the short term.

The ANC of WS9 baseflow decreased significantly over time (Table 4-6); however, the data fall into two distinct groups – those during treatment (before 1994) and those after treatment (1994-2002) (Fig. 4-25). Prior to 1994, most of the data were between 0 and 45 μeq L^{-1}. Afterwards, about half of the data were positive and half were negative, between 30 and -40 μeq L^{-1} but the ANC did not significantly change during that time (Table 4-6), so it did not recover once the N and S applications stopped. The ANC values in WS9 baseflow did not become as negative as those on WS3, because the treatment was terminated after only 8 years on WS9, and the ANC values for WS9 baseflow also did not transition to negative values as quickly as they did on WS3 (3.5 years of treatment for WS3 vs. 6 years for WS9). Baseflow on WS9 was moving toward becoming chronically acidic, but the termination of treatment allowed the regular though not consistent occurrence of positive ANC values; thus, baseflow in WS9 remains episodically acidic.

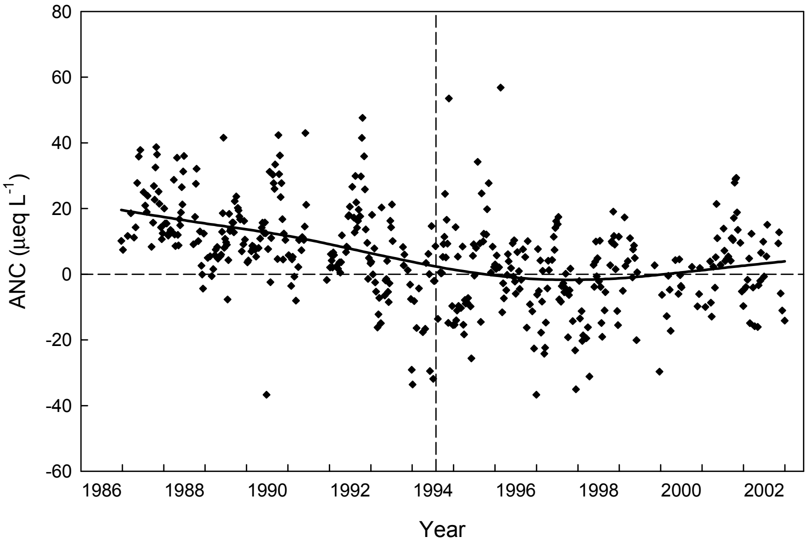

Figure 4-25. ANC concentrations of baseflow from WS9. Dashed vertical line marks end of treatment.

4.2 Concentrations at Peakflow

Episodic changes occurred on all the watersheds, including the reference WS4. The difference in concentrations between baseflow and storm peakflow concentrations for any of the analytes typically was <2 mg L^{-1}, even for the largest storms, and was often <1 mg L^{-1}. As acidification progressed, the magnitude of differences between baseflow and peakflow concentrations did not increase or decrease meaningfully, even if the data were adjusted to account for differences in flows. Instead, there was a wide variation in the differences between peakflow concentrations and baseflow concentrations within and across years.

Because storm sampling took place only from 1987 through 1997, with no sampling in 1996 and only one storm sampled in 1997, and there were many fewer observations per year than for baseflow or soil water samples, less information can be derived from the samples collected near peakflow. Furthermore, for all watersheds, including reference WS4, there was substantial variation in concentrations even over a short number of years; thus, while the trend lines suggest generally expected and explainable behavior, the variation in the data makes some of the trends less convincing than they are for soil water and baseflow.

4.2.1 WS4 Responses

Figure 4-26 shows the patterns of the concentrations of the various analytes over time from reference WS4. From these graphs, the trend lines and the data suggest that all the base cations in peakflow on WS4 went through an initial period of mobilization (in response to increasing NO_3 concentrations) followed by progressive depletion, but not all of the base cation increases or decreases were highly significant (Table 4-7). Whether SO_4 experienced true declines in concentrations after 1994 is questionable because of the limited amount of data, but the data certainly suggest that NO_3 concentrations at peakflow declined significantly beginning about 1991 (Fig. 4-26, Table 4-7). The reason for the decline in NO_3 concentrations is unknown, but the increases at peakflow in 1990 and 1991 (Fig. 4-26) also correspond to high NO_3 concentrations in baseflow (Fig. 4-17), so the same factor probably affected both flow regimes.

4.2.2 WS3 Responses

Watershed acidification appears to have induced cation mobilization (Stage II) for all four base cations through about 1992 or 1993 (Fig. 4-27). The increases in concentrations were statistically significant for all base cations (Table 4-8). Only a few samples were available after the downturns

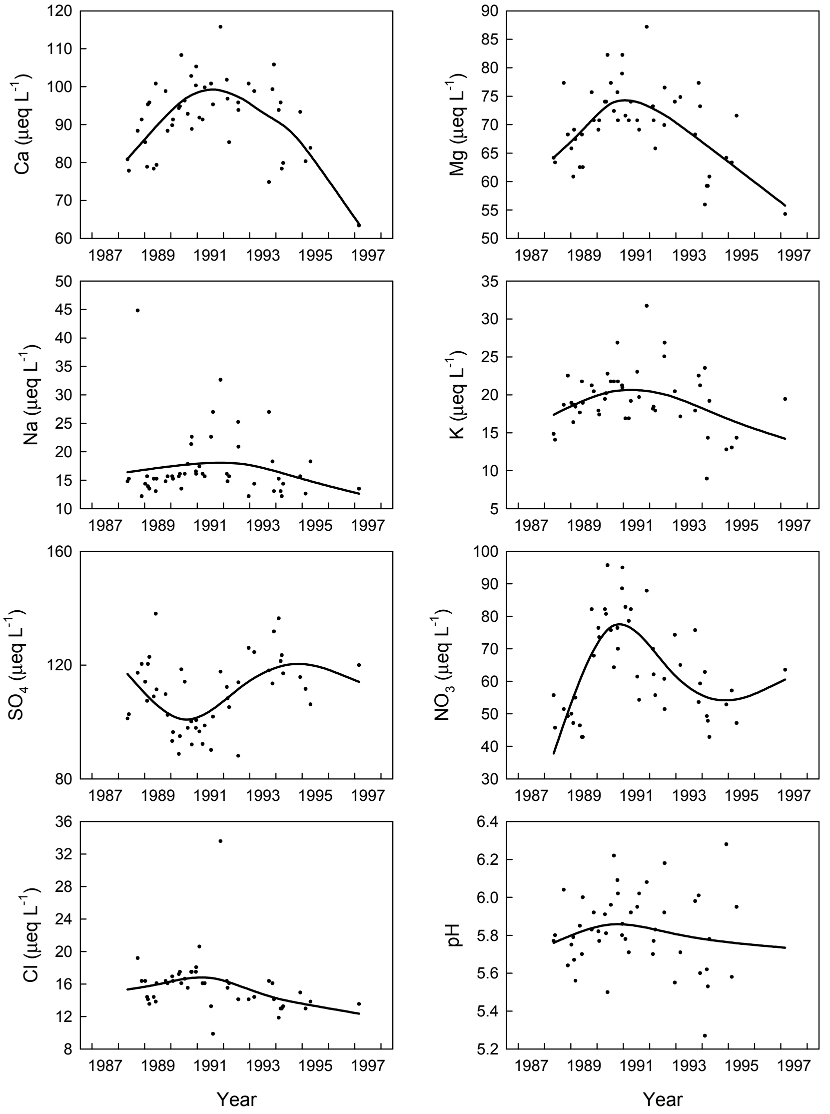

Figure 4-26. Chemical concentrations in peakflow from WS4 with trend lines overlaid.

began, so it is difficult to conclude with certainty that depletion (Stage III) of base cations was initiated, but the downturns for Mg and Na were significant. By contrast, the case for Ca and K depletion is particularly difficult to make since the downturns of those data were not significant (Table 4-8).

Table 4-7. Mann-Kendall and Sen slope results for peakflow from WS4.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1988-7/1991	0.002	5.86
	8/1991-6/1997	0.010	-5.59
Mg	1988-1990	0.000	5.49
	1991-1997	0.025	-2.46
Na	1988-7/1992	0.001	0.87
	8/1992-1997	0.274	-1.45
K	1988-3/1991	0.077	1.43
	4/1991-1997	0.045	-1.66
SO_4	1988-8/1990	0.327	-5.62
	9/1990-1997	0.001	5.76
NO_3	1988-11/1990	0.011	13.79
	12/1990-1997	0.000	-7.11
Cl	1988-11/1990	0.053	0.66
	12/1990-1997	0.002	-0.81
pH	1988-7/1991	0.506	0.04
	8/1991-1997	0.051	-0.06
ANC	1988-1997	0.505	-0.64
	1988-7/1991	0.038	2.92
	8/1991-1997	0.010	-11.56

While the SO_4 trend line for peakflow samples follows the general patterns that were seen for soil water on WS3 (i.e., increasing concentrations followed by retention), neither the increases nor decreases in concentrations were significant (Table 4-8). This lack of significance makes it impossible to show that the acidification treatment increased the mobilization of SO_4. This apparent lack of response is surprising given that SO_4 was applied in higher concentrations than N and the source of stormflow from WS3 is believed to be transported quickly through upper soil layers. The statistically unconvincing response of SO_4 in peakflow to treatment indicates that the source areas that ultimately contribute stormflow also behave different biogeochemically than the upland areas.

Nitrate and Cl responses provide strong evidence that they were affected by the ammonium sulfate additions (Fig. 4-27). Both increased significantly (Table 4-8) and did not have later downturns, though NO_3 did level off as it did in soil water. The maximum increases in Cl were only about 10-15 μeq L^{-1}, compared to ~100 μeq L^{-1} for the NO_3 trend line and as much as twice that for the actual concentrations.

The pH (Fig. 4-27) and ANC values (Fig. 4-28) for WS3 convincingly indicate increased acidification of peakflow: both declined significantly (Table 4-8). The pH dropped by about 0.5 units based on the trend line and ANC moved from almost all positive or ~0 μeq L^{-1} concentrations to all negative values with most in the -40 to -80 μeq L^{-1} range. Thus, like baseflow, chemistry at peakflow on WS3 has shifted from being episodically acidic to chronically acidic.

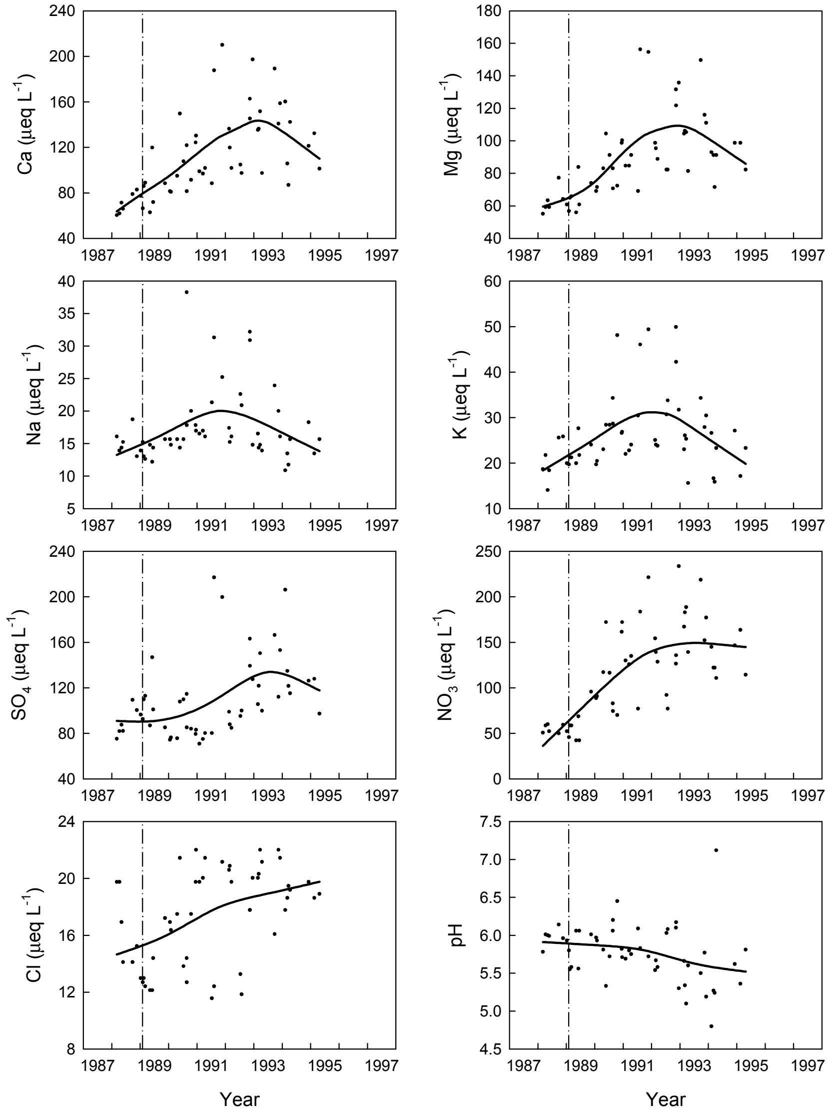

Figure 4-27. Chemical concentrations at peakflow from WS3 with trend lines overlaid. Dashed vertical line marks beginning of treatment.

4.2.3 WS9 Responses

While the trend lines for Ca and Mg concentrations in peakflow on WS9 suggest that base cation mobilization occurred through the beginning of 1991 and was followed by progressive depletion thereafter (Fig. 4-29), the Mann-Kendall tests do not show significant concentration increases or decreases for either period (Table 4-9). Thus, the results infer that the source areas that contribute stormflow on WS9 were depleted of excess Ca and Mg prior to the initiation of acidification treatments, and weathering rates were controlling Ca and Mg concentrations during storm events (Stage IV).

Table 4-8. Mann-Kendall and Sen slope results for peakflow from WS3.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1988-3/1993	0.000	15.18
	4/1993-1995	0.244	-20.18
Mg	1988-10/1992	0.000	9.23
	11/1992-1995	0.009	-15.09
Na	1988-11/1991	0.001	1.40
	12/1991-1995	0.020	-2.07
K	1988-2/1992	0.000	3.44
	3/1992-1995	0.108	-3.19
SO_4	1988-3/1993	0.059	4.70
	4/1993-1995	0.534	-17.25
NO_3	1988-6/1992	0.000	27.32
	7/1992-1995	0.861	-3.25
Cl	1988-1995	0.003	0.75
pH	1988-1995	0.003	-0.08
ANC	1988-1995	0.004	-4.08
	1988-7/1991	0.797	-0.55
	8/1991-1995	0.021	-18.02

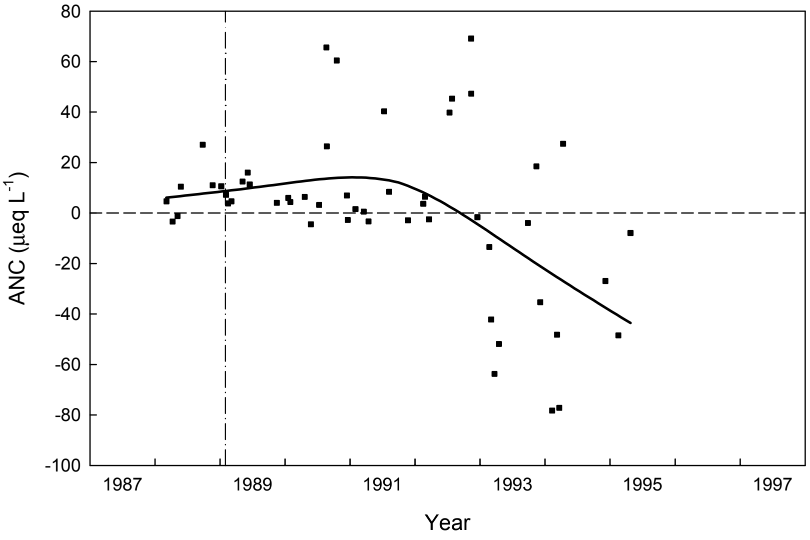

Figure 4-28. ANC concentrations of peakflow from WS3. Dashed vertical line marks beginning of treatment.

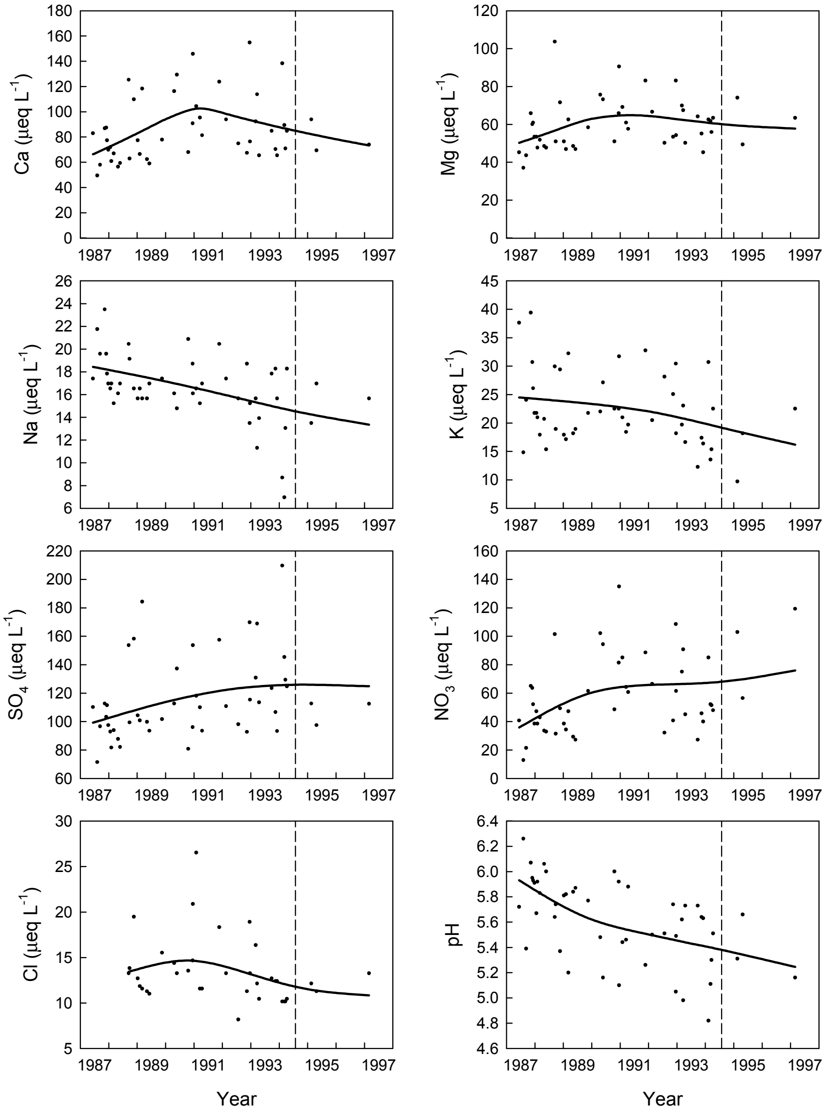

Figure 4-29. Chemical concentrations at peakflow from WS9 with trend lines overlaid. Dashed vertical line marks end of treatment.

By contrast, Na and K concentrations decreased significantly throughout the entire period that fertilizer was applied to WS9 (Fig. 4-29, Table 4-9). Consequently, exchangeable levels of Na and K were available at the

Table 4-9. Mann-Kendall and Sen slope results for peakflow from WS9.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1987-1990	0.082	7.56
	1991-1997	0.135	-3.96
Mg	1987-10/1990	0.214	3.83
	11/1990-1997	0.350	-1.54
Na	1987-1997	0.001	-0.49
K	1987-1997	0.042	-0.80
SO_4	1987-1997	0.014	3.03
NO_3	1987-1997	0.017	3.59
Cl	1987-1997	0.031	-0.35
pH	1987-1997	0.000	-0.07
ANC	1987-1997	0.000	-5.81

beginning of the study, but they were already in a depleted state (Stage III) presumably due to long-term ambient inputs of acidic deposition.

Peakflow concentrations of SO_4 and NO_3 increased during the period of treatment (Fig. 4-29). Their concentrations were distributed widely but the increases were enough to result in significant upward trends (Table 4-9). By contrast, Cl decreased (Table 4-9) and the magnitude of the change was much smaller than for SO_4 or NO_3 (Fig. 4-29).

ANC and pH responses indicate that peakflow became increasingly acidic over time. As on WS3, ANC on WS9 decreased significantly over time (Table 4-9) and ANC values transitioned from primarily positive values between 0 and 40 μeq L^{-1} in 1989 and 1990 to almost consistently negative concentrations after 1992 with values between 0 and -60 μeq L^{-1} (Fig. 4-30). The pH values at peakflow on the trend line dropped almost 0.75 units from nearly pH 6 in 1987 to about pH 5.25 in 1997 (Fig. 4-29). As a result of treatment, acidification of peakflow became chronic.

5. DISCUSSION

5.1 Application of Base Cation Results

For solution samples collected from WS3 and WS9, it is clear that different interpretations of cation availability or depletion states can result, depending upon whether soil water or stream water responses are evaluated. Even evaluations based upon chemistry from different streamflow regimes can be different. On both WS3 and WS9, soil water and peakflow results reflected processes of cation mobilization (Stage II) followed by progressive depletion (Stage III). In some cases base cation losses were great enough to move the soils to equilibrium with weathering inputs (Stage IV). By

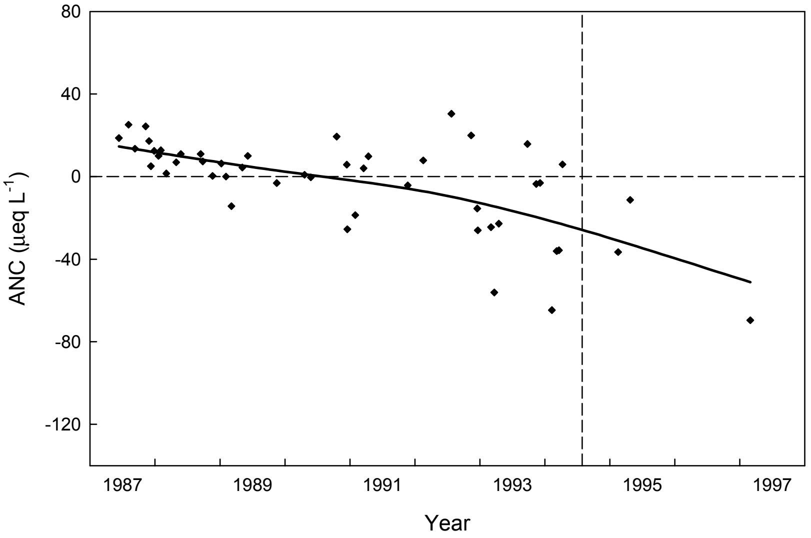

Figure 4-30. ANC concentrations of peakflow from WS9. Dashed vertical line marks end of treatment.

contrast, baseflow results generally indicated that the watersheds still had at least small reserves of exchangeable base cations (Stage II).

The dissimilarity in soil nutrients and/or biogeochemical processing of nutrients must be considered and understood to realistically evaluate the base cation and buffering status of the component of the watershed of interest. Sufficiently long time series data are more commonly available from stream water than from soil water, and stream water chemistry often is considered an integrator of all the processes within a watershed. Thus, there may be a tendency to apply those stream water data to the entire watershed. Since baseflow predominates the duration of annual flows, and groundwater can make up as much as 75-85 percent of stormflow (Hewlett and Nutter 1969, Swistock et al. 1989) in forested headwater streams, the bias of long-term stream water data sets will be toward baseflow conditions which, at least for WS3 and WS9, were much more different from soil water than concentrations at peakflow.

If the application of stream water results is to determine the acid/base status of the aquatic environment, it is reasonable to use interpretations from stream water. However, if the application is to obtain information about the soils or potential effects on vegetation or soil fauna across the greater watershed area, stream water interpretations may not be applicable if stream water is dominated by deep groundwater sources. In order to make interpretations about upland soil conditions from stream water, one should first ensure that stream water and soil water originate from the same sources or assess that they are in similar states of cation availability or depletion. If they are not, soil water should be substituted for stream water in the assessment.

We cannot speculate whether interpretations about soil base saturation levels collected from the uplands over time would have resulted in findings similar to soil water because soil samples were not collected frequently enough (Chapter 3) to examine trends closely, and the number of soil samples collected may have been too small to make a meaningful interpretation given the spatial variability of soil chemistry. However, the conceptualized base cation depletion model presented by Fernandez et al. (2003) also included conceptualized trends in base saturation.

5.2 Application of Nitrate Responses

Stoddard (1994) described N saturation in a series of stages based on seasonal stream NO_3 concentrations. In Stage 0, stream NO_3-N concentrations are near zero year round. In Stage 1, NO_3-N becomes elevated (0.5 to 0.8 mg NO_3-N L^{-1}) in the dormant season due to a lack of microbial and vegetative uptake. Stage 2 is characterized by elevated stream NO_3-N concentrations year round. WS4 has been cited as the best example of a Stage 2 N saturated watershed in the northeastern United States, exhibiting elevated year-round NO_3 concentrations (Stoddard 1994, Peterjohn et al. 1996, Fenn et al. 1998, Williard et al. 2003). At the beginning of the study, WS3 stream water (i.e., weekly grab samples and baseflow) had approximately the same concentrations of NO_3 as WS4, but WS3 now is at about three times that level (Figs. 4-17 and 4-19)**,** so it too clearly is in Stage 2 N saturation. WS9 stream water concentrations were lower at the beginning of treatment (Fig. 4-22) than on WS3 or WS4, but the most recent years of data show that NO_3 concentrations in stream water on WS9 are now approximately equal to that on WS4 and equal to that on WS3 in the mid 1980s. The degree of seasonality for WS9 NO_3 concentrations is somewhat greater than WS3 but similar to WS4. Thus, stream water concentrations on WS9 also indicate that it is now behaving in accordance with Stage 2 N saturation.

The soil water NO_3 concentrations from WS3 and WS9 show that some type of retention of NO_3 had occurred in the watershed soils even during prolonged elevated levels of N inputs. This behavior was demonstrated to a lesser extent in WS3 baseflow. That NO_3 retention can be induced after periods of elevated losses simply by continuing to add N to the system at elevated rates is intriguing because it provides a substantially different perspective on how long-term elevated atmospheric deposition may affect forest ecosystems in the long term. Other researchers have found some unexpected long-term NO_3 results in stream water (Goodale et al. 2003) and in studies with manipulated increases of N inputs (Fernandez, unpublished results). It is clear that our current understanding of N cycling in forests is incomplete. Some of the newer ideas about N retention processes are based on kinetic principles or are hypotheses (e.g., Davidson et al. 2003, Dail et al. 2001, Hansen et al. 2001) while others have been documented in soils in the field or laboratory (Fitzhugh et al. 2003), but there is still much to be learned about factors that control the processes and how important those processes are across an entire watershed (Fitzhugh et al. 2003).

5.3 Regional Susceptibility to Acidification

The geology and overlying soils on the study watersheds are considered to be only moderately sensitive to acidification (pers. comm. Stephanie Connolly, Monongahela National Forest Soil Scientist). Consequently, watersheds underlain by more acidic geologies in the area, such as Pottsville and Allegheny formations, have received the majority of attention in terms of defining critical loads, adjusting vegetation management strategies, and development of possible mitigation strategies (e.g., see the Monongahela National Forest Plan Revision). Indeed, at the start of this study, many people believed that there would be little or no measurable changes to solution chemistry because the amount of N and S added annually represented only a small proportion of the total pools within WS3 and WS9 and a moderate amount of buffering capacity existed. Consequently, the onset of acidification as evidenced by base cation depletion, decreasing pH and ANC, and perhaps most dramatically, the transition from episodic to chronic acidification in baseflow over such a short period of time was somewhat surprising.

These soils have been subjected to decades of S and N inputs that greatly exceed the cumulative loads added during treatment. That acidification effects were documented at these relatively modest input levels suggests that a large land base in this region may be more sensitive to acidification than previously believed. For example, watersheds that are classified as moderately sensitive to acidification occupy approximately 32 percent of the land base within the proclamation boundary of the Monongahela National Forest. In a synoptic survey of 27 watersheds located in close proximity to and on similar geology as the Fernow Experimental Forest, Williard et al. (2003) found that NO_3 concentrations in baseflow for many streams (Fig. 4-31) were greater than the highest NO_3 concentrations observed on WS9, and several streams had concentrations that were approximately equal to those found after 3-5 years of treatment on WS3. The latter concentrations also correspond to NO_3 concentrations that were present at the time the ANC of WS3 baseflow was transitioning from positive to negative values. The NO_3

concentrations at the beginning of the study for WS3 and WS4 were similar, and more than 10 of the streams surveyed by Williard and his colleagues had NO_3 concentrations in baseflow that were greater than WS4.

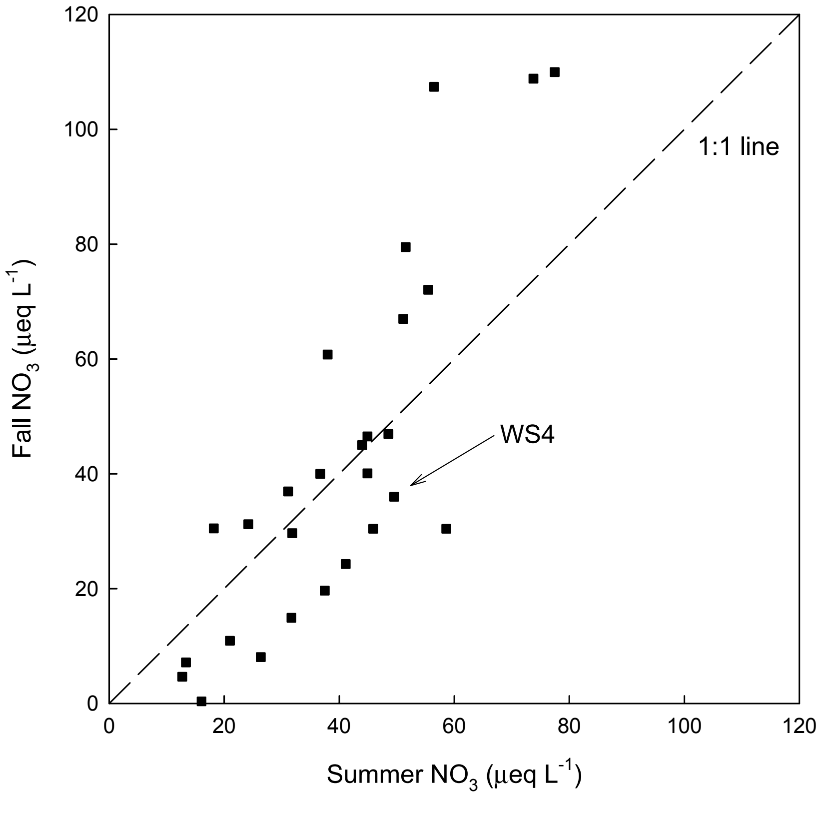

Figure 4-31. Summer and fall stream NO_3 concentrations for 27 watersheds located near WS4.

The relatively rapid progression toward acidification on these watersheds has potential implications in relation to future forest management decisions. The S and N loads added as fertilizer to the watersheds represent about 16-30 years of ambient deposition. During that treatment period, approximately 187 kg Ca ha^{-1} were exported from WS3 in stream water. This loss was, on average, 46 percent of the base cation loss and Ca was the cation that had the greatest effect on ANC. A major pool of Ca in WS3 is in the bolewood of trees. Calcium stored in the bolewood of WS3 is estimated to be approximately 155 kg ha^{-1} (see Chapter 7). Therefore, removal of all of the bolewood from WS3 by clearcutting would effectively remove about as much Ca as was exported by the elevated S and N inputs. As a result, intensive harvesting may affect the moderate to long-term susceptibility of soil to acidification even on sites classified as only moderately sensitive to acidification.

6. SUMMARY AND CONCLUSION

There was strong evidence of acidification of both soil water and stream water by the ammonium sulfate treatments on WS3 and WS9. With respect to soil water, WS3 and WS9 went through periods of increased base cation exchange and mobility due to increasing concentrations of SO_4 and NO_3, followed by periods of progressive base cation depletion in soil water. Some of the base cations in some soil horizons eventually became sufficiently depleted that they reached equilibrium levels, such that supplies of exchangeable base cations to soil solution were derived only from weathering, while others continued to be depleted through the end of data collection. Potassium concentrations increased on both watersheds due to inputs of the acid anions, but there was a lag in K increases in WS3. Exchange and mobilization of K occurred much later than for the other cations, which was surprising since it typically is exchanged more easily into soil solution than Ca and Mg. The reason for the delayed release of K is unknown.

Base cation recovery was observed in WS9 soil water following the termination of acidification treatments in 1994. Calcium and Mg concentrations in soil water declined below equilibrium concentrations as available base cations became associated with soil exchange sites. Eventually they transitioned even further through the recovery period and again moved toward equilibrium condition.

Nitrate and SO_4 leaching were obvious in soil water; the concentrations increased immediately and rapidly in response to the first fertilizer application and continued to increase for a number of years. However, as time progressed retention of both NO_3 and SO_4 were observed. The retention of SO_4 was believed to be at least partially due to the creation of anion adsorption sites by increasing SO_4 inputs and by pH-dependent charge development on clay particles that resulted in increased SO_4 adsorption as the pH decreased. The delayed retention of NO_3 was unexpected based on N-saturation theory. Nitrogen retention in forest soils occurs only if they are N deficient and should begin at the time that N inputs become elevated. The reasons for the much later retention are unknown, but are believed to be due largely to abiotic immobilization, which is a focus of contemporary N cycling research. Even after N inputs were terminated on WS9, NO_3

concentrations in soil water did not increase so, at least in the short term, N retention has not been reversible. The retention of these acid anions did not have a substantial effect on controlling base cation depletion; by the time anion retention occurred most of the base cations already had transitioned from the mobilization phase into the depletion phase.

Soil water acidity was substantially affected by the increased mobility of NO_3 and SO_4 and counterbalancing base cations. At the beginning of treatment, ANC levels on WS3 and WS9 were negative but always >-100 μeq L^{-1}. With progressive S and N additions, soil water ANC on WS9 dropped to as low as ~ -300 μeq L^{-1}, and on WS3 they fell to as low as -800 μeq L^{-1}. The smaller ANC drop on WS9 reflects the shorter period of treatment than on WS3 (8 yr vs. 15 yr). On WS9, the ANC concentrations in soil water returned toward pretreatment levels after fertilization was terminated in 1994. The increasing deficit in available counterbalancing charge by base cations relative to acid anions was believed to be fulfilled by Al^{3+}. Depending upon the horizon, approximately 60 to 80 percent of the negative charge in soil solution was counterbalanced by Al^{3+} in WS3, and in WS9 about 70 to 80 percent of the negative charge was counterbalanced by Al^{3+}.

While the patterns of base cation responses in baseflow and peakflow were not as marked as they were in soil water, acidification of both streamflow regimes was documented. On WS3, base cations were in sufficient supply in the soil source areas and bedrock that provide nutrients to baseflow so that only base cation mobilization was evidenced through the 15 years of treatment; the depletion phase was not entered for any of the four measured base cations. By contrast, on WS9, the supply of major base cations to buffer baseflow must have been substantially less because depletion of Ca and Mg began about 2-3 years into treatment. Sulfate retention, again presumably because of adsorption was observed for WS9 baseflow, but not for WS3 baseflow. Conversely, NO_3 retention was observed for WS3 baseflow but not for WS9. The pH of baseflow declined for both watersheds, but more on WS3 than WS9. On average, the drop was about 0.75 pH units on WS3 and about 0.3 pH units on WS9. The pH of baseflow on both watersheds remained above 5.0, so Al that came into solution to help fulfill cation charge deficits probably existed primarily as Al^{2+}. The changes to acidity on WS3, which was treated almost twice as long as WS9, were very significant and resulted in WS3 baseflow moving from being only episodically acidic to chronically acidic. WS9 was moving toward being chronically acidic but the termination of treatment allowed baseflow on WS9 to remain largely episodically acidic.

The base cations in peakflow on WS3 generally showed initial periods of mobilization followed by progressive depletion. On WS9, there were no significant changes to Ca or Mg, inferring these two ions largely were depleted from the source areas that contribute nutrients to streamflow during storm events, and weathering rates were controlling the amounts of Ca and Mg in peakflow. Potassium and Na concentrations showed these ions also were in limited supply before treatment began and were becoming progressively depleted over time. Increases to NO_3 were more marked and significant than for SO_4 in peakflow on WS3. The NO_3 data for peakflow also suggested retention was occurring for it, but the broad spread of the data make this a bit less certain than the NO_3 retention that was suggested especially for soil water. Sulfate and NO_3 increased throughout the entire period of record, though the data were spread rather widely. The pH of peakflow on both WS3 and WS9 fell through the period of record. The general decline on both watersheds was less than 0.5 pH units, though for individual storms the decline was as much as a full pH unit or more over the life of the study. For all but one or two storms on each watershed, the pH at peakflow remained above 5.0. The ANC of storm runoff for both watersheds moved from being only episodically acidic at the beginning of treatment to being chronically acidic by the time stormflow sampling was terminated.

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Chapter 5

VEGETATION AND ACIDIFICATION

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1. INTRODUCTION

In this chapter, the impact of watershed acidification treatments on WS3 at the Fernow Experimental Forest (FEF) and at WS9 on vegetation is presented and summarized in a comprehensive way for the first time. WS7 is used as a vegetative reference basin for WS3, while untreated plots within WS9 are used as a vegetative reference for WS9. Bioindicators of acidification impacts that will be considered include several measures of tree and stand growth rates, foliar chemistry, bolewood chemistry, and herbaceous species composition and diversity. These studies enhance our understanding of the inter-relationships of changes in soil conditions caused by the acidification treatment and the condition of forest vegetation. Treatments on these watersheds were described in Chapter 2. Scientific names of plant species mentioned by common name in the text are given in the Appendix.

Although the original objective of the Fernow acidification studies was to evaluate the effects of acidic deposition on solution chemistry and ecosystem processes, it is also important to understand the linkage between soil and solution processes and biotic effects. In particular, in this chapter we report the results of a number of studies designed to investigate the impact of soil acidification treatments on the health and growth of forest vegetation.

Productivity of vegetation is often used as a measure to detect effects of treatments on vegetation. Common measures of forest productivity include

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aboveground biomass production and stand growth. Stand growth is measured in terms of basal area, biomass or cubic volume. Growth can also be measured as individual tree growth rates, leaf area production or net primary productivity. Plants growing in chronically acidified soils may exhibit decreased calcium (Ca) uptake over time due to competition with aluminum (Al) (Cronan 1991). The effects of nutrient deficiencies on tree growth vary by species; however, severe deficiencies will adversely affect almost all tree species. If treatments on WS3 caused significant Al mobilization which led to accelerated base cation leaching and decreased availability of important nutrients to critically low levels, then radial and basal area growth for all tree species on WS3 could be significantly reduced. Diameter growth expressed as basal area increment has been routinely used to show impacts of fertilization on tree growth (Wilmot et al. 1996, Long et al. 1997, Demchik and Sharpe 2000). Species composition and diversity are increasingly important measures which are believed to be linked to productivity. The effects of various treatments can also be considered by their effects on chemical constituents of the vegetation, or on physiological processes.

Foliar chemical analysis is a tool that is commonly used to assess changes in growth rates and health of forest vegetation. Our understanding of critical foliar nutrient values is most developed for commercial conifer species, but we can evaluate treatment effects in hardwood species as well. The utility of foliar analysis is based on the assumption that adding nutrients to a stand of trees increases availability of nutrients in the soil, which, in turn, is reflected in nutrient uptake and nutrient content of the vegetation. The application of ammonium sulfate fertilizer was expected to increase the availability of nitrogen (N), which could result in growth stimulation if this stand, or a particular species within the stand, were limited by N availability. Increased N availability could also lead to nutrient imbalances, which might be manifest as growth declines. Soil chemical differences that were hypothesized as a result of the acidification treatment were expected to result in differences in availability of exchangeable cations such as Ca, magnesium (Mg), manganese (Mn) and Al. Acidification-induced reductions in base cations such as Ca and Mg may lead to decreased uptake of these nutrients and increased stress for plants, while increased levels of Mn and Al can create toxic conditions for trees.

Study of the chemical element content of bolewood xylem has been used to assess the impact on forest health in cases where the soil has been acidified or limed (DeWalle et al. 1991, DeWalle et al. 2003). Changes in the availability of cations in soil solution cause changes in ion content of tree sap. Ions in tree sap tend to become adsorbed within cell walls of xylem sap-conducting tissue. As trees grow and add a new growth ring of xylem tissue each year, the sequence of chemical element concentrations in tree rings can potentially preserve a record of soil water chemical changes.

Bolewood concentrations of Ca, Mg, Mn and molar ratios such as Ca/Mn have been commonly used to indicate changes in soil acidity. Lower levels of bolewood Ca, Mg, and Ca/Mn and higher levels of bolewood Mn are thought to be indicators of increased stress in trees. Although soil acidification may cause increased Al in soil solution, increased levels of Al in bolewood are generally not found due to exclusion at the soil-root interface (Taylor 1987) or retention by the root cortex (Tomlinson 1990).

Field studies investigating the effects of N on species diversity of plant communities, such as the Park Grass Experiment in Rothamsted, England (Silvertown 1980) and the Cedar Creek Natural Area (e.g., Tilman 1987), have found that excess N can profoundly alter species composition and decrease species diversity of plant communities. Unfortunately, most such studies have been carried out on herb-dominated ecosystems, whereas relatively few have been done in forested ecosystems (Gilliam et al. 2006). Because of the coincidence of forest ecosystems with regions of high N deposition and because most of the biodiversity of forests occurs in the herbaceous layer, it is imperative to understand the response of herb layer composition and diversity to excess N.

The response of herb-dominated communities to experimental additions of N can be rapid. Tilman (1987) reported significant changes in species composition of the Cedar Creek Natural Area to all levels of N additions within one year following treatment. Although growth and foliar nutrient concentrations of herb layer plants are generally sensitive to soil fertility (Muller 2003), it might be expected that the herb layer of forests may display a lag-response to experimental additions of N, given the structural complexity of forest ecosystems, wherein resource availability can be greatly altered by other vegetation strata.

2. VEGETATION DESCRIPTION

2.1 Fernow

2.1.1 Stand Conditions – WS3 and WS7

Interpretation of the impacts of acidification on vegetation on WS3 relative to WS7, depends in part upon understanding the status and dynamics of the species composition of the forest during the experiment. Forest vegetation on both watersheds, which was generally described in Chapter 2, was approximately the same age, having largely originated after cutting and herbicide treatments ending in 1970. However, watersheds differed in the nature of earlier vegetation treatments and aspect, which may have influenced species composition and growth at the time of treatments. Specifically, prior to 1970 WS7 was maintained barren with herbicides for several years, while WS3 was allowed to regenerate immediately following clearcutting.

Table 5-1 shows the changes in basal area for all trees greater than 2.54 cm diameter at breast height (dbh) and dominant/co-dominant trees on WS3 and WS7 during the experiment based upon inventories in 1990/91, 1996, 1999, and 2003. Basal area of black cherry, expressed as % of dominant/co-dominant trees on WS3 and WS7, gradually increased over the course of the study, in contrast to most other species. Yellow-poplar was also an increasingly important species on WS7, but a mix of other species still dominated. Red maple represented a small but relatively constant proportion of overstory trees during the experiment on both watersheds. Early successional species, such as sweet birch, fire cherry, and black locust, decreased gradually in the overstory, while more shade tolerant species, such as sugar maple and American beech, increased in relative abundance.

2.1.2 Herbaceous Layer Characteristics – WS3 and WS7

The herbaceous layer was studied initially on four watersheds of FEF – WS3, WS4, WS7, and WS13 – in 1991 and 1992, with further emphasis placed on WS3, WS4, and WS7 in conjunction with *in situ* soil incubations in 1994 (see Chapters 3 and 7). Despite large differences in stand age among these watersheds, with WS3 and WS7 trees being approximately 20 years old versus 80-100 years for WS4 and WS13 in 1991, there were minimal differences in herb layer composition, cover, biomass, and species diversity (Gilliam et al. 1995, Gilliam 2002). This was in sharp contrast to measures of tree communities, which varied more predictably with stand age along a successional gradient. Whereas WS3 and WS7 were higher in stem density, lower in basal area, and dominated by early successional species, such as yellow-poplar, black cherry, and sweet birch, WS4 and WS13 had higher basal area, lower stem density, and were dominated by late successional species, such as northern red oak and sugar maple (see Chapter 2 and Gilliam and Roberts 2003).

A complete floristic study of WS3, WS4, and WS7 was carried out by Aulick (1993). Using Sorensen's Coefficient of Similarity (Barbour et al. 1999), she found that WS3 was floristically more similar to WS4 (similarity coefficient of 0.58) than it was to WS7 (0.49). Rather than attribute this discrepancy in floristic similarity to treatment effects, Gilliam et al. (1994) concluded that it arose from the high cover of a few fern species (e.g. shield

Table 5-1. Dominant species (% basal area) for WS3 and WS7 for all stems >2.54-cm dbh and dominant/codominant stems during acidification experiment. WS3 initial=1990, WS7 initial=1991. Data obtained from 25 0.04-ha permanent growth plots on each watershed. For scientific names of trees, see Appendix A.

Species	1990/91		1996		1999		2003	
	All	Dom/ Codom	All	Dom/ Codom	All	Dom/ Codom	All	Dom/ Codom
	%							
WS3								
Black cherry	36.9	55.8	45.4	57.5	47.9	61.4	51.0	60.9
Yellow-poplar	4.5	5.8	4.6	6.3	4.9	6.8	5.7	6.1
Red maple	14.4	7.7	13.1	6.3	12.0	5.7	11.5	7
Sweet birch	5.4	3.8	5.4	3.8	4.9	3.4	5.1	3.5
N. red oak	4.5	5.8	4.6	5.0	4.9	5.7	5.1	5.2
Amer. beech	2.7	0	2.3	0	2.1	0	2.5	0
Sugar maple	1.8	0	1.5	0	1.4	0	1.3	0
Fire cherry	9.0	11.5	8.5	11.3	7.7	10.2	6.4	7.0
Black locust	2.7	1.9	1.5	1.3	1.4	1.1	1.3	0.9
Fraser magnolia	4.5	3.8	3.8	2.5	4.2	2.3	3.8	2.6
White ash	0.9	0	0.8	0	0.7	0	0.6	0.9
WS7								
Black cherry	15.1	18.6	17.3	20.6	17.9	22.4	20.5	23.6
Yellow-poplar	17.4	25.6	21.4	27.0	23.6	29.9	26.2	30.3
Red maple	8.1	2.3	8.2	3.2	8.5	3.0	8.2	3.4
Sweet birch	19.8	20.9	20.4	19.0	20.8	17.9	20.5	19.1
N. red oak	1.2	2.3	1.0	1.6	0.9	1.5	1.6	1.1
Amer. beech	0	0	0	0	0	0	0	0
Sugar maple	4.7	0	5.1	0	4.7	0	4.9	1.1
Fire cherry	9.3	11.6	7.1	9.5	5.7	7.5	3.3	4.5
Black locust	9.3	14.0	10.2	12.7	9.4	11.9	9.0	11.2
Fraser magnolia	0	0	0	0	0	0	0	0
White ash	2.3	2.3	2.0	3.2	2.8	1.5	2.5	2.2

fern, Christmas fern – see Table 5-2) on WS7 that were either absent from or of low cover on the other watersheds. The prominent fern component on WS7 was ascribed to its more north-northeast slope aspects, wherein ambient temperatures are generally lower and soil moisture generally higher than the southeast-south-southwest slope aspects of WS3 and WS4. These conditions are generally conducive to greater success of ferns (George and Bazzaz 2003). Carvell and Perkey (1997) found that wood and Christmas ferns could be used as diagnostic plants to identify mesic sites. Gilliam et al. (1994) summarized herbaceous layer cover and foliar chemistry for the 1991 sampling of WS3, WS4, and WS7, and they concluded that there were few differences among watersheds in any measured variable that could be attributed to the acidification treatment on WS3.

Table 5-2. Herbaceous layer species names and codes.

Species name	Common name	Code
Acer pensylvanicum L.	striped maple	ACPE
A. saccharum Marsh.	sugar maple	ACSA
Dryopteris marginalis (L.) A. Gray.	shield fern	DRMA
Laportea canadensis (L.) Webb	stinging nettle	LACA
Panicum spp.	panic grass	PANI
Polystichum acrostichoides (Michx.) Schott.	Christmas fern	POAC
Prunus serotina Ehrh.	black cherry	PRSE
Rubus spp.	blackberry	RUBU
Sassafras albidum (Nutt.) Nees	sassafras	SAAL
Smilax glauca Walter.	catbrier	SMGL
S. rotundifolia L.	greenbrier	SMRO
Stellaria pubera Michx.	star chickweed	STPU
Viola spp.	violet	VIOLA

2.2 Stand Conditions – WS9

The Clover Run watershed, hereafter known as WS9, was also subjected to acidification treatments following a history of mountain farming, removal of regrowing hardwood forest following farm abandonment, and reforestation with planted Japanese larch, as described in Chapter 2. Larch were planted in 1984 and acidification began in April 1987 after about three years of growth. A buffer zone of regrowing hardwoods, which received treatments was left along the perennial stream channel on the watershed. Effects of treatment on WS9 were evaluated by comparing response on six 30-m x 30-m control plots randomly located on the watershed that did not receive surface applications of chemicals with the response on the adjacent treated areas. See Chapters 3 and 4 for a map of WS9 with plot layouts and treatment assignments.

3. METHODS

3.1 Tree and Stand Growth

Two methods were employed to evaluate potential impacts of the acidification treatment on tree growth on the experimental watersheds. One method employed repeated measurements of tree diameter on growth plots located on WS3 and WS7, and measurements of height and diameter of larch trees on treatment and control plots on WS9. The second method involved annual radial growth analysis of increment cores and wood disks from trees sampled for dendrochemical analysis.

3.1.1 Growth Plot Analyses

Twenty-five randomly located 405-m^2 plots were established in 1990 (WS3) and 1991 (WS7), 1 and 2 years after treatments began, respectively. The diameter of all trees greater than or equal to 2.54 cm was recorded and the trees were permanently tagged. These plots were re-measured in the dormant season of 1996, 1999 and 2003. The data set included more than 5,600 trees. Changes in diameter over time on these plots were converted into basal area growth, volume growth using local volume tables for the FEF, and biomass growth from equations developed by Brenneman et al. (1978). Basal area and biomass included all stems $\geq$2.54 cm dbh and cubic volume included all stem $\geq$12.7 cm dbh. Analyses presented here are for net volume growth on plots including the effects of growth of surviving trees, ingrowth of trees reaching measurable size, and mortality. For comparative purposes the statistical analyses were conducted for the 1990-1996 six-year period for WS3, the 1991-1996 five-year period for WS7, and the 1996-2004 eight-year period for both watersheds. Since the total analyses included net volume growth of all species and trees on each plot, further analyses were also repeated for two clusters of plots based on the relative abundance of black cherry and yellow-poplar (n = 15 for WS3 and n = 14 for WS7) or sweet birch and red maple (n = 10 for WS3 and n = 11 for WS7). A multiple-factor repeated measures analysis of variance with watershed and species group as class variables, plot as the subject, initial plot relative density as a covariate and annual growth components as the repeated measure was used to compare annual net growth (Nowak 1996).

For WS9, the effects of the acidification treatments on the growth and development of the Japanese larch plantation were evaluated after 9 growing seasons using six 12.2 m x 15.2 m unfertilized control plots with buffers and 43 0.004-ha circular fertilized plots (Kochenderfer et al. 1995). Three condition classes were used to describe the larch trees: 1. good vigor – dominant or co-dominant trees. 2. medium vigor – intermediate trees. 3. poor vigor – low intermediate or overtopped trees. Diameter and height were measured on all trees within the measurement plots.

3.1.2 Tree Core Analysis

The objective of radial growth analysis was to determine if annual radial and basal area growth differed significantly between WS7 and WS3 over time during the experiment. No comparable radial growth studies were conducted on WS9. Radial and basal area growth for yellow-poplar, black cherry, red maple and black locust trees on WS3 and WS7 were compared after 12 years of treatment. The methods used to conduct this research are condensed here, but are discussed in depth elsewhere (Odenwald 2002). To analyze growth rates, a wood core was extracted at breast height with increment borers from ten yellow-poplar, black cherry, and red maple trees on WS3 and WS7; thus the data set included a total of 60 trees. Trees on permanent growth plots were not cored. In preparation for tree-ring growth analysis, these cores were dried, mounted on wood blocks, sanded, and examined using a high resolution scanner and WinDENDRO 6.5d software manufactured by Regent Instruments Inc. (Quebec, Canada). Alternatively, black locust trees were sampled by collecting wood disks at breast height from ten felled trees on each watershed. Black locust disk surfaces were prepared for growth analysis similar to the wood cores described above. Black locust growth data have not been previously published.

Use of radial growth increment comparisons requires correction for differences in tree age or diameter and site specific conditions. In this section use is made of relative radial growth rates (RRG) (Odenwald 2002) defined as:

$$\text{RRG} = \frac{\text{annual radial increment (mm) for a year after treatment}}{\text{mean annual radial increment (mm) in that tree over 14 years before treatment.}}$$

The RRG thus indexes growth in each tree to average radial growth in that same tree for years prior to treatment to account for site differences. The RRG is expected to gradually decline during the treatment period as radial increment declines and diameter increases. Mean RRG for all trees of a species was compared between treatment and reference watersheds year by year.

Annual basal area increments in mm^2 (BAI) were also computed for each tree in each year before and after treatment (Odenwald 2002). Using BAI data from Odenwald (2002), regression relationships for mean annual BAI between WS3 and WS7 for years prior to treatment (Fig. 5-1) were used to predict expected BAI for years after treatment for black cherry, yellow-poplar and red maple trees. Relationships in Figure 5-1 adjust for the growth effects of differences in site and tree size between WS3 and WS7 prior to treatment. The differences between predicted BAI and actual BAI measured for years after treatment began were tested for significance and used as a measure of treatment effect.

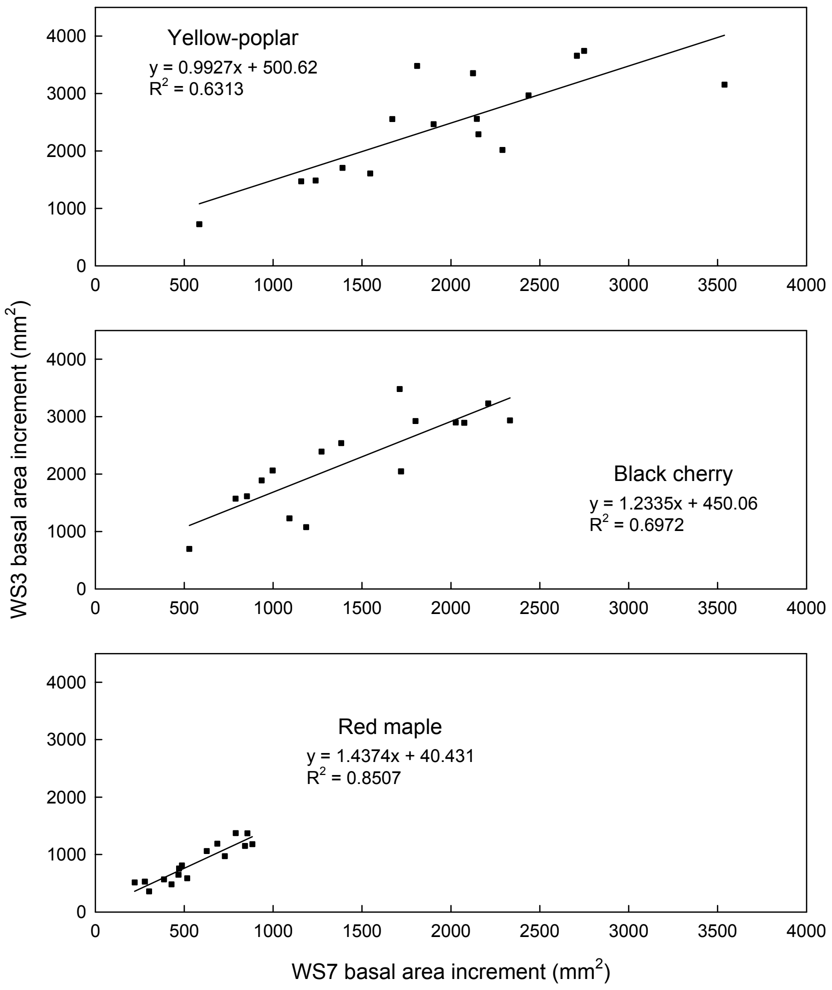

Figure 5-1. Regression relationships between mean annual basal area increment (mm^2/tree) of yellow-poplar, black cherry, and red maple trees on WS3 vs. WS7 for pretreatment years (1973-1988, 10 trees per species each year, based upon data from Odenwald 2002).

3.2 Foliar Chemistry

Foliage was sampled in 1992 from WS3 and WS7 (sweet birch, yellow-poplar, black cherry and red maple) as part of a total biomass sampling for nutrients (Adams et al. 1995). In 1997 and 2002, foliage was collected from the upper crown of five trees from each of six species (the four listed above plus northern red oak and sugar maple) from WS3 and WS7, and in 2002 from WS4. Because the data are most complete for WS3 and WS7, for the original four tree species, statistical comparisons were made between watersheds using these data. No foliar data were available for these watersheds prior to the beginning of this study. All of these heretofore unpublished data were collected by personnel with the USDA Forest Service, Northeastern Research Station at Parsons, West Virginia. All tissue nutrient analyses were conducted at the University of Maine Soil and Plant Testing Laboratory, using protocols described by Adams et al. (1995). Samples were collected from the upper crown of two trees per species per treatment plot, where present. Samples were dried and ground (1-mm mesh) and analyzed for N, Ca, potassium (K), Mg, phosphorus (P), Al, boron (B), copper (Cu), iron (Fe), Mn, and zinc (Zn).

Pickens (1995) and Pickens et al. (1995) reported on foliar chemistry of planted Japanese larch trees on WS9 sampled in 1992 and 1993, or six and seven growing seasons after treatments had begun. Thirty larch trees were randomly selected and sampled from a single 25 m x 25 m control and adjacent treated plot, each with a 5-m buffer zone, in the upper northwest corner of the catchment. All needle whorls were sampled on a lateral shoot at breast height just below the terminal shoot from selected trees in each year. Foliar samples were analyzed by inductively coupled plasma emission spectroscopy for Al, Ca, K, Mg, Mn, sulfur (S), and P, and for N using the Kjehldahl method at the Agricultural Analytical Services Laboratory, The Pennsylvania State University. Total height and dbh were also measured.

3.3 Dendrochemistry

Dendrochemistry of three tree species (yellow-poplar, black cherry, and red maple; see Appendix A for scientific names) on WS3 and WS7 was evaluated after four, eight and 12 years of treatment to help assess effects on nutritional status. Black locust was sampled after only 12 years of treatment. Results given here update those previously published (DeWalle et al. 1995, Tepp 1995, DeWalle et al. 1999, Odenwald 2002). Methods employed in the dendrochemical study are detailed elsewhere (DeWalle et al. 1999) and are only summarized briefly here. On WS3 and WS7, wood for most species was extracted as cores at breast height with increment borers from five trees of each species (four cores per tree). Wood from cores from each tree was later separated and composited into 4-yr segments. Wood tissue was destructively analyzed for chemical element content using inductively-coupled plasma emission methods. Simple t-tests were used to determine significance of differences in mean concentration or ratios between treated and control trees. Wood from black locust was only collected after 12 years of treatment. For the locust trees, wood from each annual increment was taken from wood discs collected at breast height from boles of ten felled trees on WS3 and WS7. Wood from each annual growth ring in black locust was combined among all treated and control trees for chemical analysis to give detail for each year. Due to the necessity of such compositing, differences between treated and control trees could not be evaluated statistically for black locust; however, having annual growth ring data can help to show how tree-ring chemistry changes between heartwood and sapwood regions. Some black locust dendrochemistry data have been previously published (DeWalle et al. 2002).

Dendrochemistry of young planted Japanese larch trees on untreated and treated plots on WS9 was evaluated in 1994, seven growing seasons after initiation of treatment in spring 1987. Four increment cores were taken from each of five treated and control trees. Procedures were similar to those described for the Fernow dendrochemistry comparisons (DeWalle et al. 1999). Planted Japanese larch were considered desirable for these comparisons since larch generally has narrow bands of xylem for sapflow that may preserve a record of past soil chemistry changes in heartwood. Additional dendrochemistry studies of larger sawtimber red oak and black cherry in the WS9 streamside buffer zone and nearby control areas were conducted five years after treatments began (DeWalle et al. 1995, 2003).

3.4 Herb Layer Dynamics

The methods employed have been described in detail in other publications (e.g., Gilliam et al. 2001, Gilliam 2002), so we summarize them briefly here. The herbaceous layer was sampled by identifying and visually estimating cover (%) of all vascular plants ≤1 m in height within ten 1 m^2 circular sub-plots in each of seven 0.04-ha circular sample plots in WS3, WS4, and WS7, for a total of 2100 1 m^2 sub-plots. Sampling was carried out monthly from May to October of 1994. Mineral soil was collected by hand trowel at five points within each of the seven plots per watershed to a depth of 5 cm. These five samples were composited, thoroughly mixed, and then placed in two polyethylene bags – one brought back to the laboratory for immediate extraction and analysis (see below) and the other incubated *in situ* by burying it 5 cm beneath the mineral soil surface for ~30 days during the same period described for the herb layer.

Data were analyzed in three ways, the first two to assess temporal variability at different scales and the third to assess spatial variability. First, year-to-year variability was examined by comparing mean cover for the more dominant herb layer species. This was done by combining the 1991/1992 observations with the 1994 study of Hockenberry (1996). To ensure uniformity in these comparisons, data from 1991/1992 were taken as a sub-set of the original 15 plots sampled in each watershed to match the seven plots sampled by Hockenberry (1996). Similarly, only the July samples from Hockenberry (1996) were used to match the sample time used in 1991/1992. Next, seasonal variability was analyzed specifically to address the relationship of herb layer cover to N availability, and hence test for possible responses to the N additions on WS3. Accordingly, monthly mean herb layer cover was compared to monthly rates of mean net nitrification for each watershed separately for the 1994 data.

Spatial variability was assessed with canonical correspondence analysis (Gilliam and Saunders 2003) using Canoco for Windows 4.5. This analysis was performed on each watershed separately and used available N pools (i.e., extractable ammonium (NH_4) and nitrate (NO_3)), rates of net nitrification, and foliar N and N:P ratios in *V. rotundifolia* as environmental variables. This was performed on the July sample only (see above).

4. RESULTS

4.1 WS3 vs. WS7 (Fernow) Results

4.1.1 Tree Growth

4.1.1.1 Growth Plots

In general, annual net growth on WS3 growth plots exceeded that observed on WS7 for the 14 year period. This result was consistent for basal area, biomass and cubic volume growth using repeated measurements on permanent growth plots. Stratifying the analysis by plot species composition and time period indicated that most of the differences in growth between the watersheds occurred during the period from 1990/91 to 1996 and on plots dominated by black cherry and yellow-poplar (BC/YP in Fig. 5-2). There was no evidence that productivity differed in either direction between the watersheds for plots dominated by red maple and sweet birch (RM/SB in Fig. 5-2). For the BC/YP plots, growth on WS3 was greater than WS7 for all measures and time periods ($p < 0.03$), except basal area growth during the period from 1996-2004 ($p = 0.12$). For the RM/SB plots, growth on WS3 and

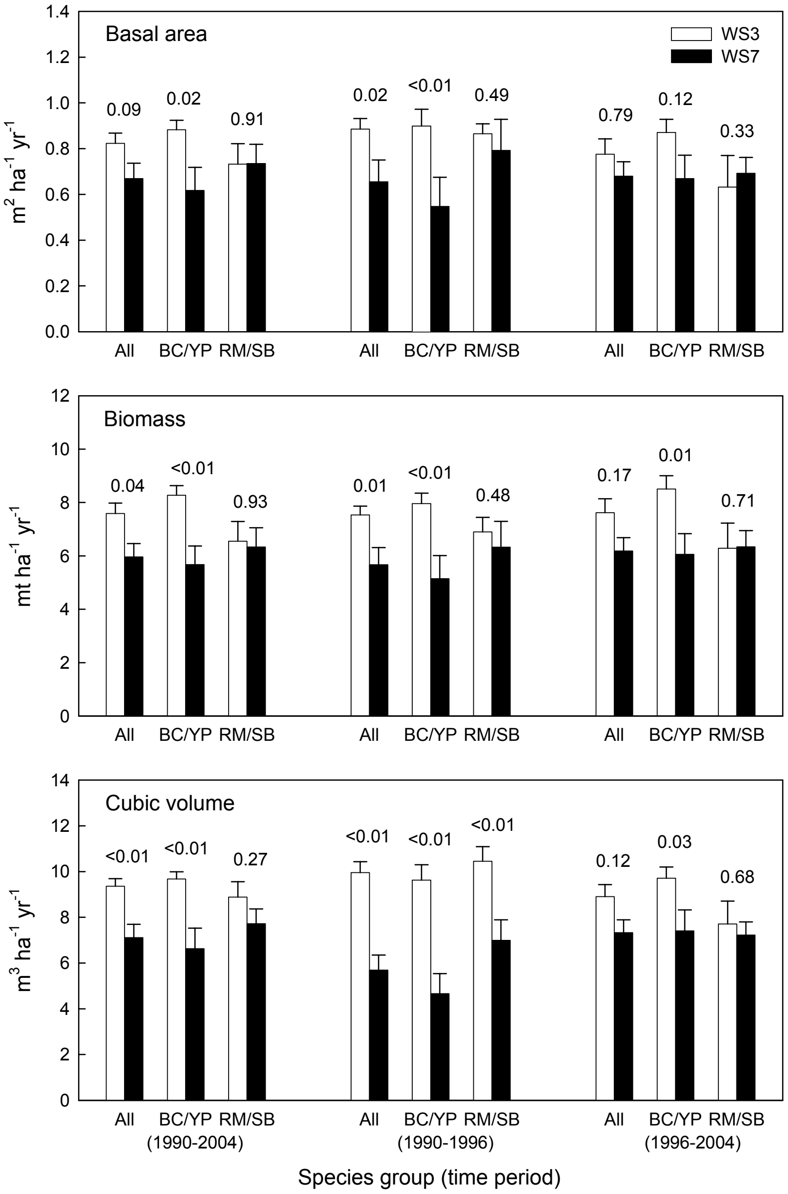

Figure 5-2. Comparison of net annual growth of trees on growth plots, by species composition and time period. Plots were stratified by a higher occurrence of black cherry/yellow-poplar (BC/YP, n = 14 or 15) or red maple/sweet birch (RM/SB, n = 10 or 11) for WS3 and WS7, respectively. Initial measurements were recorded in 1990 for WS3 and 1991 for WS7. Numbers above means and standard errors are significance levels, indicating probability >F statistic for each comparison.

WS7 did not differ by any measure or time period ($p > 0.33$), except cubic volume growth during the period from 1990-1996, where growth on WS3 was greater ($p < 0.01$).

There was no evidence that the acidification treatment reduced productivity from one time period to the next within WS3 on the BC/YP plots (Fig. 5-3). Annual basal area, biomass and cubic volume growth were virtually unchanged for all plots combined ($p > 0.07$) and for the BC/YP plots ($p > 0.59$). On the RM/SB plots, annual basal area growth ($p = 0.02$) decreased on WS3 during the period from 1996 to 2004, but biomass growth ($p = 0.26$) and cubic volume growth ($p = 0.06$) were unchanged. On WS7, both basal area and biomass growth were unchanged during the two time periods for both species groups, while cubic volume growth increased for the BC/YP plots in the second time period ($p < 0.01$).

A comparison of growth between species groups within each watershed and time period indicated that growth in the BC/YP plots was enhanced by the acidification treatment. On WS7, where no treatment was applied, the RM/SB plots grew slightly faster than the BC/YP plots during the period from 1991-1996, and grew at an equal rate during the period from 1996 to 2004 (Fig. 5-4). The growth comparison between species groups was different on WS3, where the species groups had equal growth from 1990 to 1996 and the BC/YP plots grew faster than the RM/SB plots during the period from 1996-2004. This pattern of response was consistent for annual basal area, biomass and cubic volume growth.

Net annual biomass production in 2004, when the stands were 34 years old, averaged 6.0 mt ha^{-1} on WS3 and 4.6 mt ha^{-1} on WS7. These rates are comparable to data summarized by Tritton and Hornbeck (1982), in which annual biomass production of 30-year-old beech-birch-maple stands averaged 4.7 mt ha^{-1}. Periodic net annual biomass growth since the acidification treatments began was 7.6 mt ha^{-1} on WS3 and 6.0 mt ha^{-1} on WS7 (Fig. 5-2).

4.1.1.2 Tree Cores

Results of analyses of RRG ratios indicated that growth of black cherry, red maple and yellow-poplar trees on WS3 had significantly decreased compared to those from WS7 by 1998, after nine years of treatment (Figs. 5-5 through 5-8). RRG ratios declined to levels below 1.0, as is expected with increasing tree diameter on both watersheds, but RRG ratios for each species were significantly lower on WS3 than on WS7 after nine years of treatment. The RRG ratio for black cherry in 2000 did not differ significantly between watersheds.

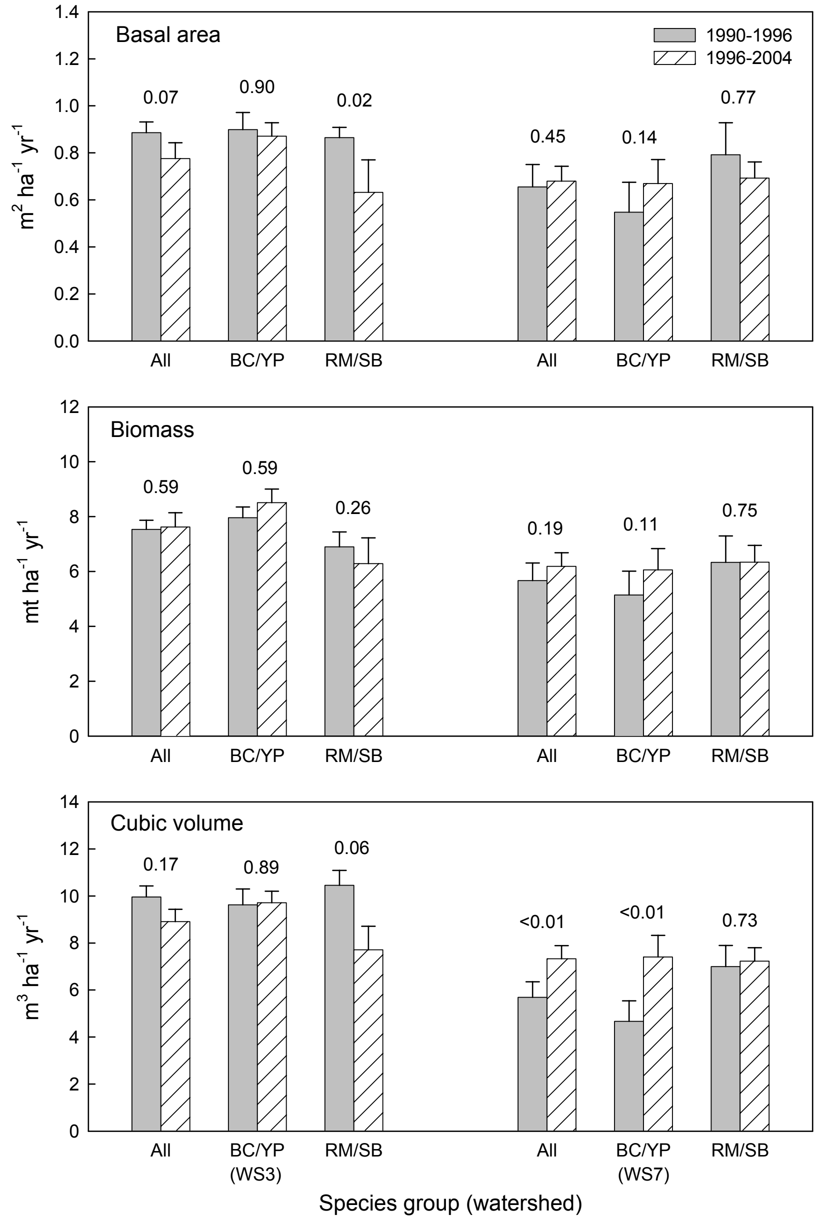

Figure 5-3. Comparisons of net annual growth between time periods for each watershed. Initial measurements were recorded in 1990 for WS3 and 1991 for WS7. Numbers above means and standard errors are significance levels, indicating probability >F statistic for each comparison.

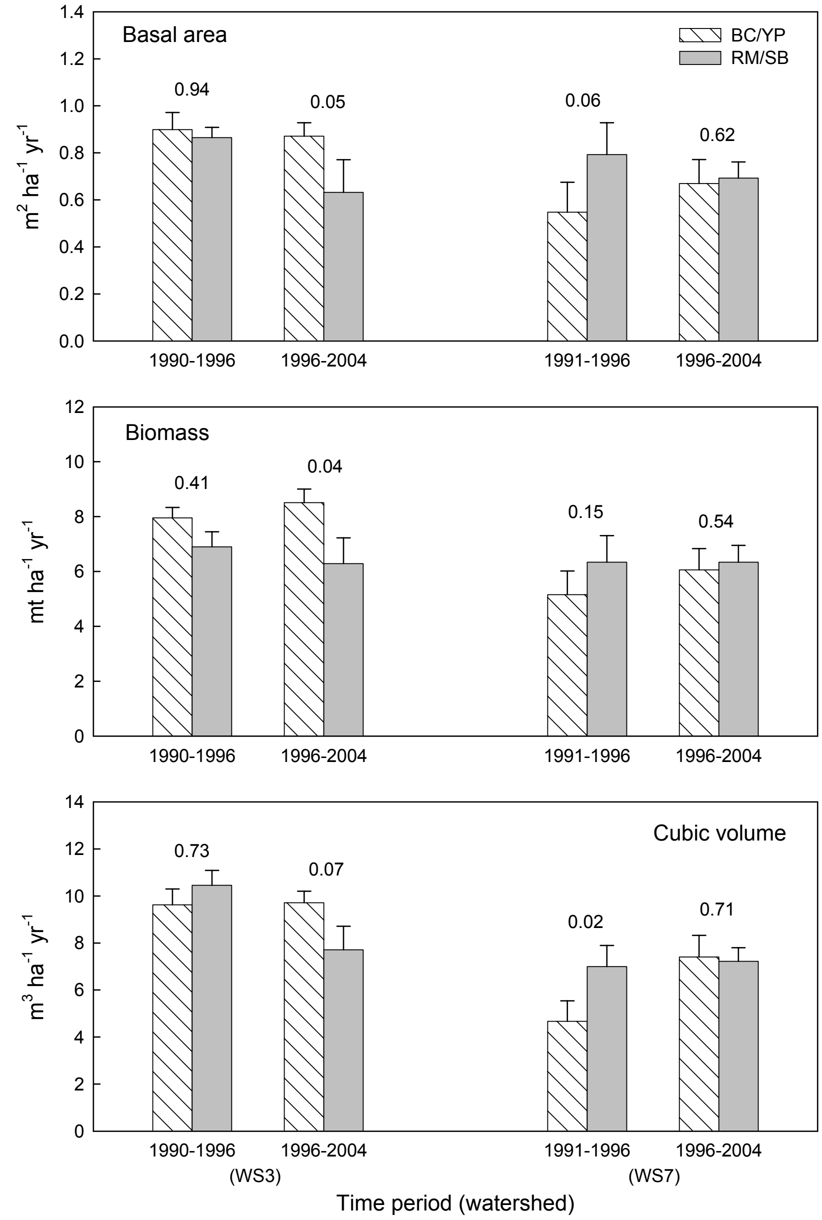

Figure 5-4. Comparisons of net annual growth by plot species group and time period for each watershed. Species groups include black cherry/yellow-poplar (BC/YP) and red maple/sweet birch (RM/SB). Numbers above means and standard errors are significance levels, indicating probability >F statistic for each comparison.

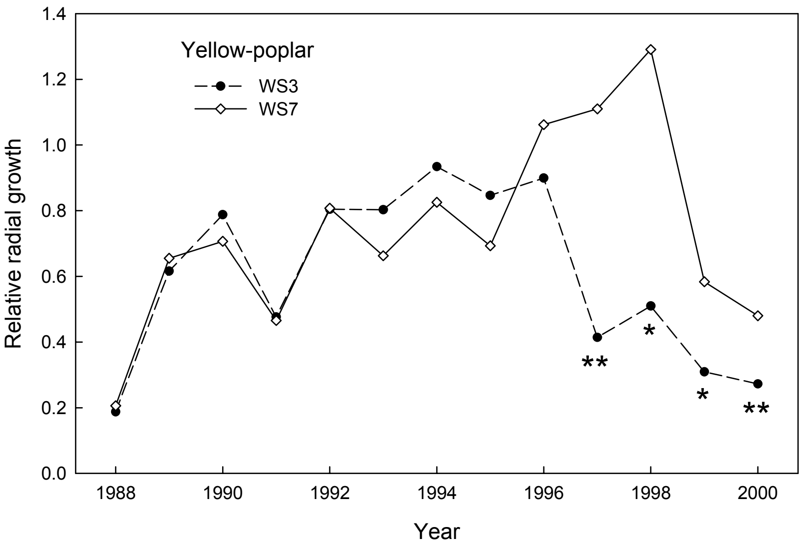

Figure 5-5. Relative radial growth patterns for 10 yellow-poplar trees on WS3 and WS7 during acidification treatments which began in 1989. Asterisks by year indicate significant differences; * $\alpha = 0.1$ and ** $\alpha = 0.05$.

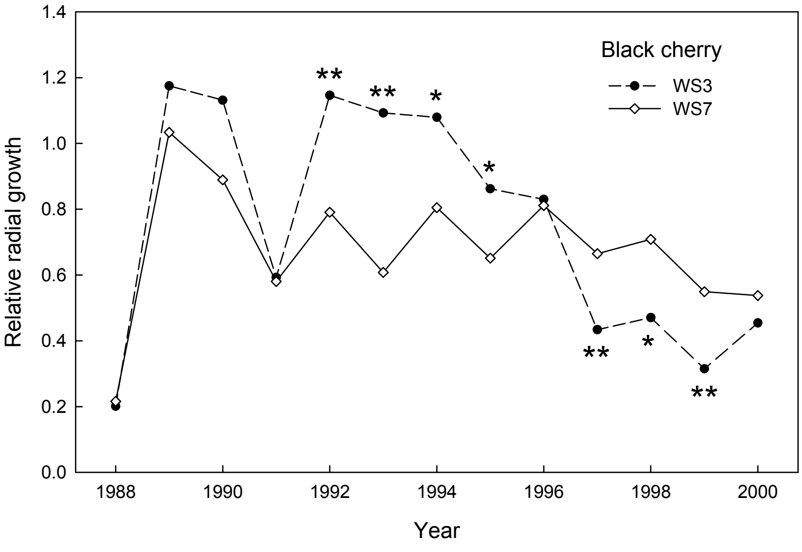

Figure 5-6. Relative radial growth patterns for 10 black cherry trees on WS3 and WS7 during acidification treatments which began in 1989. Asterisks by year indicate significant differences; * $\alpha = 0.1$ and ** $\alpha = 0.05$.

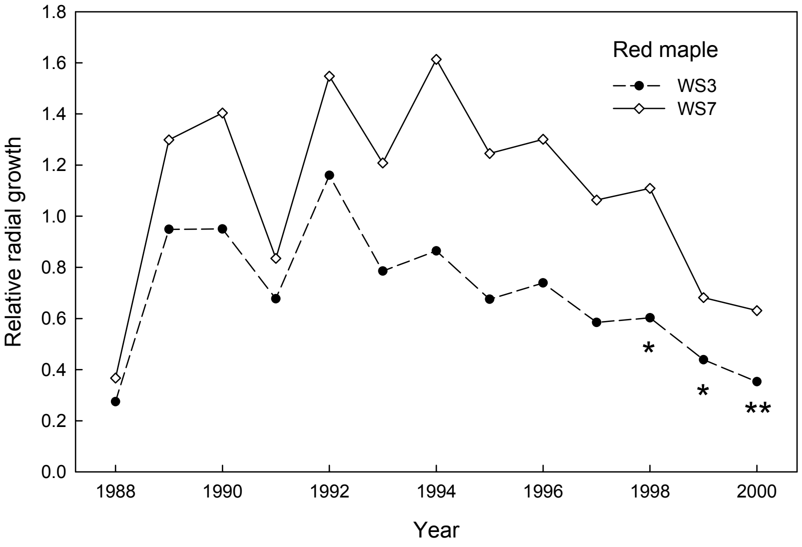

Figure 5-7. Relative radial growth patterns for 10 red maple trees on WS3 and WS7 during acidification treatments which began in 1989. Asterisks by year indicate significant differences; * α = 0.1 and ** α = 0.05.

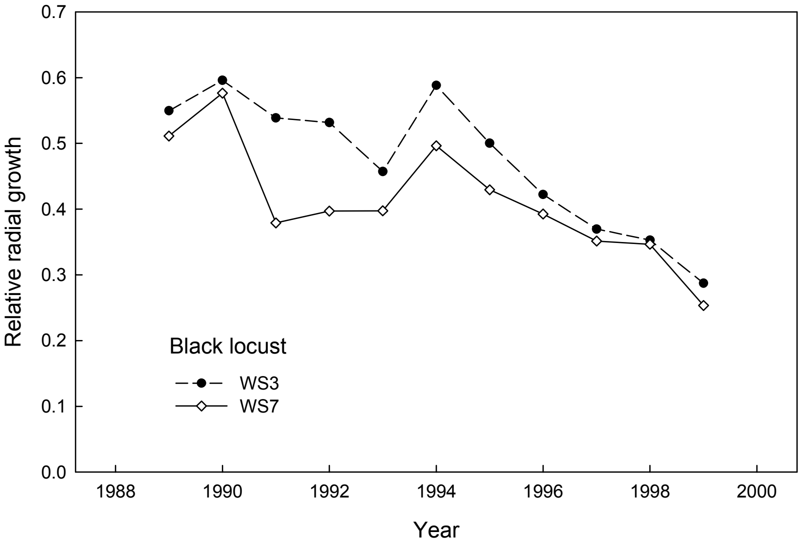

Figure 5-8. Relative radial growth patterns for 10 black locust trees on WS3 and WS7 during acidification treatments which began in 1989. Asterisks by year indicate significant differences; * α = 0.1 and ** α = 0.05.

All species, except red maple, also showed a pattern of increased growth on WS3 compared to WS7 from four to seven years after treatment began, but this early growth acceleration was only significant in black cherry trees. Black locust RRG ratios showed a trend similar to that of black cherry and yellow-poplar trees, with accelerated early growth and slowed later growth, but there were no statistically significant differences between watersheds. Black cherry RRG ratio analysis produced the greatest number of statistically significant differences between WS3 and WS7 (Fig. 5-6). Red maple trees did not show any evidence of an increase in RRG from 1989 to 2000, but did exhibit significantly lower RRG ratios during the last 3 years (Fig. 5-7).

Basal area growth patterns using tree core measurements, were similar to those obtained with the RRG. For yellow-poplar and black cherry (Fig. 5-9), actual mean basal area increments per tree were greater than predictions for about the first eight years of treatment and then became smaller than predicted from 1997 to 2000. Red maple trees exhibited lower BAI than predicted throughout the study period. After eight years of treatment, or about 1996, actual basal area was only about half the predicted values for all species. All species showed significantly lower BAI on WS3 vs. WS7 during 1997-2000 (Fig. 5-9). Actual BAI relative to predicted BAI in early

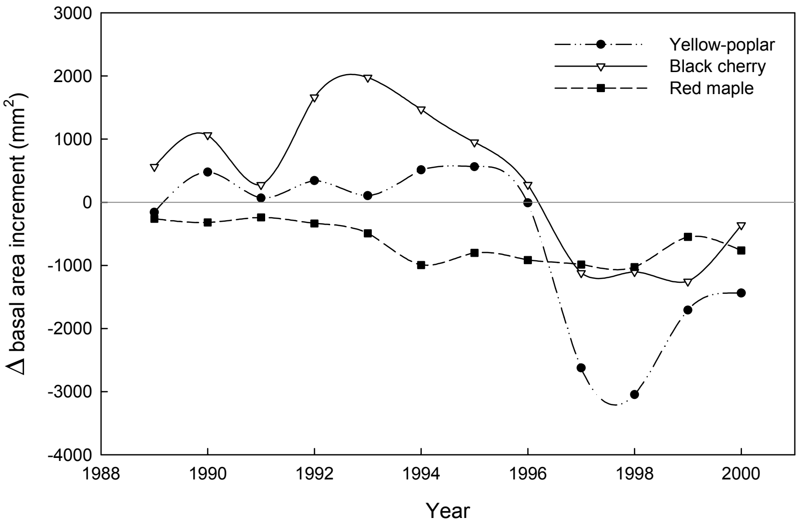

Figure 5-9. Actual minus predicted annual mean basal area increment per tree (mm^2) for yellow-poplar, black cherry, and red maple trees on WS3 for years after treatments began (based upon data from Odenwald 2002). Yellow-poplar differences were significant at the 0.01 level in 1990 and 1997-2000 and significant at the 0.05 level in 1994-95. Black cherry differences were significant at the 0.05 level in 1991 and at the 0.01 level in all other years except 1989 and 1996. Red maple differences were significant at the 0.01 level in all years except 1992.

years of treatment was equivalent to a maximum of about 2000 mm^2 or 80% increase for black cherry. Smaller positive BAI changes of up to 500 mm^2 or 20% of expected BAI were indicated for yellow-poplar in early years. As indicated in Figure 5-9 increases were significant in yellow-poplar during 3 years and in black cherry during 7 years prior to 1996.

May et al. (2005) found diameter growth on WS3 reduced by 37% compared to WS7 from 1999-2001 in three each of red maple, yellow-poplar, and black cherry trees. These data were collected late in the treatment period analyzed here and support the tree core analysis showing reduced radial growth had occurred.

4.1.2 Overstory Foliar Chemistry

Significant differences in mean foliar chemistry concentrations existed among species, as expected, and between WS3 and WS7 (Table 5-3). Trends in foliar nutrients varied over time within watershed and species suggesting that foliar condition at the time of sampling was important even though foliage was sampled in late summer each year. In 1992 and 1997, average foliar N concentrations for black cherry and red maple were greater

Table 5-3. Significant differences in foliar chemistry for four tree species between WS3 and WS7 in 1992, 1997 and 2002 which represents conditions 4, 9 and 14 growing seasons after treatments began. Species were SB = sweet birch, YP = yellow-poplar, BC = black cherry, and RM = red maple. All differences were significant at the $\alpha = 0.05$ level except that for iron (Fe) which was significant at $\alpha = 0.1$ (box).

	Analyte										
Species	N	Ca	K	Mg	P	Al	B	Cu	Fe	Mn	Zn
						1992					
SB		X					X			X	
YP		X		X				X			X
BC	X										
RM	X	X			X		X				
						1997					
SB		X									
YP		X							$\boxed{\text{X}}$		
BC		X				X		X		X	
RM	X			X	X	X	X	X		X	
						2002					
SB								X			
YP											
BC			X			X	X	X			X
RM						X				X	

on WS3 than WS7. Nitrogen concentrations decreased over time, with the exception of yellow-poplar, for which concentrations increased slightly (Fig. 5-10). Calcium was significantly greater in foliage on WS7 for all species in 1992 and/or 1997, but no significant differences occurred in 2002 (Fig. 5-11).

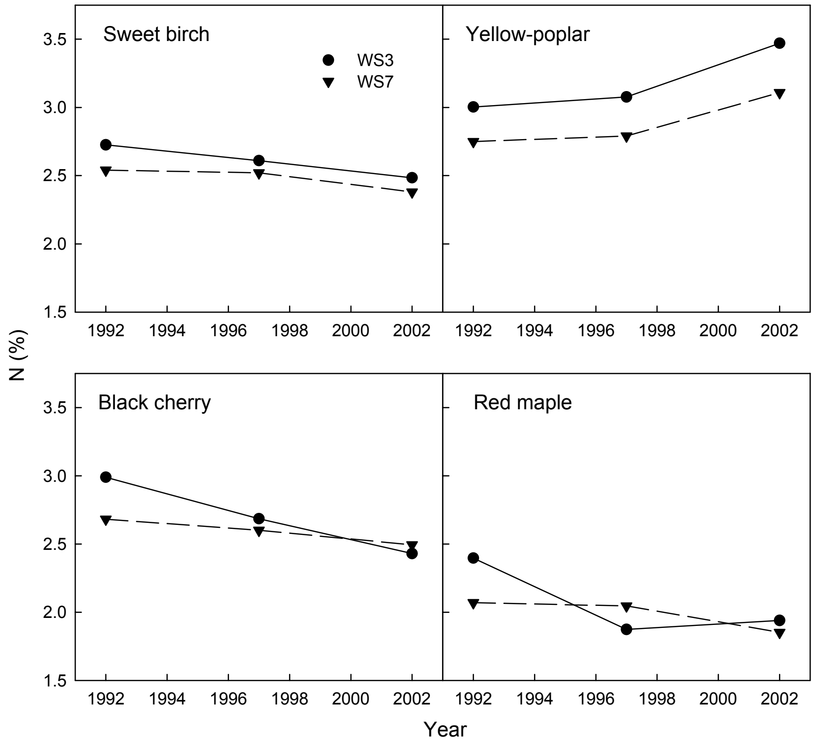

Figure 5-10. Foliar N content for sweet birch, yellow-poplar, black cherry, and red maple trees on WS3 and WS7 in 1992, 1997 and 2002 (4, 9 and 14 growing seasons after treatments were initiated in 1989).

Generally, foliar Ca increased over time, with a peak in 1997 (Fig. 5-11). WS7 yellow-poplar consistently exhibited the highest Ca concentrations – nearly twice that of yellow-poplar concentrations on WS3. For Mn there was no consistent trend in average concentrations over time, but levels in foliage were generally greater on WS3 than WS7 (Fig. 5-12) in all four species. Differences in foliar Mn concentrations between WS3 and WS7 were significant for sweet birch in 1992, yellow-poplar and red maple in 1996 and red maple in 2002 (Table 5-3). Foliar Mn concentrations in black cherry did not differ between the two watersheds.

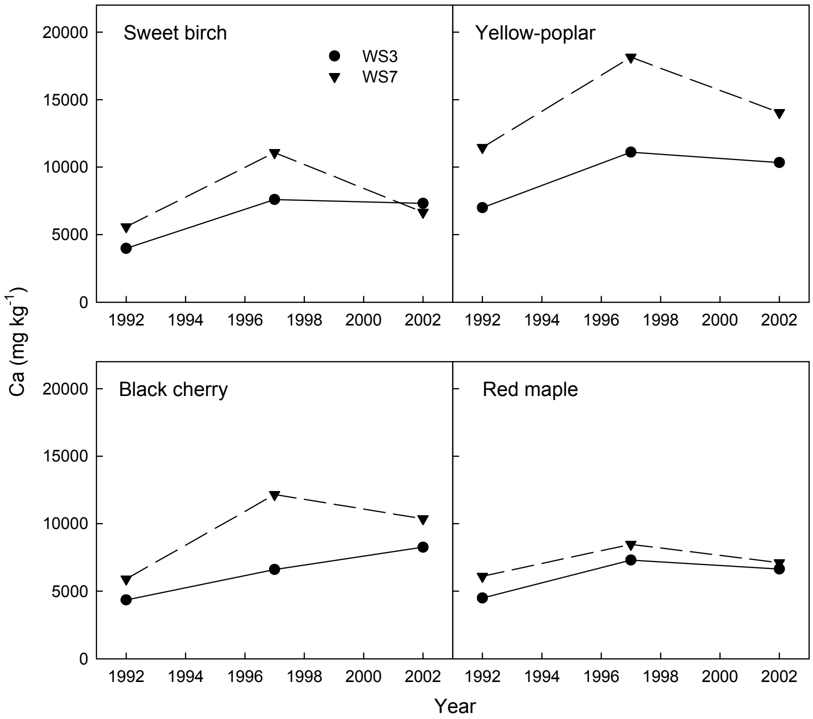

Figure 5-11. Variation in mean foliar Ca (mg kg^{-1}) in four tree species after 4, 9 and 14 growing seasons of treatment on WS3 and WS7.

For yellow-poplar, foliar Al concentrations decreased significantly in 1997, a trend opposite that displayed for foliar Ca, while all others showed at least a slight increase (data not shown). Generally foliar Al concentrations were greater on WS3 than WS7, except in 2002 for sugar maple, yellow-poplar and oak, 1992 for sweet birch, and 1997 for northern red oak.

Mean foliar nutrient concentrations were compared with regional means and extremes from the Northeastern Ecosystem Research Cooperative foliar chemistry database for those species for which there was an acceptable number of samples. Mean values for N, Ca, Mg and Al concentrations in sweet birch, black cherry and red maple foliage all fell within the range of values observed across the northeastern United States for these species (Northeastern Ecosystem Research Cooperative 2004). Foliar P concentrations in black cherry, however, were at the lower end of the range reported for black cherry in the northeastern United States. The P concentrations reported here are similar to those found elsewhere on the Fernow (Adams et al. 1995, Adams et al. 2005), and may suggest the potential for P limitation on this site. Additional data from this and other nearby sites (W. Peterjohn, unpublished data) lend support to this hypothesis.

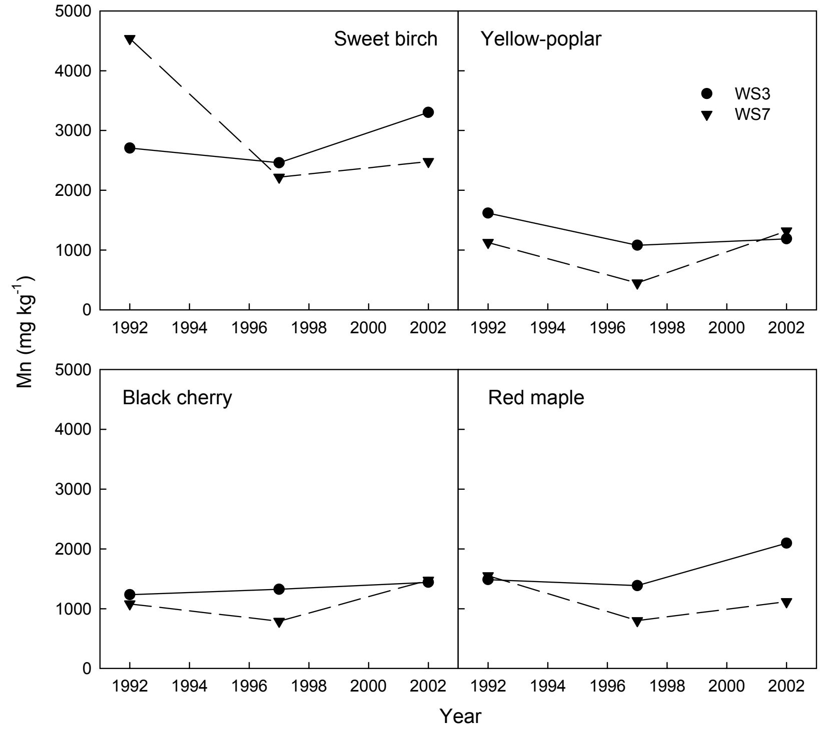

Figure 5-12. Variation in mean foliar Mn (mg kg^{-1}) in four tree species after 4, 9 and 14 years of treatment on WS3 compared to WS7.

4.1.3 Dendrochemistry

Analyses of dendrochemistry results showed shifting patterns between treated and control trees after four years of treatment as opposed to eight and 12 years of treatment. Figures 5-13 through 5-16 show patterns of Ca, Mg, Mn and Ca/Mn found in bolewood at the times of sampling on WS3 and control areas in the four tree species. Many, but not all, of these differences between treated and control tree mean concentrations and ratios were significant in t-tests by species and age segment (DeWalle et al. 1999). WS7 control tree chemical concentrations were similar over time. Only average values for control trees are shown to simplify presentation; different control

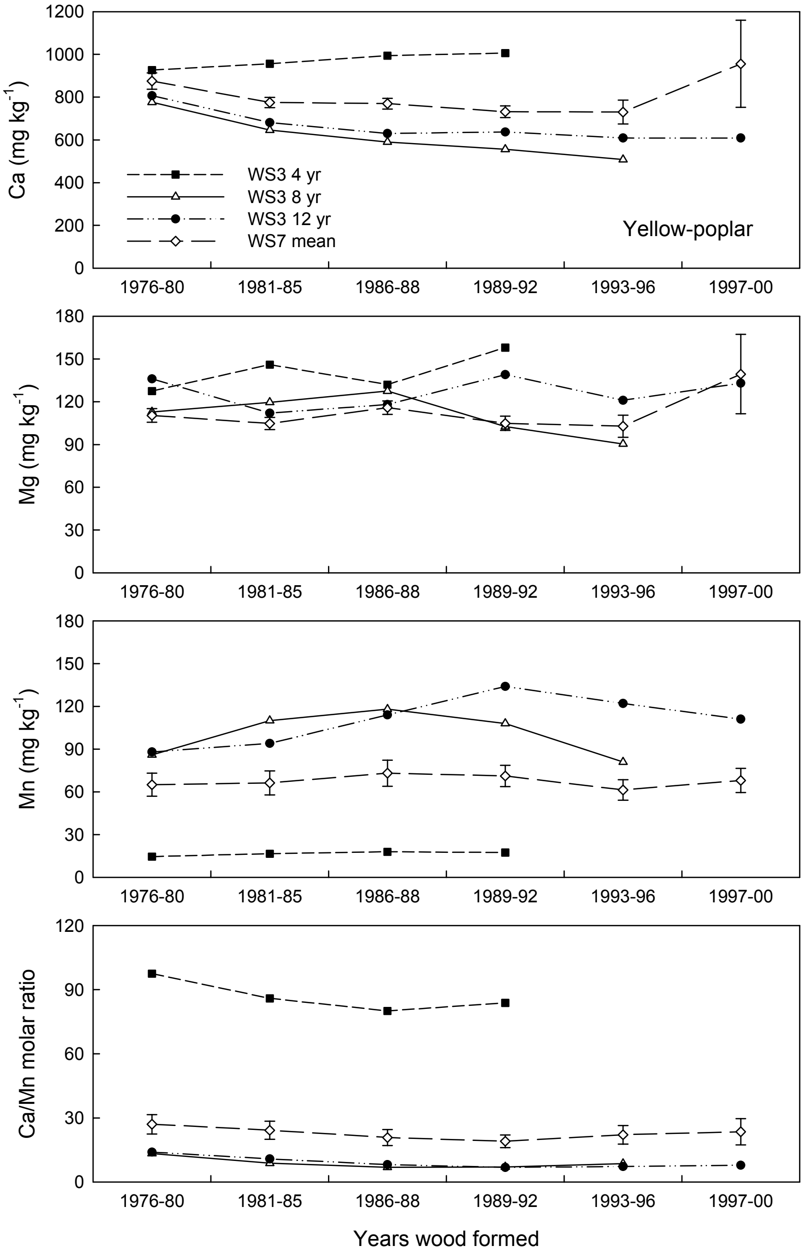

Figure 5-13. Yellow-poplar bolewood Ca, Mg, and Mn concentrations and Ca/Mn molar ratios on WS3 and WS7 measured after 4, 8 and 12 years of treatment. WS7 untreated tree data were similar over time and only means ± standard errors are shown. Treatments began in 1989.

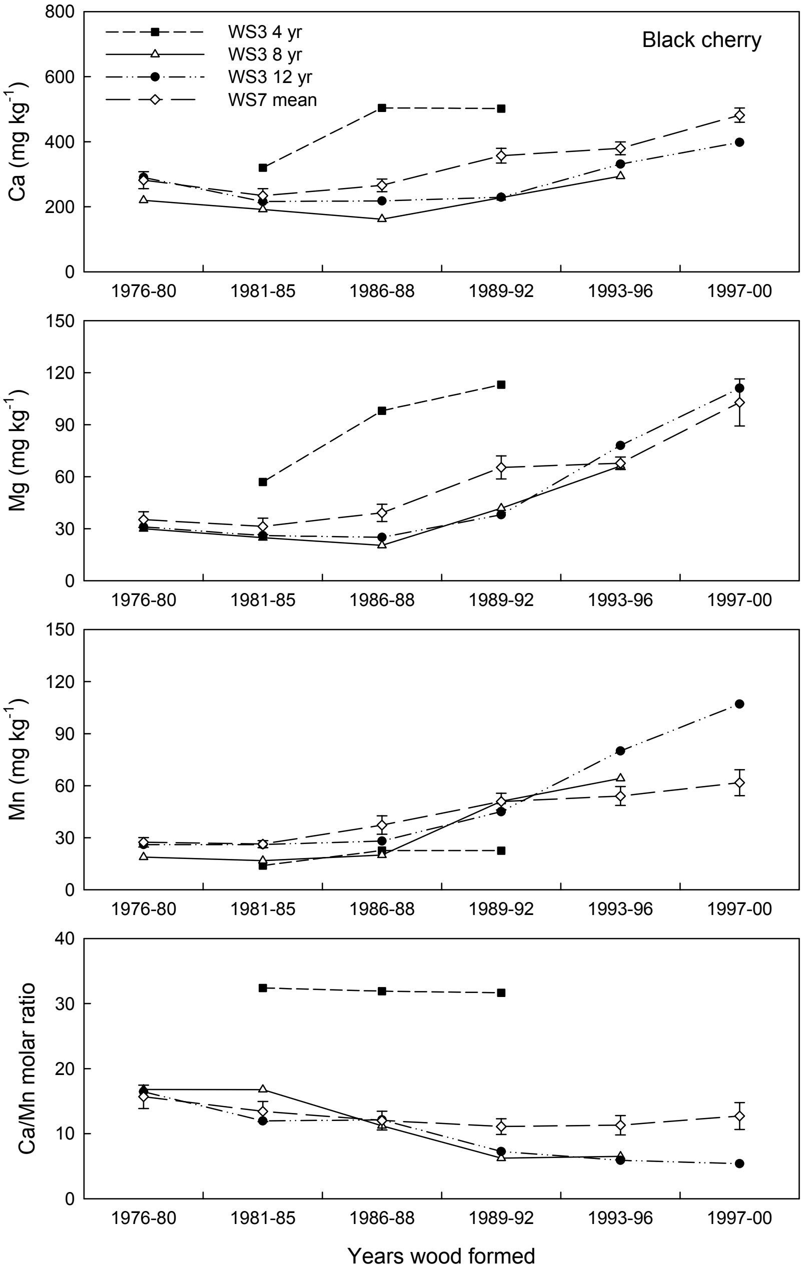

Figure 5-14. Black cherry bolewood Ca, Mg, and Mn concentrations and Ca/Mn molar ratios on WS3 and WS7 measured after 4, 8 and 12 years of treatment. WS7 untreated tree data were similar over time and only means ± standard errors are shown. Treatments began in 1989.

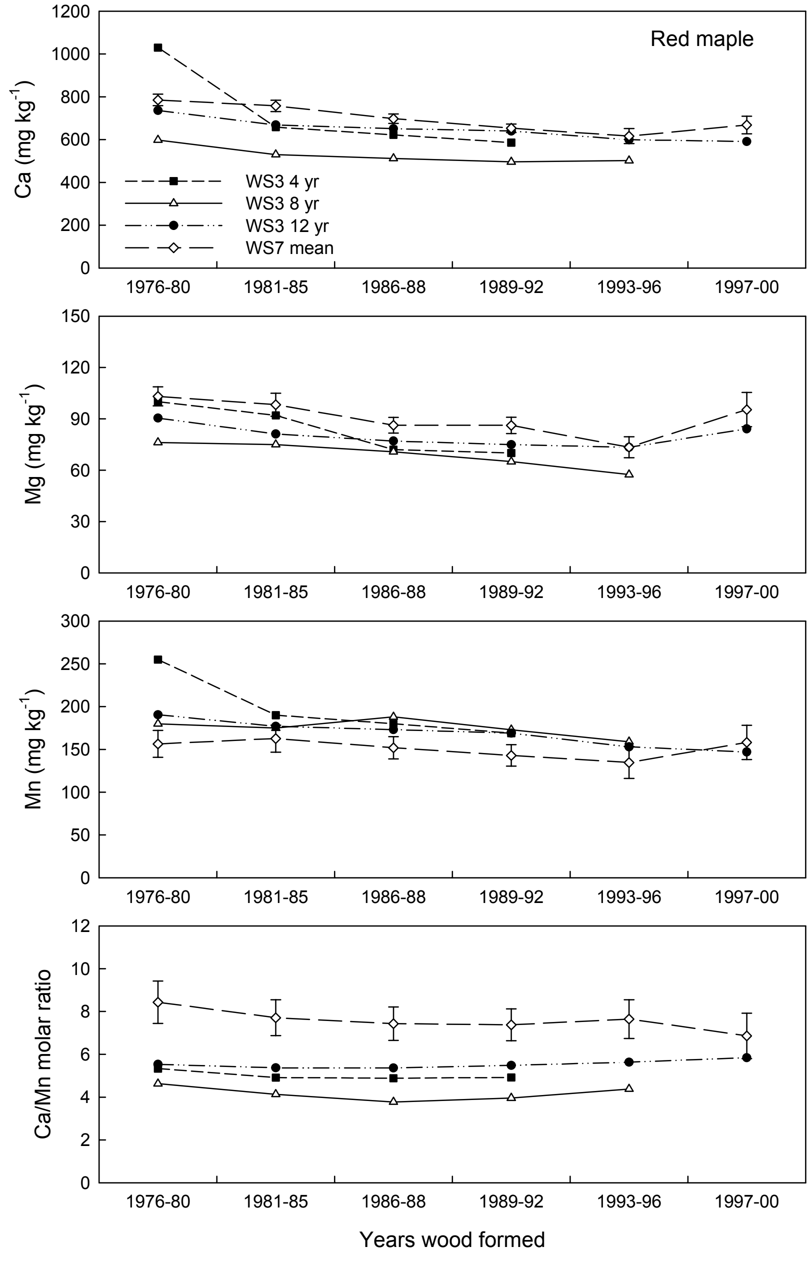

Figure 5-15. Red maple bolewood Ca, Mg, and Mn concentrations and Ca/Mn molar ratios on WS3 and WS7 measured after 4, 8 and 12 years of treatment. WS7 untreated tree data were similar over time and only means ± standard errors are shown. Treatments began in 1989.

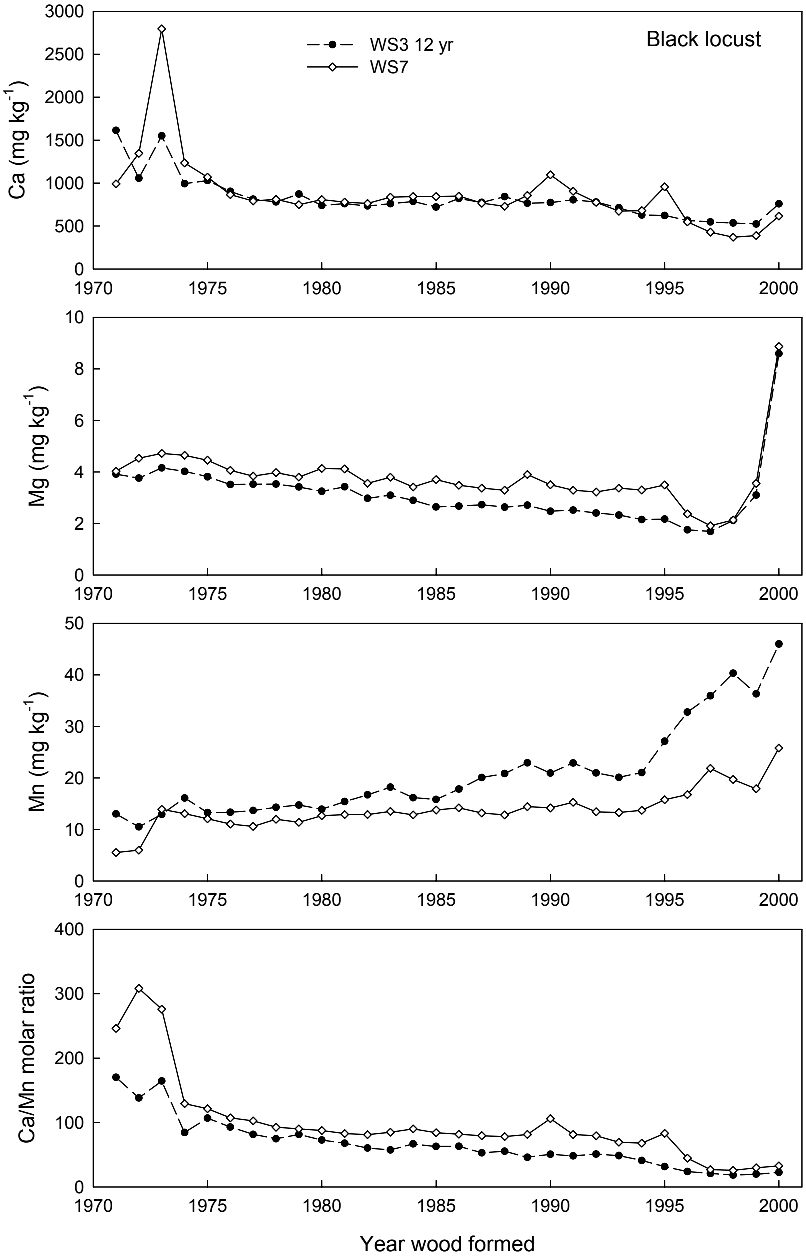

Figure 5-16. Black locust bolewood Ca, Mg, and Mn concentrations and Ca/Mn molar ratios on WS3 and WS7 measured after 12 years of treatment. Treatments began in 1989.

trees were sampled after four, eight, and 12 years of treatment. For the three species sampled repeatedly (black cherry, yellow-poplar, and red maple) mean Ca and to a lesser extent Mg concentrations were generally greater in sapwood of treated trees after four years of treatment. After eight and 12 years of treatment, treated trees generally showed lower levels of Ca and Mg content compared to control trees. Although there were some deviations from this pattern due to sample variations and species characteristics, the data appeared to suggest an initial period of base cation mobilization occurred followed by a period of base cation depletion.

Manganese trends in species sampled repeatedly were essentially the opposite with treated trees showing lower levels than controls after four years and higher levels of Mn after eight and 12 years of treatment. Ratios of Ca/Mn magnify these trends and show higher ratios in treated compared to control trees after four years of treatment and lower ratios after eight and 12 years of treatment. This suggests that base cation mobilization of Ca relative to Mn occurred after four years of treatment and cation depletion of Ca relative to Mn occurred after eight and 12 years of treatment.

Relatively small, inconsistent differences existed in dendrochemistry between eight and 12 years of treatment. However, greater levels of Mn were observed for all species, except red maple, from eight to 12 years, which suggests a continuation of soil acidification.

Dendrochemistry response to treatment varied somewhat among the various tree species. Red maple trees did not show the elevated Ca and Mg levels after four years of treatment (Fig. 5-15) observed in yellow-poplar and black cherry trees (Figs. 5-13 and 5-14). Red maple trees sampled were largely understory and intermediate canopy position trees, while all yellow-poplar and black cherry trees sampled were dominants or co-dominants. Slower growth of understory red maple trees may have limited their response to treatment due to intense competition for nutrients by the overstory trees. Red maple was the only species that did not show increased radial growth in the early stages of treatment. This suggests a linkage between bolewood chemistry and radial growth (see discussion section). Black cherry trees showed increases in Mn levels in wood formed only after four to eight years of treatment, due to the preservation of prior trends of Mn depletion in heartwood that existed from the base cation mobilization phases (Fig. 5-14).

The response of black locust trees to the fertilization treatment deserves special mention (Fig. 5-16). Sapwood in this species was only 3-4 growth rings wide and this species was expected to better preserve a record of soil chemical changes in its rings than other species. However, sapwood rings did not show expected lower base cation levels on WS3. In addition, the heartwood on WS3 that was formed well before treatments began appeared to show elevated Mn and reduced Ca/Mn ratios due to treatment. This suggests black locust heartwood may not be chemically stable. Black locust trees appeared to be unsuited to recording chemical changes in the soil, possibly due to its nitrogen fixing capability.

4.1.4 Herb Layer Effects

Gilliam et al. (2001) suggested that one of the main effects of the acidification treatment on WS3 was to decrease spatial heterogeneity of N processing, using several measures that included net N mineralization and nitrification, available N pools, and tissue concentrations of nutrients of an herb layer species – *Viola rotundifolia* – that occurred on all sample plots in the study. It was concluded that foliar nutrient concentrations in *V. rotundifolia* represented a useful and adequate indicator of soil nutrient availability, including N, P, Ca, Mg, and K. Spatial variability in virtually all measures of soil N dynamics (particularly foliar N in *V. rotundifolia*) was substantially less in WS3 than in WS4 and WS7 (Gilliam et al. 2001). Mechanisms potentially controlling spatial variability on these watersheds, including soil chemistry and degree of soil weathering, were investigated further by Gilliam et al. (2005).

Hockenberry (1996) repeated assessment of the herbaceous layer of WS3, WS4, and WS7 in 1994, but used a different sampling approach than those used in the first two years of the study. The 1991 and 1992 samplings were carried out on 15 plots per watershed, but only done once (July) in the year. By contrast, Hockenberry (1996) did monthly measurements of herb layer cover and composition (from May to October) in a seven-plot sub-set of the original 15 used in 1991 and 1992. Yurish (1996) carried out monthly *in situ* soil N incubations on the same seven plots as Hockenberry (1996). To date, no study has synthesized these two studies to better assess the potential effects of the acidification treatment on the herbaceous layer of WS3. Accordingly, we report the results of further analysis of data collected in 1994, five years after treatments began. In doing so we assess (1) temporal patterns of herbaceous layer cover and net nitrification on a plot-by-plot basis, and (2) spatial patterns of herb layer composition, soil N processing, and foliar nutrients of *V. rotundifolia*.

Comparisons of mean cover for individual species of the herbaceous layer among watersheds and years of sampling, despite being based on more extensive sampling comprising a four-year period, support the findings of earlier studies (e.g., Gilliam and Turrill 1993, Gilliam et al. 1994), which were based on one-time sampling (Table 5-4). In particular, there were (1) notable similarities in the herb layer between these watersheds that differ greatly in forest stand age and history, and (2) negligible, if any, responses of the herb layer to the N additions to WS3 during the first five growing seasons after treatments began. Dominance of the herbaceous layer by fern species on WS7 did not change in the four-year period of the study, with Christmas fern and shield fern combining for 20-25% cover (Table 5-4). This is substantial, considering that it is approximately the same as the total herb layer cover for each of WS3 and WS4. There were no significance differences among years for WS3, except for black cherry seedlings in 1994, strongly indicating that there has been little measurable response of herb layer composition to the acidification treatment on WS3 (Table 5-4).

Table 5-4. Percent cover for dominant species/species groups in July of 1991, 1992, and 1994 (>1% cover on any watershed in any year) on WS3, WS4, and WS7. Values given are mean cover ± 1 SE of mean. Yearly means for a given watershed followed by the same letter are not significantly different at $p < 0.05$. See Table 5-2 for species codes. Data from Hockenberry (1996).

Species code	1991	1992	1994
	%		
WS3			
LACA	–	–	–
STPU	–	–	–
POAC	–	–	–
DRMA	0.5 ± 0.2a	0.5 ± 0.1a	0.6 ± 0.3a
VIOL	3.8 ± 1.1a	2.9 ± 0.9a	3.9 ± 1.0a
SMRO	3.0 ± 0.9a	2.3 ± 0.7a	3.4 ± 1.0a
RUBU	0.7 ± 0.4a	1.3 ± 0.6a	2.3 ± 0.7a
ACPE	1.7 ± 0.8a	2.7 ± 0.5a	1.8 ± 0.6a
PRSE	0.4 ± 0.2a	0.3 ± 0.1a	0.9 ± 0.2b
WS4			
LACA	3.5 ± 2.5a	1.8 ± 1.4a	2.4 ± 2.4a
STPU	–	–	–
POAC	1.7 ± 1.0a	1.1 ± 0.6a	0.8 ± 0.3a
DRMA	1.1 ± 0.5a	1.7 ± 0.7a	0.4 ± 0.1a
VIOL	3.0 ± 1.1a	1.3 ± 0.6a	4.6 ± 1.4a
SMRO	1.0 ± 0.2a	0.9 ± 0.3a	1.0 ± 1.2a
RUBU	1.9 ± 1.0a	0.8 ± 0.7a	1.7 ± 1.0a
ACPE	2.2 ± 0.7a	0.9 ± 0.5a	1.0 ± 0.4a
PRSE	1.2 ± 0.9a	1.0 ± 0.5a	0.9 ± 0.3a
WS7			
LACA	2.7 ± 1.8a	0.4 ± 0.4a	0.8 ± 0.6a
STPU	1.0 ± 0.9a	2.9 ± 1.0a	2.6 ± 0.2a
POAC	5.6 ± 2.5a	6.7 ± 2.7a	3.9 ± 1.4a
DRMA	15.2 ± 5.3a	20.5 ± 6.8a	15.2 ± 5.1a
VIOL	3.8 ± 1.1a	5.2 ± 0.9a	5.9 ± 1.5a
SMRO	1.1 ± 0.6a	3.5 ± 1.0a	1.0 ± 0.5a
RUBU	0.5 ± 0.3a	1.0 ± 0.4a	1.3 ± 0.6a
ACPE	0.2 ± 0.1a	0.2 ± 0.1a	0.2 ± 0.1a
PRSE	0.2 ± 0.1a	0.3 ± 0.1a	0.5 ± 0.1a

Although species composition and cover of the herb layer do not appear to have responded to five years of the acidification treatment, other results suggest that it may have altered plant and soil relationships, especially the relationship between soil N availability and herb cover. This can be seen in differences in patterns of correlation among watersheds for net nitrification versus mean herb layer cover. Monthly rates of net nitrification were significantly correlated among watersheds. For WS4 versus WS7 this was significant at $p < 0.01$ ($r^2 = 0.88$), whereas for WS4 versus WS3 it was significant at $p < 0.001$ ($r^2 = 0.98$), indicating the seasonal patterns in soil net nitrification were essentially identical among watersheds (Fig. 5-17). By contrast, mean cover for the herb layer was significantly related to net nitrification only for WS4 and WS7 (despite higher overall cover and large fern component on WS7) but not for WS3 (Fig. 5-18). Thus, the seasonal pattern of change in herb cover that is consistent with seasonal patterns of change in net nitrification on WS4 and WS7 appears to be absent on WS3, likely related to decoupling of N cycle from biotic controls due to acidification treatments, as noted by Gilliam et al. (2001).

Multivariate analysis also revealed alterations in spatial patterns of plant – soil relationships potentially caused by the acidification treatment on WS3. We used canonical correspondence analysis (CCA), a multivariate technique that performs a least-squares regression of plot scores (species' weighted averages) as dependent variables onto environmental variables as independent variables (ter Braak 1988). Thus, CCA is a form of direct gradient analysis (Palmer 1993). In addition to generating ordination diagrams with plot and species locations, CCA also generates environmental vectors originating from the center of the ordination space. The lengths of these vectors represent the gradient lengths of each measured environmental variable, such that vector length is proportional to the importance of an environmental gradient in explaining species' patterns. Thus, shorter lines represent gradients of lesser importance; longer lines represent gradients of more importance (ter Braak 1988, Palmer 1993, Gilliam and Saunders 2003).

The environmental factors included in our analyses were chosen to represent aspects of soil N availability and cycling at treated and untreated watersheds at FEF: extractable N pools (NH_4 and NO_3), rates of net nitrification, and foliar N and N:P ratios in *V. rotundifolia*. The latter (N:P ratios) was included to assess the likelihood of P-limitation on herb layer vegetation. Gilliam et al. (2001) found higher N:P ratios, indicative of P-limitation (Koerselman and Meuleman 1996), in *V. rotundifolia* on WS3 compared to that on WS4 and WS7.

Although the individual species appearing in the ordinations (Figs. 5-19 through 5-21) varied among watersheds, N:P ratio was the shortest (i.e. least important) vector on the two untreated watersheds (Figs. 5-20 and 5-21).

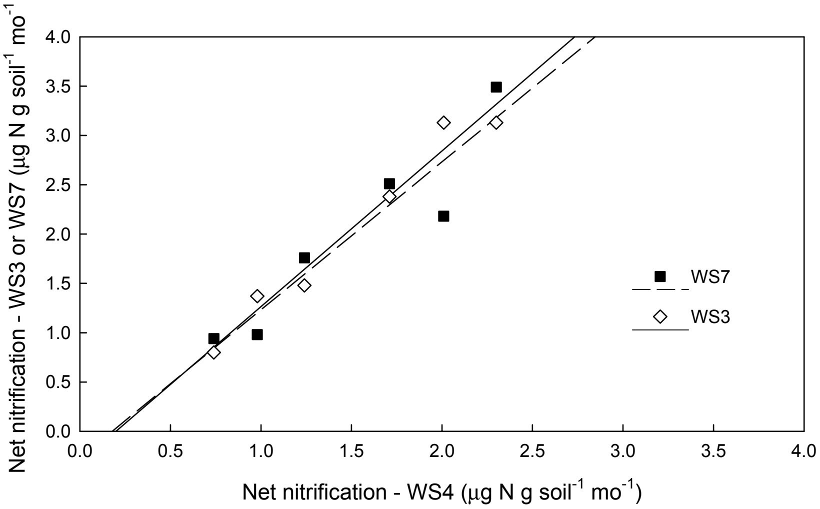

Figure 5-17. The relationship between net nitrification on WS3 and WS7 versus WS4. Each point represents mean monthly values, May to October 1994. Solid line represents significant linear relationship between net nitrification on WS3 and WS4: $y = -0.31+1.57x$, $r^2 = 0.98$, $p < 0.001$; dashed line represents significant linear relationship between net nitrification on WS7 and WS4: $y = -0.27+1.50x$, $r^2 = 0.88$, $p < 0.01$.

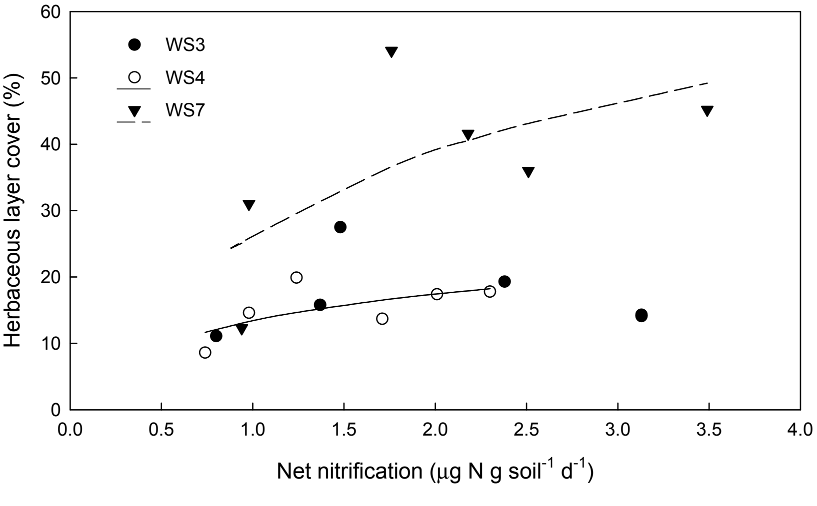

Figure 5-18. The relationship between herbaceous layer cover and net nitrification in mineral soil for WS3, WS7 and WS4. Each point represents mean monthly values, May to October 1994. Lines represent significant logarithmic relationships for WS7 ($Y = 18.4(\ln X) + 26.2$, $r^2 = 0.45$, $p < 0.05$), and WS4 ($Y = 5.8(\ln X) + 13.4$, $r^2 = 0.41$, $p < 0.05$). Relationship was not significant ($p > 0.10$) for WS3.

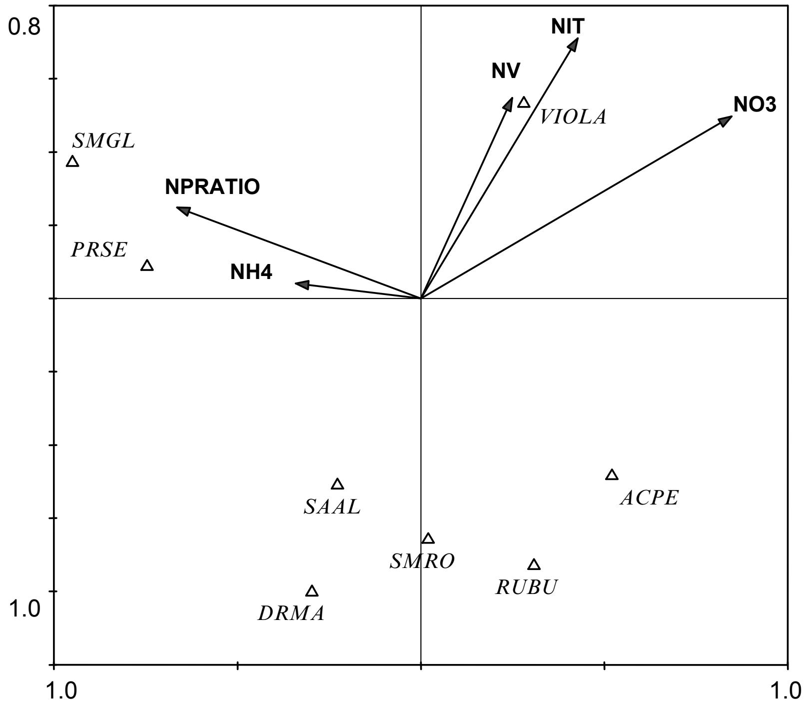

Figure 5-19. Canonical correspondence analysis of herbaceous layer species and indices of N availability/dynamics on WS3. NH4 and NO3 are extractable pools of soil NH_4 and NO_3, respectively; NIT is net nitrification; NV is foliar N in *Viola rotundifolia*; NPRATIO is foliar N:P ratio in *V. rotundifolia*. See Table 5-2 for species codes.

However, N:P ratio was among the longer (i.e. more important) vectors for treatment WS3 (Fig. 5-19). This suggests that the acidification treatment, particularly the N content of the treatment, has created P limitations by saturating the plant demand for soil N. As a result, P availability (measured in the case by foliar N:P ratios) exerts a significant influence on the spatial patterns of herbaceous layer species on WS3, but not on WS4 or WS7, likely the result of the excess N being added to WS3.

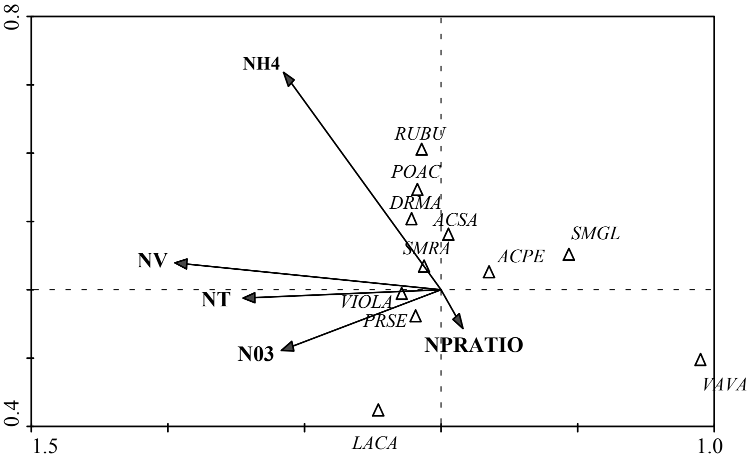

Figure 5-20. Canonical correspondence analysis of herbaceous layer species and indices of N availability/dynamics on WS4. See Figure 5-19 for meaning of environmental vectors and Table 5-2 for species codes.

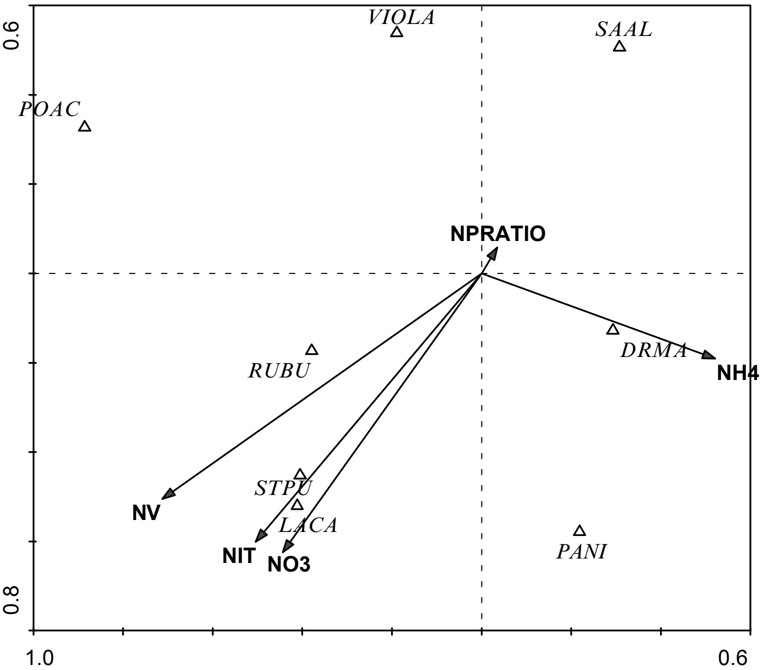

Figure 5-21. Canonical correspondence analysis of herbaceous layer species and indices of N availability/dynamics on WS7. See Figure 5-19 for meaning of environmental vectors and Table 5-2 for species codes.

4.2 WS9 (Clover Run) Results

4.2.1 Tree Growth

In 1993, after nine growing seasons of treatment, Kochenderfer et al. (1995) reported that average height of the treated larch trees was significantly lower ($\alpha = 0.05$) than that for the control trees in high, medium and low condition classes (Table 5-5). There was no significant difference in height of larch trees growing on the treated area and control plots prior to initiation of treatments (1986) for any of the condition classes (Table 5-5). The mean height of all larch trees after nine growing seasons was 5.7 m on the control plots and 4.8 m on the treated area. Average diameter of treated trees in condition class 1 and 2 was significantly smaller than that of control trees in 1993 (Table 5-5). Growth of the WS9 larch after nine growing seasons compared favorably with that reported at other locations, but acidification treatments appeared to cause a significant reduction in both height and diameter growth.

Table 5-5. Comparison of height (m) and diameter (cm) growth of treated and control larch trees for three condition classes on WS9. Values are means with standard errors in parentheses. For a given year and condition class, means followed by different letters are significantly different α=0.05 (analysis of variance followed by Tukey's HSD test).

Condition Class	Pretreatment (1986)[a]		Post-treatment (1993)	
	Treated	Control	Treated	Control
		Height m		
1	1.2 (0.03)a	1.2 (0.03)a	5.8 (0.09)b	6.7 (0.09)c
2	0.8 (0.03)a	0.8 (0.03)a	4.4 (0.12)b	5.1 (0.12)c
3	0.5 (0.03)a	0.5 (0.03)a	2.9 (0.15)b	3.4 (0.18)c
		Diameter cm		
1	–	–	5.3 (0.3)a	6.1 (0.3)b
2	–	–	3.0 (0.3)a	3.8 (0.3)b
3	–	–	2.3 (0.3)a	2.0 (0.3)a

[a] Treatments began in April 1987.

Pickens (1995) also compared the height and diameter of larch trees within one of the untreated control plots on WS9 that did not receive treatment and an adjacent treated plot in 1992 and 1993 after six and seven years of treatment, respectively. Mean larch tree height and diameter in the Pickens (1995) study were significantly greater ($\alpha \leq 0.05$) on the control plot than the treated plot in 1992 and 1993 (Fig. 5-22). On the treated area, mean larch tree height was about one meter less and mean diameter at breast height was about 1-2 cm less than on the control area. These differences agree with those found after nine years of treatment shown in Table 5-5 and indicate that acidification treatments with ammonium sulfate reduced larch height and diameter growth during the first six to seven years of treatment.

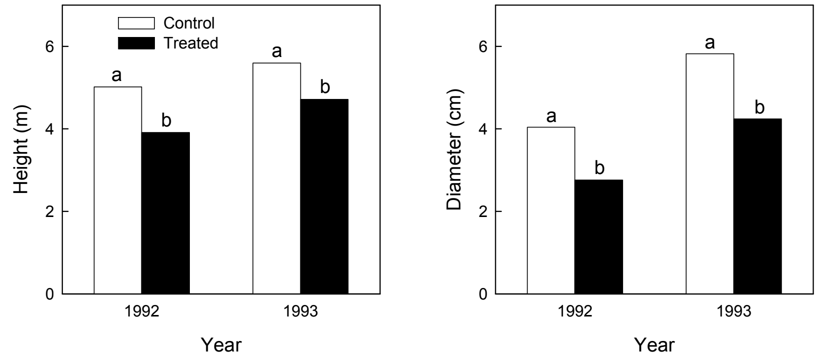

Figure 5-22. Mean heights (m) and diameters at breast height (cm) of Japanese larch trees on a control and treated plot measured in 1992 and 1993, six and seven years, respectively, after initiation of treatment on WS9 (Pickens 1995). Different letters above bars indicates significant difference at the $\alpha = 0.05$ level between control and treatment plots in that year.

Although it has been more than 60 years since farming ceased, soil analysis indicated that the soils on WS9 are very nutrient-deficient and highly acidic, with an average pH of 4.5 in the top 30.5 cm of soil. The average concentration of Mn extracted from soil samples collected in 1994 at the same locations where foliar samples were collected, indicated no significant difference ($\alpha = 0.05$) between treated and control soils (Kochenderfer et al. 1995). However, average concentrations of Mn were significantly different in both soils between the 0-15.2 cm soil layer (56.5 mg kg^{-1}) and the deeper 15.2-30.5 cm layer (21.2 mg kg^{-1}). In contrast, soils analyzed using a strontium chloride ($SrCl_2$) extraction method (Chapter 3, Table 3-4 and Fig. 3-14) showed significantly reduced exchangeable Ca and Mg and significantly increased Al and Mn in treated soils. Acidification of soil water by ammonium sulfate treatments on WS9 was also indicated, based upon soil lysimeter data (Chapter 4, Fig. 4-12 and Table 4-2) and based upon stream water sampling at baseflow and peakflow (Chapter 4, Tables 4-5 and 4-9, Figs. 4-24 and 4-29). Thus, it appears the reduced growth of Japanese larch observed on WS9 could be related to low levels of soil fertility that were exacerbated by the acidification treatment.

Unfortunately, no detailed analysis of tree cores was conducted on Clover Run to determine if patterns of increasing growth followed by decreasing growth occurred in Japanese larch. Since growth was already reduced after six years of treatment (Pickens, 1995), the period of accelerated growth, if any, would have to have been relatively short compared to Fernow WS3.

4.2.2 Foliar Chemistry

An analysis of foliar samples collected from dominant and co-dominant larch trees (Kochenderfer et al. 1995) indicated that concentrations of macro-elements and most metals were within the medium range of concentrations reported for coniferous tree species. Of the foliar elements analyzed, only the concentration of Mn was significantly greater on the fertilized plots. Pickens (1995) also found significantly reduced Mg and P and elevated Mn and Al in larch foliage on the treated portions of WS9 and DeWalle et al. (1999) showed both depleted Ca and increased Mn in bolewood of treated trees (see Section 4.2.3 of this chapter).

Results from Pickens et al. (1995) showed that trees on the treated plots had significantly lower foliar Mg and P and significantly higher foliar Mn and Al content in 1992 and 1993 than those from the control plots (Fig. 5-23). No significant differences in foliar K and Ca between treated and control larch trees were found. However, Ca in treated red maple seedling, blackberry and mountain laurel foliage on WS9 was significantly lower than in control leaves during the same years. Foliar N was significantly greater in treated than control trees in 1993.

4.2.3 Dendrochemistry

For WS9, dendrochemistry analyses suggest that Japanese larch trees appeared to preserve a record of dendrochemical changes due to treatment over time (Fig. 5-24, DeWalle et al. 1999). Wood formed in treated trees after 4-5 years of treatment showed higher concentrations of Ca and Mg relative to control trees, while wood formed more than five years after treatments began, showed relative depletion. Differences in mean Ca and Mg concentrations were significant only in 1996. Manganese concentrations were elevated relative to control trees in all years (significant in 1992-1994) and Ca/Mn showed significant reductions in all years. Depletion in bolewood base cations may have occurred a few years sooner on WS9 than on WS3, due to differences in soil buffering capacity, but precise timing of these changes is difficult to determine.

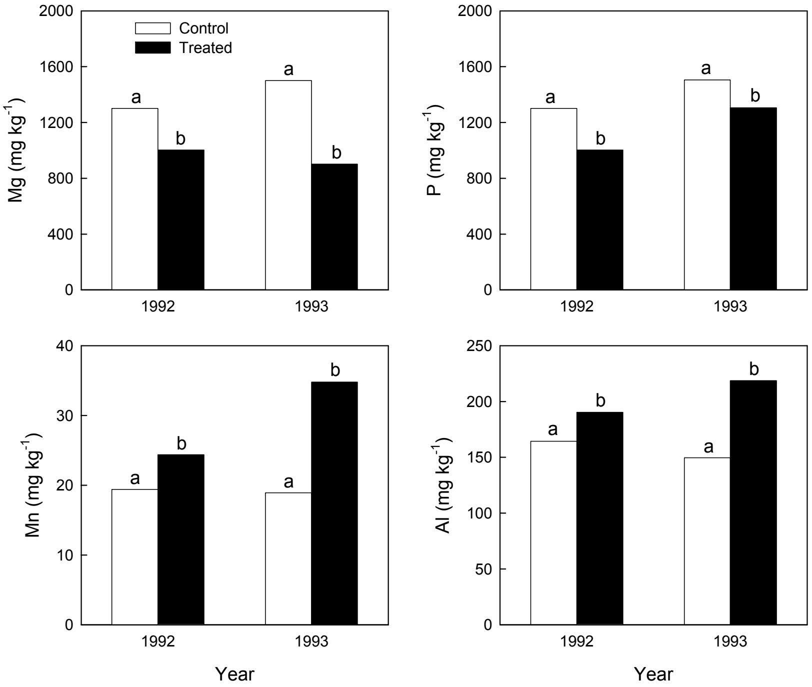

Figure 5-23. Comparison of Japanese larch foliar chemistry on WS9 treated and control plots in 1992 and 1993 (Pickens 1995). Significant differences between treated and control trees ($\alpha = 0.05$) are shown by different letters above the bars.

5. DISCUSSION

The results of analyses of treatment effects on forest growth, based upon inventory growth plot and tree core data analyses at Fernow WS3 and WS7 did not completely agree. Tree core analysis indicated that radial and BAI growth was species specific and either increased or remained unchanged in the early stages of treatment, and in later stages of treatment tree cores showed that growth was reduced in all species. Growth plot data generally only showed increased growth or no reductions in stand productivity due to treatment. All measurements of treatment effects on growth of Japanese larch on WS9 Clover Run showed reduced growth. Possible reasons for these differences in research results on treatment effects on forest growth and comparisons with results from other research are discussed below.

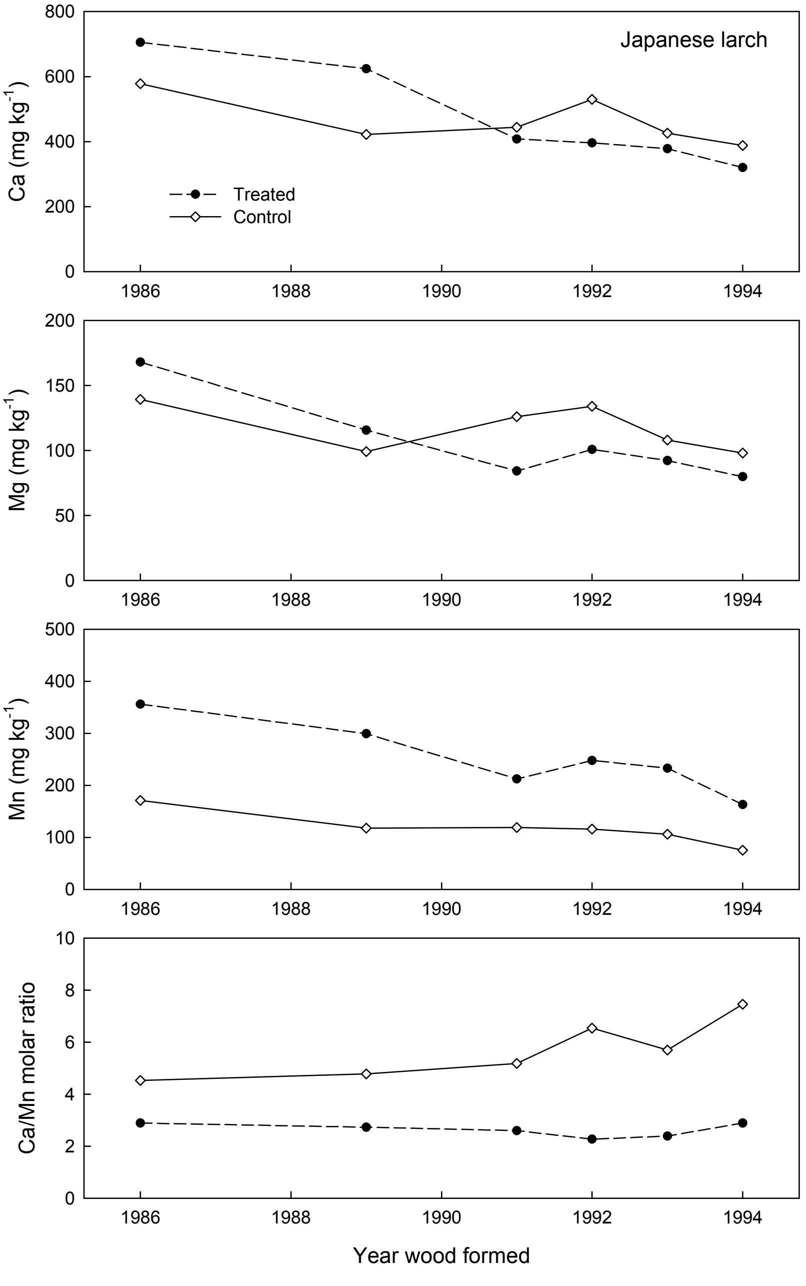

Figure 5-24. Japanese larch bolewood Ca, Mg, Mn and Ca/Mn molar ratios on WS9 treated and untreated plots after seven years of treatment. Treatments began in spring 1987.

Comparisons of annual radial growth data from tree cores with stand level growth plot results is problematic due to differences in measurement approach, as well as differing time periods available for comparisons. Since the micro-site conditions, competitive status, and genetic makeup of each tree determines its growth rate, direct comparisons between net volume growth of a mix of trees of varying size and species on plots over a multi-year time period, incorporating larger-scale effects of mortality and ingrowth, and annual radial growth or basal area increment based upon tree-core analysis of individual tree specie should be made with caution.

Forest growth/productivity is not constant in forest stands and follows consistent trends represented by a sigmoid curve described by Assman (1970). Growth in the young stand increases at an increasing rate to an inflection point where growth essentially increases at a constant rate for a number of years. Beyond the inflection point, growth increases at a decreasing rate until it reaches a peak and begins to decline. Although the trend is robust, the actual timing can be affected by site quality, species composition, stand density, and disturbance regimes. Since these two watersheds differed in initial stand density, volume, species composition and biomass, interpreting differences between watersheds to determine growth effects is complicated. For example, Auchmoody (1985) obtained the greatest response to a N+P fertilizer treatment in Allegheny hardwood stands when the fertilizer treatment was combined with a thinning. Some of the growth differences between WS3 and WS7, could have resulted from the stands being in slightly different stages of development. Stand development on WS7 may have lagged behind WS3 due to the herbicide treatments that preceded the acidification study. However, with no conclusive evidence of significant changes in growth over time, it is clear that stand development in both watersheds is characteristic of the middle stages of stand development described by Assman (1970).

Regardless, some similarities in growth results between plots and tree cores at Fernow were found. Greater annual net volume growth on WS3 growth plots with more black cherry and yellow-poplar (BC/YP) from 1990/91-2004 and greater cubic volume growth on plots with more red maple and sweet birch (RM/SB) during 1990/91-96 agreed in general with the greater relative radial growth and BAI in tree cores found for black cherry, yellow-poplar and black locust during this period. Black cherry typically responds positively to N inputs in the study region (Auchmoody and Filip 1973), thus was more likely to be affected by improved soil fertility conditions due to treatment in the base cation mobilization period. Increased foliar N was found on WS3 in 1992 early in the treatment period which suggests N fertilization could have been influencing growth. It appears that ammonium sulfate treatments had a positive impact on growth of some species in this mixed hardwood stand.

Similar positive growth response to N additions have been found in other studies. BAI growth responses to ammonium sulfate treatments have been reported in sugar maple in Maine (BBWM) during the first eight years of treatment (Elvir et al. 2003). Magill et al. (2000) also reported significant increases in wood production due to high experimental levels of N deposition (150 kg N ha^{-1} yr^{-1}) in Massachusetts hardwood stands dominated by oak species. Nellemann and Thomsen (2001) likewise found significant increases in radial increment in Norway spruce trees after 20 years of atmospheric N deposition in southern Norway. Solberg et al. (2004), also working in southern Norway, similarly concluded that atmospheric deposition may have increased conifer forest growth by up to 25%. All of these results show that initial stages of enhanced atmospheric deposition can increase growth of forests due to the fertilizer effect of the added nitrogen and other related changes in ecosystem biogeochemistry.

Not all species studied showed an initial positive growth response to treatment in the West Virginia experiments, however. Red maple RRG and BAI results from tree cores at WS3 and Japanese larch height and diameter measurements at WS9 showed generally reduced growth due to treatment throughout the treatment period. RM/SB growth plot data analysis for Fernow WS3 (Figs. 5-2 through 5-4) also showed no significant differences in growth due to treatment for the 1996-2004 later growth period, unlike the BC/YP plots. Thus, Fernow growth data did suggest that some differences in the response to treatment exist among tree species over time.

Species differences in response to acidification or N treatments have also been found elsewhere. For example, Magill et al. (2000) reported that wood production in a Massachusetts red pine forest was reduced experimentally by high N and N+S additions, while hardwoods responded positively to the same treatment. No significant increases in BAI of red spruce trees were found at BBWM due to ammonium sulfate treatments (Elvir et al. 2003) even though a positive response was found for sugar maple. Other research has suggested that conifer species are more susceptible to effects of soil acidification than hardwoods (Fenn et al. 1998, Fernandez et al. 2003). Differing response to treatments between species groups, especially conifers vs. hardwoods, is not uncommon in the literature.

What is most surprising in the Fernow study of vegetative growth is the pattern of the initial radial growth increases followed by radial growth decreases in hardwood species based upon tree core analysis (Figs. 5-5 through 5-9). This pattern of growth changes was not supported by the growth plot data at Fernow. However, a similar pattern of radial growth increases and decreases attributed to effects of acidification, N deposition and climate stress was found by Nelleman and Thomsen (2001) based upon radial growth analysis on >31,000 Norway spruce growth plots in southern Norway. McNulty et al. (1996) also reported a shift from positive to negative net growth response due to experimental N additions in a high elevation spruce-fir stand including some birch and maple trees. Boxman et al. (1998) also found that reducing N deposition in throughfall on roofed plots at Ysselsteyn, Netherlands resulted in significantly improved radial growth of Scots pine, suggesting that growth was being suppressed by ambient throughfall. Finally, May et al. (2005) also noted reduced diameter growth in black cherry, yellow-poplar, and red maple trees at Fernow from 1999 to 2001, during the period of decline in growth noted by the tree cores. Theories of forest ecosystem acidification discussed in Chapter 1 suggest that a pattern of increased followed by decreased growth can result from prolonged exposure to acidic deposition. The cause of this response pattern may be either development of N saturation or base cation depletion with Al mobilization and can not be determined from the available data. The Fernow tree core results are the first to show a pattern of increasing followed by decreasing tree growth in mixed hardwood species.

The pattern of increasing then decreasing tree growth matches the pattern exhibited by soil solution chemistry and stream chemistry (Chapter 4) and the patterns of treatment effects on bolewood chemistry reported in this chapter. In Chapter 4, a base cation mobilization phase during the first four years of treatment was hypothesized based on solution chemistry. Such a mobilization of base cations could have altered bolewood chemistry and improved the nutritional status of trees relative to control conditions. Mobilization of base cations in soil solution was followed by a base cation depletion phase; we hypothesize that after eight years of treatment this depletion of cations had impaired the relative nutrient status of these same trees. The early positive effect on net annual volume growth of WS3 could be attributed to this mobilization of base cations or to improved N status. However, the growth plot data do not indicate a decrease in growth with the apparent cation depletion, as growth has remained significantly higher on WS3 in the 1996-2004 period, especially on the BC/YP plots. Treatment of Fernow WS3 beyond eight to 12 years only produced marginally greater reductions in nutrient status of trees, suggesting that an equilibrium was approached after eight years.

Larch on WS9 exhibited decreases in growth in response to treatment. One might have expected increased growth in response to treatment unless other nutrients are limiting such that the trees could not utilize the increased available N. The overall poor fertility of the eroded soils on WS9 may be limiting in other nutrients, including P or Mg. Visible symptoms of Mg deficiency were observed on WS9 (Fig. 5-25).

Foliar chemistry analyses on WS3 and WS7 provide some support for the idea that early growth response on WS3 was due to N response (Fig. 5-10) but also provide support for the mobilization of base cations (Fig. 5-11), depending on the particular tree species. The foliar data do not provide clear indications however, of a base cation depletion stage. There is a suggestion that P may be limiting to black cherry on both watersheds. Other supporting data (Gilliam et al. 2001, W.T. Peterjohn, unpublished data) also provide evidence of a P limitation.

Figure 5-25. Yellow needle tips on Japanese larch indicate Mg deficiency on WS9 (Photo courtesy of W. E. Sharpe).

WS9 foliar chemistry results showed the differences that were hypothesized due to treatment. We hypothesized that additions of NH_4, which was converted to mobile NO_3 anions by nitrification, along with applied SO_4 anions in excess of soil SO_4 adsorption capacity, would leach base cations such as Ca and Mg and ultimately reduce their availability to plants. A decrease in soil base cation availability would lead to soil acidification, making Mn and Al more available. Increased tissue N due to the added NH_4, may have led to reduced P availability due to formation of Al-PO_4 precipitates (Pickens 1995, VanGoor 1953). Recommended N:P ratios for larch needles ranged from 4 to 5, while treatment and control plots had foliage with ratios of 17 and 15, respectively, indicating reduced P availability.

Altered nutrient availability due to mobilization of Al and depletion of Ca in soils on WS3 caused by accelerated soil acidification processes may explain growth differences between trees on WS3 and WS7 based upon tree core analysis. The observed increases in relative radial growth of yellow-poplar and black cherry trees on WS3 a few years after treatment was initiated, may be due to a temporary increase in base cations in soil solution (see Chapter 4) that resulted in concurrent increases in bolewood Ca and Mg levels. Seven to eight years after treatments began, trees of both species on WS3 declined in radial growth significantly, concurrent with a change in Ca status from a mobilized phase into a depletion phase (DeWalle et al. 1999). The lack of mobilization response by red maple trees to the treatment may be due to their understory status or due to a species-specific lack of responsiveness. Published evidence suggests that sugar maple is much more sensitive to base cation availability than red maple.

In order to examine concurrence of trends in growth and bolewood chemistry, relative radial growth rates (RRG) from the above analysis can be combined with changes in bolewood chemistry (Ca/Mn ratios) for black cherry, yellow-poplar and red maple after four, eight, and 12 years of treatment. Although it is natural for RRG to decline with time, bolewood Ca/Mn decreases were accompanied by larger decreases in RRG on WS3 than on WS7 from treatment year 4 to treatment year 8 (Fig. 5-26). Patterns of change for black cherry and yellow-poplar on WS3 suggested a delay or threshold of Ca/Mn decline beyond which RRG rapidly decreased. Because each species has a characteristic range of bolewood Ca/Mn it is difficult to specify a threshold, but RRG declines occurred approximately when ratios fell below the minimum Ca/Mn found on WS7 for that species. Again, red maple did not show a base cation mobilization response and experienced RRG declines that were not closely linked to Ca/Mn. Lack of relationship for red maple may be due to the intermediate to suppressed canopy position of this species in this stand or to the relative lack of response of this species to changes in Ca availability.

A different pattern of changes in relative radial growth rates vs. bolewood Ca/Mn ratios from treatment years 4 to 12 was found on the WS7 reference watershed. Ca/Mn ratios actually increased with time of treatment for both black cherry and yellow-poplar even though RRG declined as expected. Thus it appeared that bolewood chemistry was linked differently to RRG on WS3 compared to WS7.

The Japanese larch dendrochemistry results were similar to those for WS3 vs. WS7 comparisons with the added benefit that the larch trees seemed to preserve a record of soil changes over time. The only exception was that Mn levels appeared to be elevated even during the base cation mobilization phase, unlike results on WS3 where bolewood Mn appeared to be reduced during base cation mobilization. Soils on WS9 had lower levels of exchangeable bases and higher exchangeable Al than those at Fernow WS3 and WS7 and exhibited higher levels of Mn in soil solution even before treatments began. No soil Mn data are available for comparison, but Table 3-1 in Chapter 3 does show lower exchangeable Ca and Mg and higher exchangeable Al on WS9 than either WS3 or WS7 in the 0-10 cm layer.

Thus, Mn ions already present were likely mobilized along with base cations in the early stages of treatment. Otherwise, dendrochemical responses for larch on WS9 were quite similar to those of other species on WS3 at Fernow.

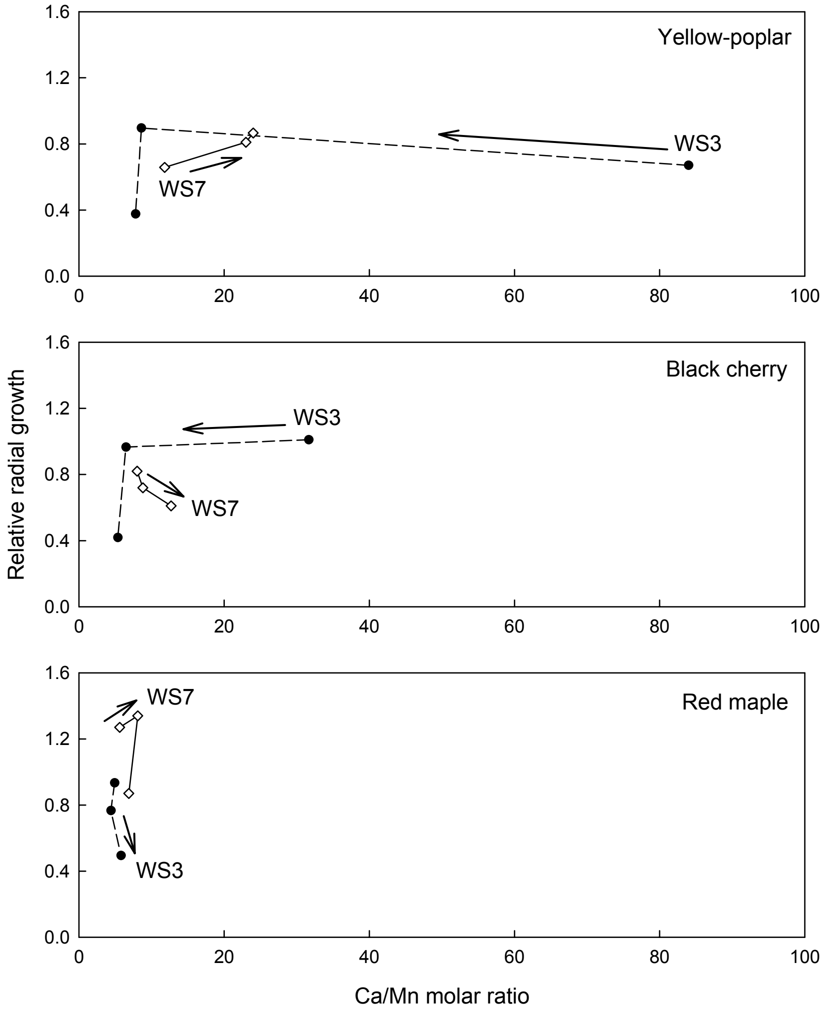

Figure 5-26. Patterns of mean relative radial growth rate and bolewood Ca/Mn ratio changes after 4, 8, and 12 years of treatment for three tree species on WS3 and WS7. Arrows indicate the direction of progression from treatment year 4 to treatment year 12.

The similarities between WS3 and WS9 results also extended to the time required for base cation mobilization and depletion to occur. Larch tree rings began to show base cation depletion in about 1991 or about five years after treatments began. Since tree ring wood was only analyzed for individual years as the planted larch trees grew large enough for rings to be easily sampled, the exact timing of mobilization and depletion can only be detected within about ± 2 years. Regardless, despite the differences in soils and past land use history between WS3 and WS9, the time required for trees to show base cation mobilization and depletion effects were about the same. A resampling of larch trees on WS9 to determine later trends in dendrochemistry could be fruitful.

Dendrochemistry response time of the forest ecosystem to a change in deposition can be roughly scaled based upon total loading from this experiment. The estimation was developed based upon assumptions that ecosystem change occurs over a time interval that is proportional to the total loading of acid computed as the product of the magnitude of the deposition change and the number of years over which it acts. Thus, a small deposition change (say 10% increase in annual deposition rate D from 1.0D to 1.1D) would take a longer time to reach an equilibrium condition (X years) than the eight years of essentially triple the atmospheric deposition load (D + 2D = 3D) that was imposed by the experimental Fernow treatment, e.g.

$$1.1D \bullet X \text{ years} = 3D \bullet 8 \text{ years}$$
$$X = 21.8 \text{ years.}$$

The dendrochemical response time (X) indicated for a 10% deposition increase was thus 21.8 years. If 12 years were needed to produce the same change, rather than eight years, then the response time to a 10% increase in deposition would be scaled up to about 33 years. Regardless, data suggest that the impacts of a relatively small 10% increase in atmospheric deposition would require a time scale of two to three decades for a dendrochemical response to occur. Thus, long-term monitoring would be required to detect impacts of such a fairly small deposition change and results could vary from Fernow response time depending on site fertility.

6. CONCLUSIONS

Forest basal area, biomass, and cubic volume growth was increased by experimental additions of ammonium sulfate at FEF (WS3 vs. WS7) on growth plots with more black cherry and yellow-poplar trees during 1990-2004 and cubic volume growth was increased on growth plots with more red maple and sweet birch during 1990-1996. Growth plot analyses included the effects of growth of all trees on the plots, including the effects of ingrowth and mortality, and represent an expression of changes in site productivity over multi-year time periods.

Tree core analysis suggested BAI growth was increased for black cherry and yellow-poplar overstory trees on WS3 during the first six to seven years of treatment (1989-1996), followed by decreased BAI in these species plus red maple during the last four years of treatment (1996-2000). Similar declines in growth were not found on permanent growth plots. Tree core analysis showed BAI treatment response for individual tree species for each year.

Red maple growth on WS3 did not positively respond to treatment, based upon tree core analyses. Our results support previous work that generally show positive response of hardwood species to N fertilization, but shows that individual hardwood species, like red maple, may respond differently.

Japanese larch diameter and height growth on WS9 (Clover Run) was significantly reduced by ammonium sulfate treatments. The WS9 results are consistent with several past studies showing reduced conifer growth in response to N fertilization and soil acidification. Reductions in growth on WS9 may have been exacerbated by past abusive farming that left the soil depleted of nutrients.

Patterns of bolewood chemistry over time on both WS3 and WS9 showed a period of relative base cation mobilization during the early years of treatment followed by a period of base cation depletion for overstory black cherry, yellow-poplar, and Japanese larch. Periods of bolewood base cation depletion were accompanied by increased concentrations of Mn. Only red maple showed bolewood base cation depletion throughout the experiment. Since red maple also did not show increased radial growth during the early stages of the experiment, a similarity in patterns of bolewood chemistry change and radial growth change is suggested. Black locust sapwood did not show effects of treatment on base cations and this species did not appear suitable for dendrochemical detection of acidification.

Acidification treatments to both WS3 and WS9 resulted in changes in foliar chemistry of trees, although larch on WS9 seemed to be more responsive than the hardwood trees on WS3. Where statistically significant differences were detected, concentrations of Ca and Mg were generally decreased and levels of Mn and/or Al were elevated in foliage. Foliar chemistry response was inconsistent and did not show initial periods of base cation mobilization followed by base cation depletion, that were found with bolewood chemistry.

The acidification treatments, through the effects of elevated N, also may have created P limitations for the herbaceous and overstory plant species on WS3. The seasonal changes in herbaceous cover that are normally linked to net nitrification were absent on WS3 due to a decoupling of N cycle from biotic controls due to treatments.

The pattern of increasing growth followed by decreasing growth found in tree cores was synchronous with changes in bolewood chemistry and other temporal patterns of soil solution and stream chemistry described in Chapter 4. The pattern of changes in growth (tree cores only), soil solution and stream chemistry fits the expected response of forest ecosystem to acidification described in Chapter 1. Ecosystem response time for bolewood chemistry changes in these experiments suggests that two to three decades would be required for detection of a 10% decrease in deposition in ecosystems similar to the FEF.

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Chapter 6

RESPONSE OF SALAMANDERS TO EXPERIMENTAL ACIDIFICATION TREATMENTS

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1. INTRODUCTION

Forests provide habitats for groups of plants and animals that serve as bioindicators, organisms that can alert biologists to obvious as well as subtle changes in forest health and ecology. Plants that function in this capacity include lichens and mosses and such animal groups include macro-invertebrates, fishes and amphibians. Amphibians play a particularly important role as bioindicators because: (1) most have complex life cycles with aquatic and terrestrial stages which expose them to perturbations in both environments; (2) they have permeable skin, gills, and eggs that are susceptible to environmental alterations; (3) their dependence on ectothermy for temperature control makes them vulnerable to environmental fluctuations; (4) many hibernate or aestivate in soils that may expose them to toxic conditions; and (5) they are both predators and prey in terrestrial and aquatic food webs (Dunson et al. 1992).

Of the amphibian groups in northeastern US forests, lungless salamanders (family Plethodontidae) are perhaps the most ecologically important. Because these salamanders are lungless, they respire through their integument and this often requires that they reside in moist, cool forests. Two subfamilies of Plethodontidae, Desmognathinae and Plethodontinae, comprise most of the salamander species in these forests. Desmognathinae includes dusky salamanders (genus *Desmognathus*), which inhabit predominantly first- and

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second-order streams. Dusky salamanders remain in or near streams throughout their lives. They deposit eggs under objects at the stream's edge or in seeps within the banks. There is a free-swimming larval stage of a few weeks to several months. Plethodontinae consists of woodland salamanders (genus *Plethodon*) as well as several aquatic to semi-aquatic species. Woodland salamanders, on the other hand, are totally terrestrial and deposit their eggs under rocks and logs, in decaying logs, or in subterranean cavities.

1.1 Salamanders on the Fernow Experimental Forest

Five species of dusky salamanders are known occur in West Virginia and 3 of these (Allegheny Mountain Dusky Salamander, *D. ochrophaeus;* Seal Salamander, *D. monticola*; Northern Dusky Salamander, *D. fuscus*) are common in the appropriate habitats on the Fernow. *Desmognathus ochrophaeus* and *D. monticola* are the dominant species in first-order streams.

Of the 11 species of woodland salamanders in West Virginia, 3 (Northern Red-backed Salamander, *P. cinereus*; Northern Slimy Salamander, *P. glutinosus*; Wehrle's Salamander, *P. wehrlei*) occur locally. *Plethodon cinereus* is the dominant woodland species on the Fernow.

Other plethodontid species that occur within forest habitats on the Fernow are Northern Two-lined Salamanders (*Eurycea bislineata*), Northern Spring Salamanders (*Gyrinophilus p. porphyriticus*), and Northern Red Salamanders (*Pseudotriton r. ruber*), Red-spotted Newts (*Notophthalmus v. viridescens*), and Spotted Salamanders (*Ambystoma maculatum*) in the family Ambystomatidae also are present on the Fernow. All of these are relatively common in appropriate habitats.

1.2 Biology and Ecology of Salamanders

Distribution of plethodontids is regulated or restricted due to moisture requirements of their permeable skin, gills, and eggs and ectothermy (Thorson 1955). The Allegheny Mountain physiographic province of West Virginia, where the FEF is located, has the lowest mean annual temperatures (11.5^{o}C) and the highest mean annual precipitation (110.2 cm) in West Virginia (U.S. Department of Commerce 1973). These environmental conditions result in cool, moist forests with an abundance of first-order streams and seeps, which provide ideal habitats for plethodontid salamanders.

Salamanders are one of the least familiar vertebrates in our forests because of their secretive behavior and nocturnal activity. This unfamiliarity results in a lack of understanding of their ecological roles in forests. Knowledge of salamander identification and natural history can provide significant information to help protect and conserve the region's forests. Salamanders are abundant in aquatic and terrestrial habitats to the magnitude where terrestrial species may represent twice as much standing biomass as birds and an amount equivalent to that of small mammals (Burton and Likens 1975a). The significance of the biomass of salamanders has been demonstrated in several population studies that have estimated large numbers of salamanders per hectare in northeastern deciduous forests. Such estimates include 5,535 *P. cinereus* per hectare (Burger 1935), 2,100 *P. cinereus* (Klein 1960), 2,324 *P. glutinosus* and 8,611 *P. jordani* (Merchant 1972), and 838 *P. cinereus* (Werner 1975). Larval densities in optimal habitats often exceed two to three individuals per m^2 (>20,000 per ha) and adult densities may exceed one to two salamanders per m^2 (>10,000 per ha) on the forest floor or streambed (Petranka 1998). Salamander larvae are important predators on stream macroinvertebrates (Huang and Sih 1991).

Ecologically, salamanders are predators that prey primarily on invertebrates. They are highly efficient (60%) at converting ingested energy into new tissue and 20% of the energy available to birds and mammals passes through salamanders (Burton and Likens 1975b). Thus, salamanders are key components in trophic cycling in northeastern deciduous forests and thereby contribute to overall forest health and ecosystem integrity.

1.3 Effects of Disturbance on Salamanders

Considering the significance of ecological niches salamanders occupy, declines in populations would be devastating to many ecosystems. Studies that illustrate the deleterious effects of anthropogenic stress provide evidence for the cause of some amphibian population declines. Both atmospheric deposition and timber harvesting have been hypothesized to have deleterious impacts on some salamander communities. Declines and extirpation of local amphibian populations and in some cases, extinction of entire species, have been reported throughout the world (Barinaga 1990, Milstein 1990, Phillips 1990, Wyman 1990, Wake 1991). We will consider both of these disturbances, as both have occurred on the FEF, and the experimental watersheds (See Chapter 2).

Some studies have shown that low soil and water pH have a detrimental affect on amphibians, but others have been inconclusive in correlating amphibian declines with soil and water acidity (Corn and Vertucci 1992). In areas where soil substrates lack buffering capacity, such as the Sierra Nevada region of California, there is some concern that acidic deposition may adversely influence amphibian populations (Harte and Hoffman 1989). Other research in this geographic region suggests that pH may not greatly influence amphibian populations because acidic pulses from snowmelt occur at times when amphibians are not developing or because of environmental variables (Muths et al. 2003, Corn and Vertucci 1992, Bradford et al. 1994). In the Blue Ridge Mountains of Virginia, Mitchell (1999) found no correlation between buffering capacity of streams and amphibian diversity. Long et al. (1995) showed that pH and UV-b light interact in a synergistic fashion in the mortality of amphibian eggs in the laboratory. Most of these studies examined either the tolerance of a few species to low pH values or associated declines in populations with soil or water acidity. Low pH values have been linked to abnormalities in embryos of ambystomid salamanders and other amphibians (Pough 1976, Pough and Wilson 1977, Singer 1982, Freda and Dunson 1984, 1985, Pierce 1985, Harte and Hoffman 1989, Kiesecker 1996). Cook (1983) found no correlation between pH and embryonic mortality for *Ambystoma maculatum* from ponds in Massachusetts and he suggested that some populations of *Ambystoma* may be resistant to low pH. Mushinsky and Brodie (1975) tested eight species of plethodontid salamanders for pH substrate preference and found that six preferred basic substrates and two showed no preference. Low soil pH values can lower amphibian densities and species richness (Wyman and Jancola 1992) and alter osmoregulation causing physiological stress (Frisbie and Wyman 1992). In forests where litter pH values were below 3.7, the density and distribution of *P. cinereus* were significantly reduced (Wyman and Hawksley-Lescault 1987). Wyman (1988) studied 16 species of amphibians in south-central New York and found that in addition to soil pH significantly influencing the distribution of *P. cinereus,* distributions of *E. bislineata, D. fuscus*, and *A. maculatum* also were restricted. Following a laboratory study, Kiesecker (1996) suggested that pH might have sublethal effects that decrease predatory success in *A. tigrinum*. Decreased predatory success may reduce fitness and survival rate of salamanders subjected to low pH.

The potential for detrimental effects of timber harvesting on forest salamanders has been a subject of interest to amphibian biologists since the 1970s (Blymyer and McGinnes 1977, Rice et al. 1979). While few studies on the impact of timber harvest occurred in the eastern US (Enge and Marion 1986, Pough et al. 1987, Ash 1988, Bonney and McComb 1988, DeGraaf and Rudis 1990, Raymond and Hardy 1991), during the 1980s and early 1990s many studies were conducted in the western United States (Murphy et al. 1981, Bury 1983, Rosenburg and Raphael 1986, Childs and Flint 1987, Andrus and Froehlich 1988, Bury and Corn 1988, Conner et al. 1988, Corn and Bury 1989, Scott and Ramotnik 1992, Walls et al. 1992). Work by Petranka et al. (1993) in the southern Appalachians sparked a debate within the ranks of forest managers and amphibian biologists (Ash and Bruce 1994, Petranka 1994, Ash and Pollock 1999). Subsequent studies on the effects of logging on forest salamanders have resulted in some answers as to the effects of silvicultural practices on forest salamanders.

Clearcutting, for the most part, has been found to have immediate detrimental effects on terrestrial and aquatic forest salamanders (Blymyer and McGinnes 1977, Silsbee and Larson 1983, Enge and Marion 1986, Pough et al. 1987, Bury and Corn 1988, Ash 1988, 1995, 1996, Raymond and Hardy 1991, Scott and Ramotnik 1992, Petranka et al. 1993, Petranka et al. 1994, Dupuis et al. 1995, Harpole and Haas 1999, Adams et al. 1996, Clawson et al. 1997, Mitchell et al. 1996, 1997, Sattler and Reichenbach 1998, Duguay and Wood 2002, Ford et al. 2002). Clearcutting exposes the forest floor to increased insolation, which results in higher soil temperature, lower soil moisture of the upper 3 cm, lower relative humidity, and reduced litter mass and depth (Troendle 1970, Swank and Vose 1988, Ash 1995, Raymond and Hardy 1991, Pauley 2005). Clearcutting also increases temperature of first-order streams (Brown and Krygier 1970, Beschta et al. 1987), and also increases sediment loads that can negatively affect microhabitats and suffocate eggs and larvae (Beschta 1978, Corn and Bury 1989, Lowe and Bolger 2002).

2. SALAMANDER RESEARCH ON THE FERNOW EXPERIMENTAL FOREST

In addition to the Watershed Acidification Research dealing with the ecology and natural history of salamanders and the effects of insecticides used to control gypsy moths on forest salamanders have been conducted at the FEF. Natural history studies examined nesting habits and development of three Desmognathinae species, aspects of larval natural history of two aquatic Plethodontinae species, and niche partitioning between a Desmognathinae species and a Plethodontinae species (Kees 1994, Marcum 1994, Ordiway 1994). Results of these studies have provided baseline data to assist biologists in proper forest management practices that will protect salamanders on the FEF.

Salamander studies reported in this book deal primarily with the effects of acidic deposition. The treated watershed (WS3) had been clearcut in 1970 prior to initiation of the acidification study, and because of the potential effects of clearcutting on salamander populations, we report the results of two areas of research. Studies were conducted separately to evaluate the effects of clearcutting, and the effects of the acidification treatment on salamanders.

In the acidification study described in this book, we hypothesized that lower pH values in the treatment watershed would cause physiological stress on salamanders which would result in loss of fat (energy) reserves, and this loss would reduce ovarian egg numbers or volumes to potentially reduce population densities. We describe a field experiment that examines the effects of watershed acidification on *P. cinereus, D. monticola* and *D. ochrophaeus*, the three most common plethodontid salamanders in the FEF.

3. METHODS

3.1 Effects of Watershed Acidification

To determine potential effects of acid deposition on salamander populations, we examined three watersheds (WS3, WS4, and WS7) for salamander surface density, prey items, percentages of fat in tails and carcasses, and ovarian egg sizes, volumes, and numbers. Surface densities of the terrestrial species *P. cinereus* and *D. ochrophaeus* were determined by capturing specimens under five coverboards (25 cm x 15 cm x 2.5 cm pine) and 5 natural objects in seven 25 m^2 quadrats placed at 10 m intervals (Pauley 1995) located along two 100 m transects positioned 20 and 40 m upslope from the stream in each watershed. To minimize the influence of weather conditions, surface density studies were conducted 24 to 48 hours after precipitation.

Soil pH was determined by collecting samples in September and October of each year of the study from the first 3 cm of soil at alternate quadrats along each transect. Soil was placed in plastic bags, then packed in ice and taken to the lab within 4 hours for pH analyses.

Surface densities of the aquatic species *D. monticola* were determined in a 25 m section of each stream. To capture specimens, we searched beneath 100 rocks (approximately 250 cm^2) and 10 rocks (approximately 500 cm^2) artificially stacked on top of larger rocks (approximately 900 cm^2). Terrestrial and aquatic sites were sampled monthly from May through October. For each specimen captured, we determined snout-vent length (SVL) and gender; we toe clipped each specimen, and then released it at the site of capture.

Adult *P. cinereus*, *D. ochrophaeus*, and *D. monticola* from all watersheds were collected from September through November each year. Specimens were placed in plastic bags, packed in ice, and taken to the lab and frozen at $-20^{o}C$. All diet items were removed from the stomach of each specimen and identified to taxonomic order. To determine the percentage of fat in the tail, the first 18 mm (Fraser 1980) of the tail was removed, weighed (wet weight), dried in a convection oven (dry weight), bathed in petroleum ether for 8 hours and weighed (lean weight) (Fitzpatric 1972, Kerr, et al. 1982, Reznick and Braun 1987). Ovarian egg numbers were determined by removing the ovaries and counting all eggs. Egg volumes were established by placing eggs in a 10 ml volumetric flask filled with water and measuring the amount of water displaced with a 1.0 ml syringe. Fat percentages and ovarian egg data were analyzed by a one-way ANOVA with Newman-Keuls multiple comparisons (significance level = 0.05).

3.2 Effects of Clearcutting

To assess effects of clearcutting on salamander populations, we studied surface density of salamanders on 4 watersheds (WS1, WS3, WS4 and WS7) from 1989 through 1990. Watersheds were cut 84 (WS4), 31 (WS1), 22 (WS7), and 19 (WS3) years prior to 1989. Therefore each watershed drains forest stands of different ages For descriptions of the watershed treatments see Table 2-1.

4. RESULTS

4.1 Effects of Watershed Acidification on Salamanders

The upper 3 cm of soil in WS3 was significantly more acidic than on the two reference watersheds. *Plethodon cinereus* were generally less abundant in WS4 than WS3 and WS7 and *D. ochrophaeus* were more common in WS4 than in WS3 and WS7. *Desmognathus monticola* occurred in about equal numbers in all watersheds.

Food items found in *P. cinereus* stomachs (Table 6-1) were similar in each watershed. Non-winged hymenopterans (referred to as ants hereafter) were the dominant taxa in all watersheds followed by coleopterans and arachnids. Except for winged hymenopterans, *D. ochrophaeus* generally had fewer items of each food category in all watersheds than did *P. cinereus*. The dominant food items found in *D. monticola* included ants, winged hymenopterans, and coleopterans. A greater percentage of stomachs of *D. ochrophaeus* and *D. monticola* were empty in all watersheds compared to *P. cinereu*s. All three species of salamanders had a higher percentage of empty stomachs in WS7 than in WS3 and WS4.

Percentages of tail fat in females (Table 6-2) were not significantly different for *P. cinereus* and *D. ochrophaeus* among the watersheds. *Desmognathus monticola* females had a greater percentage of tail fat in WS7 than in WS3. Ovarian egg numbers (Table 6-3) did not differ significantly for either terrestrial or aquatic species. Female *D. ochrophaeus* and *D. monticola* in WS3 produced a higher number of ovarian eggs than females of either species in WS4 or WS7. Females of both species produced fewer eggs in WS7. *Plethodon cinereus* produced fewer eggs in WS3 than in either of the reference watersheds. Ovarian egg volumes were significantly greater in *D. ochrophaeus* and *P. cinereus* in WS3 than in WS7, but not WS4 (Table 6-3). There was no significant difference in egg volumes for *D. monticola* among the watersheds.

Table 6-1. Distribution (percent) stomach content of prey items in stomachs of *D. monticola*, *D. ochrophaeus*, and *P. cinereus* from WS3, WS4, and WS7. 1989, 1990, 1991, 1992 data pooled.

Prey Items	WS3	WS4	WS7
D. monticola			
Hymen-ants	21.4	13.6	9.1
Hymen-wing	17.9	20.5	29.5
Lepidoptera	1.2	0.0	0.0
Diptera	10.7	5.7	4.5
Coleoptera	20.2	22.7	20.5
Centipede	2.4	0.0	2.3
Millipede	0.0	5.7	0.0
Mollusca	0.0	2.3	2.3
Collembola	0.0	1.1	0.0
Pseudoscorpion	0.0	0.0	0.0
Arachnida	6.0	1.1	4.5
Salamander	1.2	2.3	2.3
Other	3.6	5.7	4.5
Empty	39.3	38.6	43.2
Total	(84)	(88)	(44)
D. ochrophaeus			
Hymen-ants	18.3	9.0	13.7
Hymen-wing	13.3	16.3	5.9
Lepidoptera	3.3	1.8	2.0
Diptera	5.0	5.4	5.9
Coleoptera	13.3	12.0	7.8
Centipede	1.7	0.0	0.0
Millipede	3.3	2.4	2.0
Mollusca	1.7	5.4	0.0
Collembola	0.0	1.8	2.0
Pseudoscorpion	0.0	0.0	0.0
Arachnida	0.0	7.2	3.9
Salamander	0.0	0.0	0.0
Other	8.3	2.4	2.0
Empty	36.7	49.4	60.8
Total	(60)	(166)	(51)
P. cinereus			
Hymen-ants	43.9	60.9	46.7
Hymen-wing	5.3	3.1	3.6
Lepidoptera	1.5	0.8	2.4
Diptera	5.3	7.8	6.0
Coleoptera	25.0	14.1	13.2
Centipede	2.3	0.8	1.2
Millipede	3.8	0.0	0.0
Mollusca	4.5	0.8	4.2
Collembola	1.5	0.0	0.0
Pseudoscorpion	3.0	0.0	0.6
Arachnida	11.4	9.4	7.8
Salamander	0.0	0.0	0.0
Other	0.8	1.6	3.0
Empty	22.7	25.8	32.9
Total	(132)	(128)	(167)

Table 6-2. Comparison of tail fat of study species by watershed.

	Percent fat		
Watershed	*D. monticola*	*D. ochrophaeus*	*P. cinereus*
3	$13.52^{a} \pm 6.86$	$24.76^{a} \pm 8.38$	$13.52^{a} \pm 6.88$
	(n = 33)	(n = 16)	(n = 45)
4	$17.54^{ab} \pm 8.44$	$27.82^{a} \pm 6.99$	$13.78^{a} \pm 7.68$
	(n = 13)	(n = 38)	(n = 41)
7	$19.25^{b} \pm 9.63$	$24.49^{a} \pm 6.61$	$11.21^{a} \pm 5.56$
	(n = 18)	(n = 16)	(n = 66)

Mean percent fat (± 1 SD) extracted from first 18 mm of the tail in female *Desmognathus monticola*, *D. ochrophaeus*, and *Plethodon cinereus*. Within columns, mean values with different superscripts were found to be significantly different as indicated by one-way ANOVA and Newman-Keuls multiple comparison tests ($\alpha = 0.05$). 1989, 1990, 1992 data pooled.

Table 6-3. Egg numbers and egg volumes of study species by watershed.

Watershed	***D. monticola***	***D. ochrophaeus***	***P. cinereus***
		Egg number	
3	$29.7^{a} \pm 11.2$	$16.6^{a} \pm 3.3$	$7.7^{a} \pm 2.2$
	(n = 27)	(n = 17)	(n = 42)
4	$27.1^{a} \pm 8.3$	$15.8^{a} \pm 3.9$	$8.7^{a} \pm 2.1$
	(n = 11)	(n = 34)	(n = 34)
7	$22.9^{a} \pm 7.2$	$15.4^{a} \pm 3.3$	$8.2^{a} \pm 3.2$
	(n = 15)	(n = 12)	(n = 42)
		Egg volume	
3	$248.1^{a} \pm 175.7$	$101.9^{a} \pm 50.2$	$25.6^{a} \pm 19.1$
	(n = 27)	(n = 16)	(n = 39)
4	$209.5^{a} \pm 214.7$	$88.2^{ab} \pm 50.7$	$19.4^{ab} \pm 11.3$
	(n = 11)	(n = 34)	(n = 29)
7	$237.0^{a} \pm 125.0$	$51.7^{b} \pm 14.6$	$16.3^{b} \pm 14.8$
	(n = 15)	(n = 12)	(n = 37)

Mean egg number (± 1 S.D.), and mean egg volume (± 1 SD) expressed in microliters for *Desmognathus monticola*, *D. ochrophaeus*, and *Plethodon cinereus*. Within columns, mean values with different superscripts were found to be significantly different as indicated by one-way ANOVA and Newman-Keuls multiple comparison tests ($\alpha = 0.05$). 1989, 1990, 1991, 1992 data pooled.

4.2 Effects of Clearcutting on Salamanders

Ninety-one *P. cinereus* (42 in watersheds with mature stands and 49 in watersheds with young stands) and 160 *D. ochrophaeus* (117 in mature forest and 43 in immature forest) were observed. Approximately the same number of *P. cinereus* was observed in all three watersheds but more *D. ochrophaeus* were found in watersheds with mature stands than in watersheds with young stands.

Based on these data, *P. cinereus* populations at the FEF presumably recover to their original numbers in clearcut areas in 20 years. Our data concur with the conclusions of Ash (1996) and Duguay and Wood (2002). Dugay and Wood (2002) determined that it may take more than 15 years for red-backed salamanders in harvested stands in the Monongahela National Forest to reach abundance numbers found in mature hardwood forest.

Desmognathus ochrophaeus showed an interesting difference compared to *P. cinereus*. In WS3 and WS7, the most recently cut watersheds, fewer *D. ochrophaeus* were found than in older clearcuts. Based on surface density, species such as *D. ochrophaeus* that are less tolerant of dry conditions created by clearcutting are slower to recover to original densities. This species is less tolerant of dry conditions (Pauley 2005) probably because they deposit eggs in wet areas (creeks, seeps, etc.) and have a short aquatic larval stage of approximately two weeks (Marcum 1994). Because *D. ochrophaeus* are more dependent on water for reproduction, they are slower to repatriate habitats where disturbances open the canopy and reduce soil moisture.

5. DISCUSSION

Although soil pH values were significantly different among watersheds, surface densities of the terrestrial species (*P. cinereus* and *D. ochrophaeus*) and aquatic species (*D. monticola*) were not significantly different. Our findings for soil pH and species occurrence differ from previous soil pH studies (Mushinsky and Brodie 1975, Wyman 1988, Wyman and Jancola 1992), which showed an effect on species composition.

Jaeger and Barnard (1981) showed that passage time through the digestive tract of *P. cinereus* is much faster for prey items with thinner chitinous exoskeletons (dipterans) than prey with thicker chitinous exoskeletons (ants and coleopterans). Jaeger (1990) concluded that salamanders that ingest prey with thin exoskeletons can pass more prey through the digestive system in a given period of time. Jaeger suggested that salamanders avoid consuming heavy armored hymenopterans and coleopterans, which will move more slowly through the digestive tract than softer prey. Since hard-bodied prey items were the major food items of *P. cinereus* and *D. ochrophaeus*, it is doubtful that acidification had an influence on prey item availability.

The lower percentage of all food items taken in WS7, as well as the higher percentage of empty stomachs in *P. cinereus* and *D. ochrophaeus* in this watershed, could suggest that some other factor (such as disparate stand age and previous vegetation treatments) is present in WS7 that influences food availability.

Although the percentages of tail fat of female *D. ochrophaeus* and *P. cinereus* were not significantly different among the watersheds, lower fat percentage in WS3 and WS7 could suggest some stress from past forest harvesting and lower soil pH as a result of the acidification treatment.

The size (SVL) of all salamander species in WS3 did not appear to be affected by the acidification treatment. Because of the longevity of the adult stage of plethodontid salamanders (many live 15 to 20 years), and the probability that acidic deposition does not affect any particular age class, size may not be the most important parameter to determine effects of acidic deposition. If, however, acidic deposition has a detrimental effect on egg production and hatching, juveniles and subadult sizes may comprise a significantly smaller component of the population in the next few years.

Studies have shown that growth and reproductive success may be associated with the type of habitat and energy availablity. Tilly (1974) compared the size of gravid *D. ochrophaeus* and egg numbers between populations in a woodland habitat to those that inhabited a rockface. Females from the woodland habitat were significantly larger and produced clutch sizes that were on average 50% greater. Fraser (1980) kept female *P. cinereus* on either high or low food regimes and found that the amount of food did not affect the number of ovarian eggs and that the number of ovarian eggs was not correlated to SVL. He found, however, that ovarian egg number was significantly correlated to initial body weight and tail volume.

Ovarian egg numbers were not significantly different in *P. cinereus* and *D. ochrophaeus*, or *D. monticola* between treatment and reference watersheds. Ovarian egg volume data for terrestrial species did show significant differences in *P. cinereus* and *D. ochrophaeus*. Both species had significantly smaller eggs in WS7 than in WS3. The smaller eggs in WS7 may reflect the past history of the watershed. It is somewhat confusing why WS3 females produce larger eggs than those in WS7 and WS4 (although not significantly larger in WS4). It may be that females are under stress through direct contact with lower soil pH. Females under such stress may produce larger ovarian eggs as a strategy to increase hatching success.

6. CONCLUSIONS

From this study we could not demonstrate an effect of the acidification treatment on the fat content of woodland or stream salamanders. Although there were differences in the diets and predatory success (based upon the number of empty stomachs) no differences were found for fat content. This suggests the physiology of the organisms was sufficient to compensate for any changes in the diet produced by the treatments. Although there were differences in the size of eggs between treatments, the biological significance of the size difference is unknown at this point. Therefore this study did not document any direct effect of acidification on woodland or aquatic salamanders on the FEF.

Two potential concerns with this study involve the length of the study and the stand histories of the watersheds. In order to detect effects of anthropogenic change on forest salamanders, it is recommended that studies of at least 10 years need to be conducted (Dunson et al. 1992). Because this was a 4-year study, it may have been too brief for acidification effects to be detected in long-lived, high trophic level animals. Although the past treatment of WS3 may confound the acidification effects, making comparisons with a reference watershed (WS7) with a similar history should allow us to observe effects from the acidification treatment.

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Chapter 7

ACIDIFICATION AND NUTRIENT CYCLING

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1. INTRODUCTION

Additions of acid anions can alter the cycling of other nutrients and elements within an ecosystem. As strong acid ions move through a forest, they may increase the concentrations of nitrogen (N) and sulfur (S) in the soil solution and stream water. Such treatments also may increase or decrease the availability of other anions, cations and metal ions in the soil. A number of studies in Europe and North America have documented increases in base cation concentrations such as calcium (Ca) and magnesium (Mg) with increased N and S deposition (Foster and Nicolson 1988, Feger 1992, Norton et al. 1994, Adams et al. 1997, Currie et al. 1999, Fernandez et al. 2003). Experiments in Europe also have evaluated the response of forested watersheds to decreased deposition (Tietema et al. 1998, Lamersdorf and Borken 2004). In this chapter, we evaluate the effects of the watershed acidification treatment on the cycling of N, S, Ca, Mg and potassium (K) on Fernow WS3.

To accomplish this goal, we primarily will examine trends in annual nutrient fluxes. For these analyses, inputs were calculated on a calendar year basis, using data from the Fernow Fork Mountain deposition monitoring site, located near the top of WS4, and from the Parsons NADP site located in the Nursery Bottom in Parsons, West Virginia. Both of these sites and methods are described in Adams et al. (1994) and Gilliam and Adams (1996). Briefly, precipitation samples were obtained using Aerochem Metric automated wet/dry collectors, and open bucket "bulk" collectors. Inputs for N and S were calculated as the sum of total wet and dry deposition (http://www.epa.gov/castnet/data.html). Estimates of dry deposition are not available for Ca, Mg,

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and K, therefore inputs were calculated for these analytes based on bulk deposition (see Chapter 1). Bulk deposition samples were collected weekly and analyzed for pH, Ca, Mg, sodium (Na), K, ammonia-N (NH_3-N), chloride (Cl), nitrate (NO_3) and sulfate (SO_4), according to NADP protocol as described in Stensland et al. (1980). Stream water exports were calculated using flow rates for the individual watersheds and weekly grab sample nutrient concentrations, summed over a calendar year. Further information on sampling methods and analytical techniques can be found in Chapter 2, Chapter 4, and Adams et al. (1994). The calculation of watershed-specific precipitation and loadings is described in Adams et al. (1994). Additional published sources also are used to describe internal cycling. We focus primarily on WS3 (treatment watershed), WS4 (reference watershed), although we use information from studies of other watersheds, most notably WS7 (vegetative reference). See Chapter 2 for a description of these watersheds.

2. NITROGEN CYCLING

2.1 Inputs

Sources of N inputs include both wet and dry deposition. Approximately 45% of N is deposited as wet NO_3, and approximately 26% as wet ammonium (NH_4). Dry nitric acid (HNO_3) makes up about 22% of N deposition, about 6% of N deposition occurs as dry NH_4, and less than 1% is dry NO_3 (NADP 2004). Wet deposition of N has declined slightly since 1978, the first year of record for the Nursery Bottom NADP site, from an annual average of about 8 kg N ha^{-1} yr^{-1} to about 5 kg N ha^{-1} yr^{-1}. Most of this decline is the result of decreases in wet NO_3 deposition, since NH_4 deposition has remained relatively constant on average, but with considerable inter-annual variability. Total N deposition (wet plus dry deposition) at the Fork Mountain monitoring station averaged 10.4 kg N ha^{-1} yr^{-1} between 1986 and 2002, the period of data used in the analyses of nutrient budgets (Fig. 7-1). Atmospheric inputs of N at Fernow vary with elevation, the result of both higher concentrations of NH_3 and NO_3 in wet deposition and higher amounts of precipitation at greater elevations (Gilliam and Adams 1996).

Nitrogen fixation is another possible source of N in eastern forested watersheds. The only native N-fixing tree, black locust, is relatively sparse on the study watersheds, 15 stems ha^{-1} on WS3 and 2.5 stems ha^{-1} on WS4 (Gilliam et al. 1995, see Chapter 2). Because of the scattered nature of the locust trees, the closed canopy on both watersheds and the acidic soils, the N fixed is likely to be minimal on a watershed scale (Boring et al. 1988).

Presence of leguminous herbs is also negligible (Aulick 1993, Hockenberry 1996).

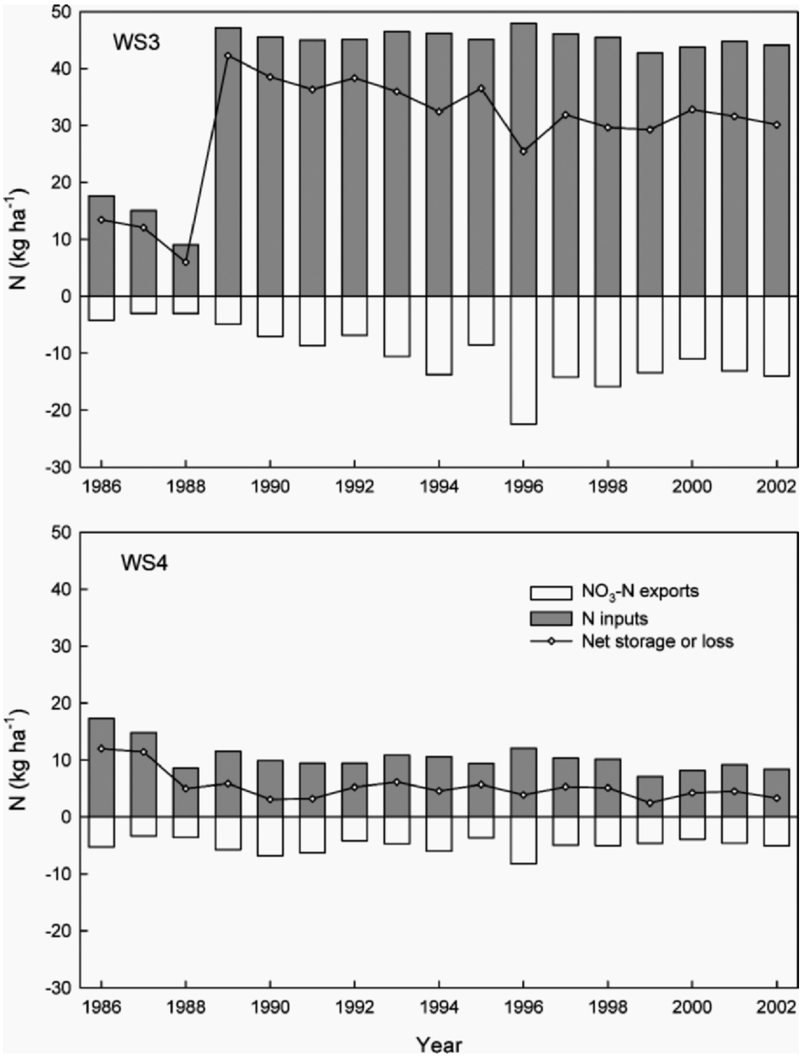

Figure 7-1. Inputs, exports and storage of N from WS3 and WS4. Treatments were initiated in 1989.

2.2 Outputs

Nitrogen outputs from the watersheds include ammonium, nitrate, and dissolved organic N (DON) in stream water, and gaseous losses of N (Fig. 7-2). Ammonium concentrations are consistently low, generally near the detection limits of our equipment, and so exports are generally negligible. Most of the N exported from the watersheds is in the form of NO_3. Pretreatment NO_3-N exports from WS3 (1986-1988) averaged about 3.3 kg ha^{-1}, and WS4 exports averaged 3.9 kg ha^{-1}. Exports on WS3 increased quickly after treatments began, to an average of 12.5 kg ha^{-1} during the treatment period. Exports from WS4 averaged 5.3 kg ha^{-1} during the same time period.

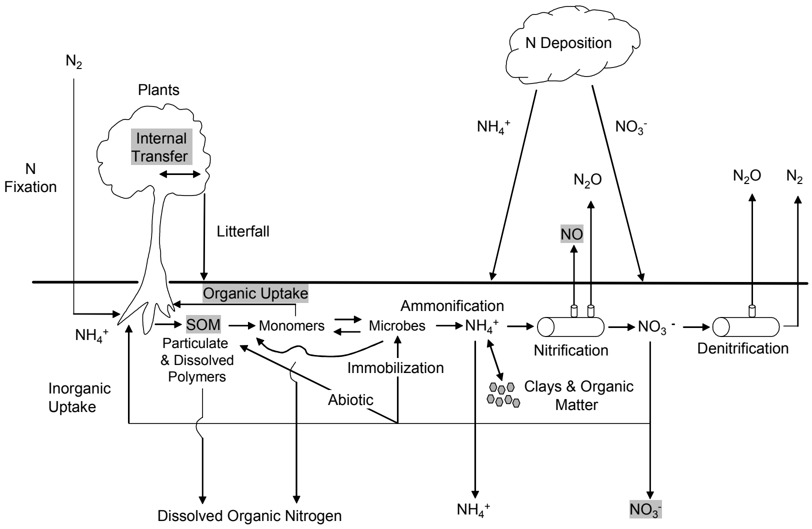

Figure 7-2. N cycle. Highlighted fluxes or pools are those which were affected by the watershed acidification treatment.

Although estimates of dissolved organic N (DON) exports are not available for WS3, DON is not expected to contribute a dominant portion of total annual N exports. DON is mostly retained in soils even when it is present in reasonably high levels (Davidson et al. 2003). Foster (1997) estimated that DON exports from Fernow WS10 and WS4 ranged from 0-50% of total N exports, and averaged 23% for WS10 and 13% from WS4. She attributed the difference between the two watersheds to differences in organic matter content of the soil, particularly the forest floor (see Chapter 3).

Therefore, based on soil organic matter concentrations in WS3 (91 g kg^{-1}) compared with WS4 and WS10 (112 and 62 g kg^{-1}, respectively), we may conclude that DON export does not contribute greatly to N leaching losses.

Some N is exported from the watersheds in gaseous emissions, although this flux is estimated to be relatively small. Soil emissions of nitric oxide (NO) were higher in WS3 relative to WS7, the vegetative reference watershed containing similar soils and a stand of hardwoods the same age as WS3 (Venterea et al. 2004). Increased NO emissions also were observed for the N-amended West Bear Brook watershed in Maine, providing evidence that increased soil NO emissions are a characteristic response in forests subjected to elevated N inputs. Venterea et al. (2004) estimated that NO emissions represented <1.6% of total inputs to Fernow WS3 and to West Bear Brook (both receiving ammonium sulfate fertilizer). Assuming all NO produced is released to the atmosphere, these emissions represent a flux of less than 1 kg N ha^{-1} yr^{-1}.

Nitrous oxide (N_2O) production was measured in WS3 and WS4 by Peterjohn et al. (1998). Although N_2O production was 22% greater for WS3 than WS4, these differences were not significantly different. Mean monthly rates of N_2O production (3.41-11.42 μg N m^{-2} hr^{-1}) were consistent with measurements from other well drained forest soils but were much lower than those of N-rich sites with poorly drained soils, and probably represents a flux of less than 1 kg N ha^{-1} yr^{-1} (Peterjohn et al. 1998, Bowden et al. 1990, 1991). Thus, increases in gaseous emissions in response to elevated N additions are not likely to contribute significantly to losses from the system.

2.3 Budgets

Nitrogen inputs to WS3 prior to the start of fertilization averaged approximately 8-10 kg N ha^{-1} yr^{-1}, including dry deposition of approximately 2 kg N ha^{-1} yr^{-1}. The significant increase in inputs to WS3 after 1989 reflects the addition of 35.5 kg N ha^{-1} yr^{-1} in the fertilization treatment (Fig. 7-1). Stream water exports of NO_3-N began increasing shortly after the first fertilizer applications. By contrast, WS4, receiving only ambient N and S inputs, experienced relatively little annual variation in N inputs or exports (Fig. 7-1). Since the treatments began, 53% to 89% (average of 73%) of the added inorganic N has been retained on WS3. Between 1989 and 2002, WS3 has retained, either through uptake, immobilization, or abiotic fixation (Fig. 7-2), approximately 470 kg N ha^{-1}. Pretreatment retention (1986-1988) of N by WS3 was around 65%; immediately after treatment began, almost 90% of the N inputs were retained. Percent N retained has declined steadily with continued treatment to around 70% in 2002, approaching pretreatment levels.

During this same time period, WS4 retained from 30% to 60% (average = 45%) of the total inorganic N deposited in deposition. Two other Fernow reference watersheds, WS10 and WS13, retained 85% and 44% of inorganic N, respectively (Campbell et al. 2004). It is notable that in a study of inorganic N budgets for 24 undisturbed forested watersheds across the northeastern United States, Fernow WS4 was the only watershed exhibiting a net loss (of 0.7 kg N ha^{-1} yr^{-1}; Campbell et al. 2004). Note however, that those estimates do not include dry deposition, thus do not incorporate all inputs to the watershed. Nonetheless, WS4 does demonstrate some of the lowest retention of N in the northeastern U.S.

The addition of N to WS3 via the ammonium sulfate fertilizer clearly increased the NO_3-N export from the watershed (Adams et al. 1997, Edwards et al. 2002, see Chapter 4). However, there was no detectable effect on NH_4 concentrations in stream water; indeed, NH_4 remains at very low levels in the stream water draining both WS3 and WS4. Apparent net storage of inorganic N on WS3 has declined over time, suggesting that less of the fertilizer N is being taken up and/or retained by the watershed, in response to continuing elevated N inputs. Conversely, during the period of analysis, in response to ambient deposition only, WS4 exports and apparent net retention have remained nearly constant.

2.4 Internal Cycling

Studies of N dynamics in the soils of the Fernow watersheds have shown that rates of net mineralization and net nitrification are high on both WS3 and WS4, compared with other forested ecosystems (Gilliam et al. 2001b). Net nitrification on WS3, WS4, and WS7 was 141, 114, and 115 kg N ha^{-1} yr^{-1}, respectively (Gilliam et al. 2001b, Christ et al. 2002), and essentially equal to 100% of net mineralization for these watersheds. These rates do not differ significantly among watersheds. Thus, NH_4 deposited via precipitation or fertilizer is mineralized and nitrified equally rapidly on WS3, WS4 and WS7. However, the lack of statistically significant differences may be due to high spatial variability, which may mask an important source of N available for export. The difference in mean net nitrification rates between WS3 and WS7 (26 kg N ha^{-1} yr^{-1}) is more than 2.5 times the amount needed to account for the approximately 10 kg N ha^{-1} yr^{-1} increase in stream water N output observed due to fertilizer treatment on WS3.

Soil emissions of NO were higher in WS3 relative to WS7 (Venterea et al. 2004), with nitrification hypothesized as the dominant source of NO. However, there were no significant differences in nitrification rates between WS3 and WS7 (Venterea et al. 2004), similar to the results of Gilliam et al. (2001b). Therefore, Venterea et al. (2004) speculated that a slight decrease in the pH of the upper soil horizon on WS3 (this was also noted in Chapter 3, a decrease of 4.34 to 4.20 in the 0-10 cm horizon during 1994-2002) may have caused increased protonation of nitrification-derived NO_3, and the subsequent abiotic formation of NO, which contributed to the differences in NO emissions between WS3 and WS7.

Nitrous oxide production, as measured in WS3 and WS4 by Peterjohn et al. (1998), was also found to be related to soil N processing. The mean rate of N_2O production was greater for WS3 than WS4, but these differences were not significantly different. Again, chemoautotrophic nitrification was important in both watersheds, accounting for 60% and 40% (WS3, WS4 respectively) of total N_2O production.

Evidence for effects of the fertilization treatment on N uptake by vegetation is equivocal. Differences in foliar nutrient concentrations were observed (Adams et al. 1995, May et al. 2005), which suggests there may have been differences in N uptake by the vegetation. Specifically, N concentrations of foliage collected in 1992 from WS3 were generally higher than from WS7 for four tree species: red maple, black cherry, yellow-poplar, and sweet birch – but were only significantly greater on WS3 relative to WS7 for black cherry and red maple. In 1997, foliar N concentrations were significantly greater on WS7 for red maple, relative to WS3. No other significant differences in foliar N concentrations were detected between the watersheds (Fig. 7-3). Foliar N concentrations generally decreased slightly or remained the same over the course of the study (Fig. 7-3), with the exception of yellow-poplar foliage, which showed a slight increase in N concentration over time. A sustained increase in foliar N concentrations would have provided support for the idea of continued high rates of N uptake as availability continued to increase.

May et al. (2005) also evaluated three of the same tree species in 1992 and 2001. In 1992, foliar N concentrations for red maple, yellow-poplar and black cherry were approximately 11% greater in WS3 relative to WS7. However, by 2001 mean foliar N was greater in WS7 for all three of these species for the trees that were sampled. Such a shift in foliar concentrations implies a change in the N uptake and/or allocation by these trees. This could be due to an increase in uptake by trees on WS7, decreased uptake by trees on WS3, or both, or could be due to changes in nutrient use and retranslocation of N once within the tree.

Mean foliar N values of all of the tree species examined fell within the range of values observed across the northeastern United States for these species (Northeastern Ecosystem Research Cooperative 2004), pointing to no obvious N deficiencies. Note however that in the 1970s, Auchmoody and Smith (1977) reported a 47% increase in basal area of small sawlog-sized yellow-poplar in response to N fertilization, which suggests the trees may have been N limited. We may further theorize that N availability, as reflected in foliar concentrations, has changed over time.

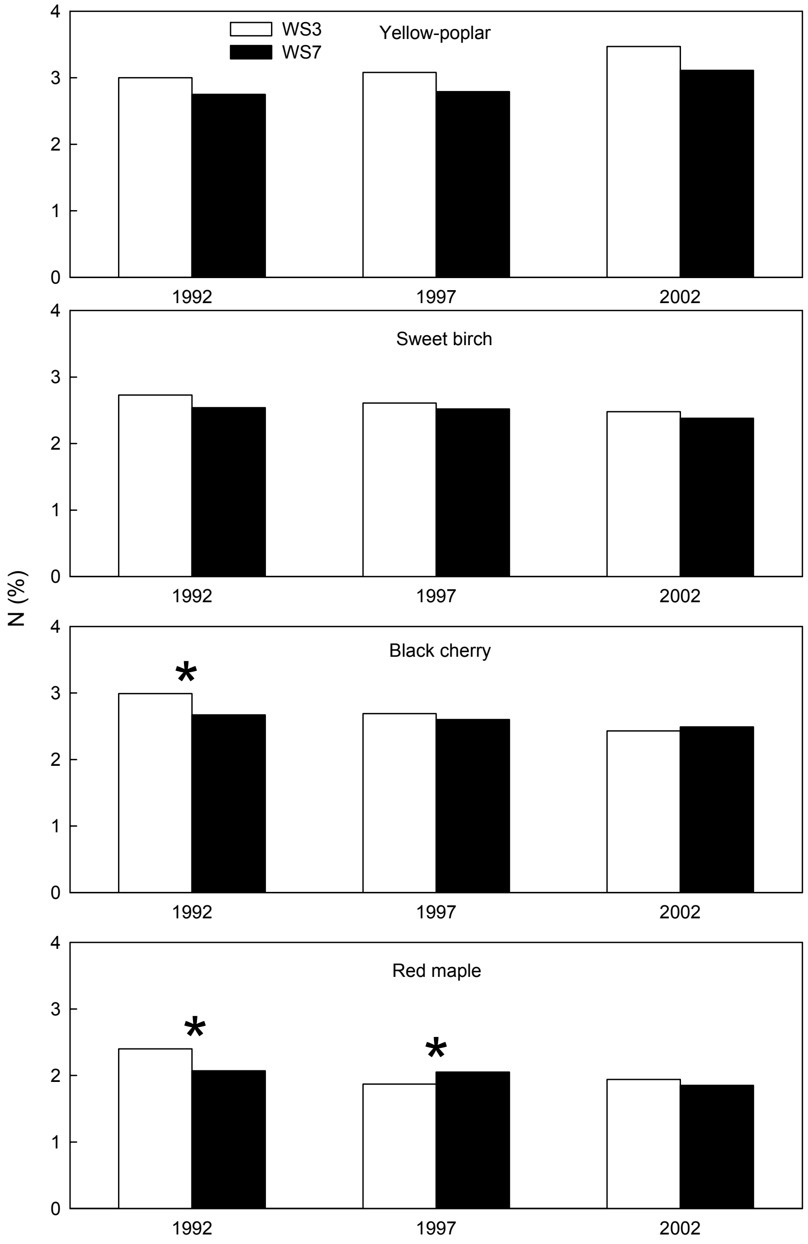

Figure 7-3. Mean foliar N concentrations for four tree species on WS3 and WS7, over time. * indicates statistically significant differences between watersheds ($p < 0.10$).

A comparison of concentrations of other foliar nutrients with the regional foliar data base suggests that phosphorus (P) may be limiting to black cherry, sweet birch and red maple, on both WS3 and WS7. Most forests are considered to be N-limited. However, once the demand for N has been met or exceeded, then another nutrient, most often P, becomes the nutrient limiting productivity. Data from fertilized root ingrowth core assays on WS4 (Foster 1997) and from phosphomonoesterase activity assays in roots of violets from WS3, WS4, WS10 and WS13 (W.T. Peterjohn, unpublished data) provide some support for this hypothesis. Thus, it may be long-term elevated ambient N deposition has led to a limitation by P, which could lead ultimately to decreased uptake of N.

Changes in nutrient allocation within the trees could also reflect altered nutrient availability. May et al. (2005) reported that the acidification treatment decreased nutrient resorption efficiencies on WS3. The resorption of N averaged 30% lower in WS3 for red maple and black cherry than in WS7, but there were no significant differences in N resorption efficiency between watersheds for yellow-poplar. For WS7, resorption efficiencies remained within the high end of published values, averaging 73-81% for N. Decreases in N reabsorption could be indicative of excess N uptake, with the tree decreasing retranslocation as a means to balance internal nutrient concentrations. Such changes in nutrient reabsorption and translocation may have significant implications for nutrient cycling in the forest floor and soil.

Changes in N uptake or nutrient resorption also could result in changes in litter quality. Although litter from yellow-poplar, black cherry, and sweet birch on WS3 decayed more slowly than on WS7, N loss rates from the leaf litter did not vary between the two watersheds after 3 years of treatment (Adams and Angradi 1996). Increases in total soil N concentrations over time were observed on WS3 (Chapter 3) and provide some support for the idea of increased uptake of N by the vegetation. The O horizon was the most responsive of the soil horizons to the fertilizer treatment, which could be partly explained by the application of fertilizer to the ground where the topmost horizon would receive and capture the additional N, but it could also be due to increased N uptake by vegetation leading to higher N foliar concentrations, ultimately resulting in greater N content of the litter layer.

After 3 years of the acidification treatment, aboveground N content of WS3 was slightly higher than WS7, except in the herb layer (Adams et al. 1995), although this difference was not statistically significant. WS3 contained 255 kg N ha^{-1} aboveground, compared with 233 kg N ha^{-1} for WS7. To some extent, this reflects greater aboveground biomass on WS3, which could not be attributed to treatment due to lack of pretreatment information (Adams et al. 1995).

All of these observations suggest that while vegetation on WS3 has responded to the N fertilization through increased uptake and some changes in allocation of nutrients, the response is highly variable, temporally, spatially within the watersheds, and among plant species. Chapter 5 details the responses of vegetation, some of which support the idea that uptake of N was increased, at least early on in the experiment.

Important and unresolved questions regarding N cycling remain. In particular, what accounts for the apparent storage of ~70% of N inputs? This was unexpected, particularly in a system that has many of the symptoms of N saturation (Peterjohn et al. 1996, Fenn et al. 1998). Other studies suggest incorporation into soil organic matter (Magill et al. 2000), but the mechanism by which this occurs is still unclear. Specifically, the role of abiotic immobilization of N (Fitzhugh et al. 2003) in forest soils requires further consideration.

3. SULFUR CYCLING

3.1 Inputs

West Virginia and western Pennsylvania receive some of the highest deposition of S in the eastern United States. However, S deposition has declined markedly since monitoring began in Parsons, from a high of >50 kg S ha^{-1} yr^{-1} in wet deposition to a current level of approximately 28 kg S ha^{-1} yr^{-1}, nearly a 45% decrease. Note that while such declines have been recorded at most monitoring stations in the northeastern United States (Hedin et al. 1994, Lynch et al. 2000), suggesting some success in regulating emissions, SO_4 deposition is still greater at the FEF than for either Hubbard Brook Experimental Forest, or Coweeta Hydrologic Laboratory, two other Appalachian sites (Fig. 7-4). Total S inputs to WS3 averaged approximately 23 kg S ha^{-1} yr^{-1} prior to the initiation of the acidification treatment. This increased to 59 kg S ha^{-1} yr^{-1} as a result of the acidification treatment. Sulfur inputs to WS4 averaged 19 kg S ha^{-1} yr^{-1} for the same period (Fig. 7-5).

The majority of the S deposition is delivered via wet SO_4 deposition (56%), with another 39% deposited as dry sulfur dioxide (SO_2). The remainder is dry SO_4. Helvey and Kunkle (1986) estimated average annual bulk deposition of 13.3 kg S ha^{-1} yr^{-1} with an additional 4.4 kg S ha^{-1} yr^{-1} delivered in throughfall. More recent estimates suggest that dry deposition contributes an average of 6.3 kg S ha^{-1} yr^{-1} to deposition, or approximately another 34%, to forest ecosystems above wet deposition (http://www.epa.gov/ castnet/data.html).

Similar to wet deposition of N, wet deposition of S increases with elevation at the FEF, the result of higher concentrations of SO_4 combined with higher amounts of precipitation at greater elevations (Gilliam and

Adams 1996). Wet inputs of S also exhibit a distinct seasonal pattern at Fernow, increasing in late spring to a maximum during summer months (June to August). From 1983 to 1989, wet inputs of S from June to August averaged nearly twice that of the other months. This has important implications for impacts on these forests, which are more metabolically active during this time of the year. Also, because of the contribution of S inputs to deposition of acidity to the forest, there are also implications for inputs of H^+, which increased from a minimum of 0.05 keq H^+ ha^{-1} in January to a maximum of 0.14 keq H^+ ha^{-1} in July (Gilliam and Adams 1996).

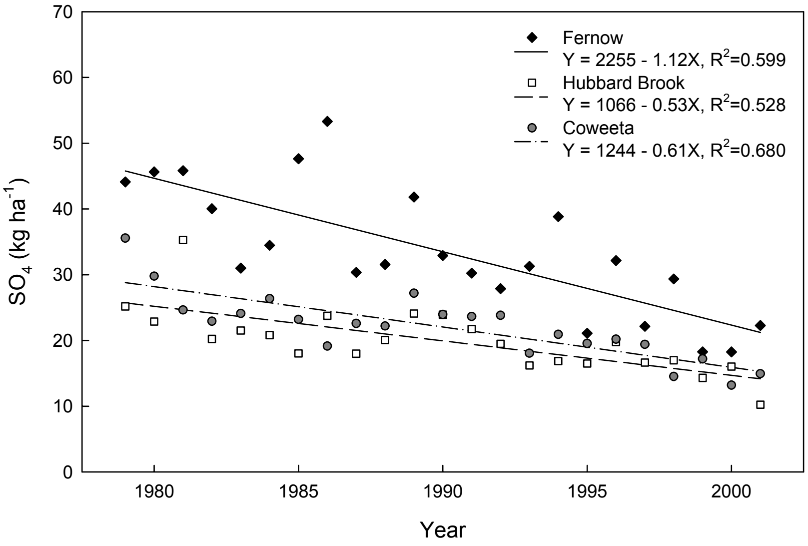

Figure 7-4. SO_4 deposition at three Appalachian monitoring stations, 1979-2001.

3.2 Outputs

Sulfur is usually exported from a watershed in the form of SO_4 in stream water, although there also may be some loss as hydrogen sulfide (H_2S) from wet soils with anaerobic conditions. Hydrogen sulfide however, is uncommon in well-drained forest soils such as found on the FEF because it is rapidly oxidized to SO_4. Exports of SO_4-S from WS3 in the three years prior to the treatments were about 6.5 kg ha^{-1} yr^{-1}. Exports increased to an average of 11.1 kg ha^{-1} yr^{-1} during the treatment period. Exports from WS4 averaged 8.0 kg ha^{-1} yr^{-1} (pre-treatment years) and 10.5 kg ha^{-1} yr^{-1} during the treatment period. Baseflow SO_4 concentrations increased from 1986 to approximately 1996 (Chapter 4), then decreased through 2002, and these changes may be attributable to the 1990 CAAA. The pattern of SO_4 exports from WS4 follows a similar pattern (Fig. 7-5).

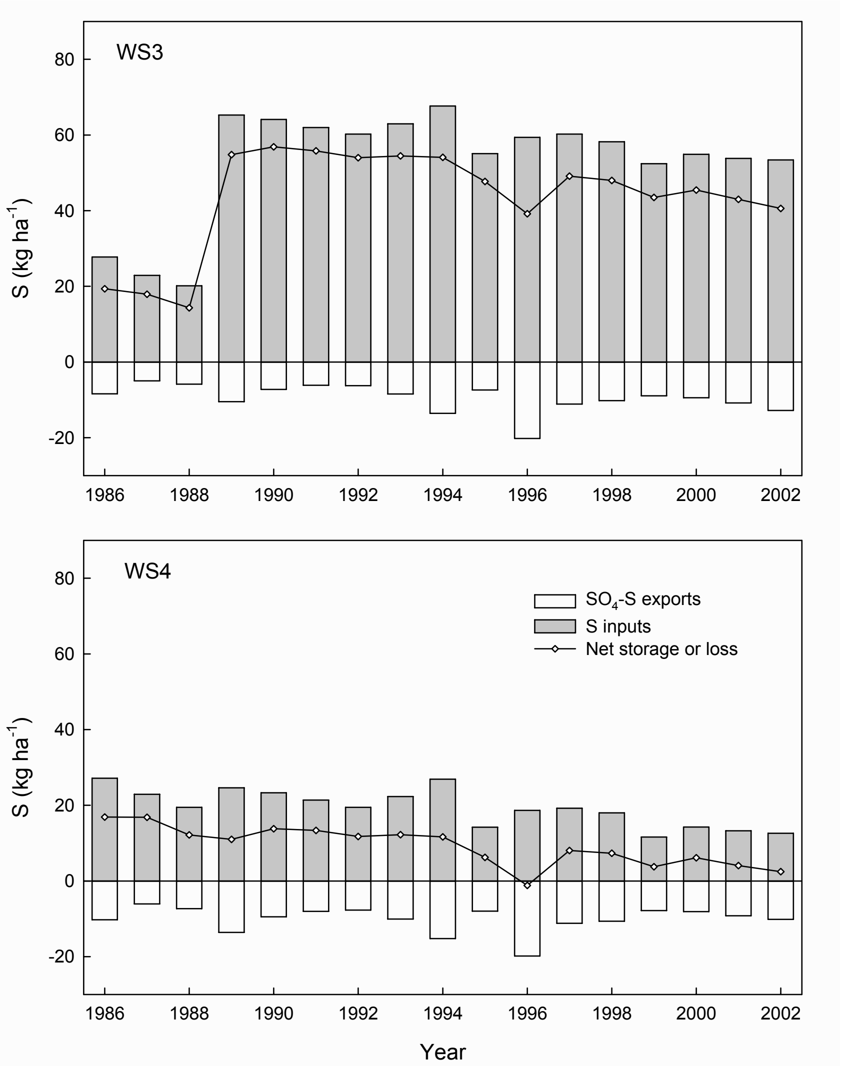

Figure 7-5. Inputs, exports and storage of S from WS3 and WS4. Treatments were initiated in 1989.

3.3 Budgets

Sulfate inputs, exports and net storage or loss for WS3 and WS4 are shown in Figure 7-5. Sulfate can be retained within a catchment through vegetative uptake, immobilization via microbial assimilation, incorporation into organic matter or through physical adsorption onto soil colloids (Fig. 7-6; Reuss and Johnson 1986, Edwards 1988). Early work by Helvey and Kunkle (1986) showed that during the mid-1980s, WS4 was retaining S. Total inputs were 17.7 kg SO_4-S ha^{-1} yr^{-1} in bulk deposition, and exports in stream water were 8.4 kg S ha^{-1} yr^{-1} for an estimated retention of 47% of the SO_4-S inputs at the deposition levels occurring at that time. However, Polk (1991) suggested that the soils on Fork Mountain were no longer able to adsorb SO_4, although there were differences in adsorption capacity among soil horizons.

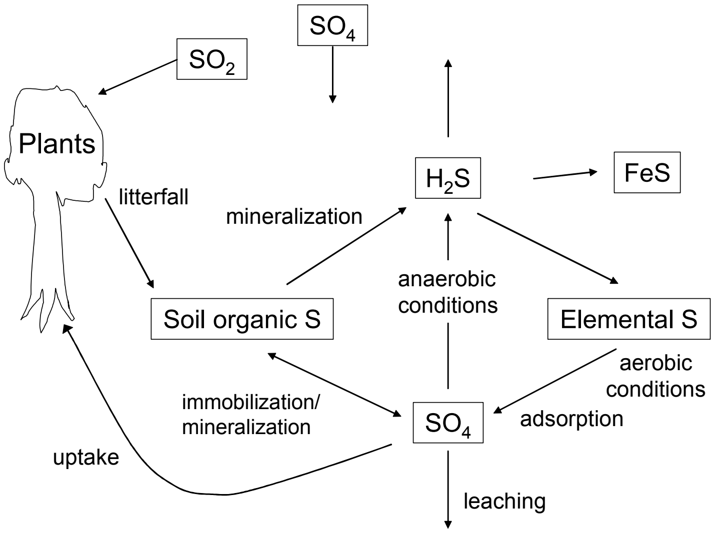

Figure 7-6. S cycle in forest ecosystems.

On an annual basis, both WS3 and WS4 were retaining SO_4-S prior to initiation of treatment in 1989, although net storage was slightly less for WS4 (66%) than for WS3 (73%). The application of ammonium sulfate increased inputs to WS3, without a concomitant increase in SO_4-S exports. Retention of SO_4-S by WS3 immediately after treatments began was high (about 90% of total inputs), but declined slightly, and by 2002 was around 80%. Baseflow SO_4 concentrations have increased throughout the study (Chapter 4), suggesting saturation of SO_4 adsorption capacity, at least in the streamside zone. WS3 soil water concentrations suggest that adsorption, perhaps via pH changes and/or increasing SO_4 concentrations, is occurring in the majority of the watershed, but the concentrations in streamside areas do not suggest significant retention (Chapter 4). The streamside areas act as respositories for materials leached from the uplands over longer time periods, such that soils in the streamside areas have no more ability to retain S even through there still appears to be retention ability in the uplands. Note a similar pattern of retention occurring on WS4 (Fig. 7-5) and WS7 (Fig. 7-7), despite the absence of fertilizer additions. This provides some support for our hypothesis of desorption due to decreased atmospheric inputs and, ultimately, effects on solution concentrations.

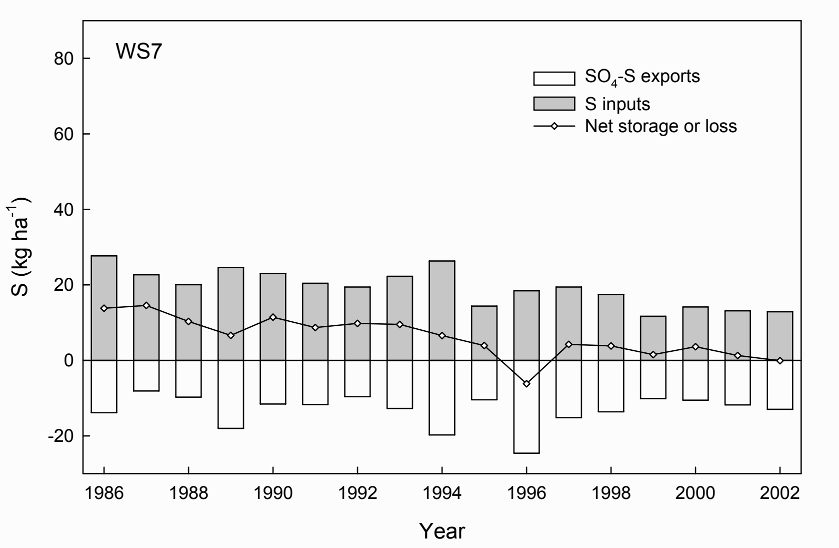

Figure 7-7. Inputs, exports and storage of SO_4-S from WS7.

3.4 Internal Cycling

Sulfur deposition usually exceeds the S uptake requirements for a forest (Reuss and Johnson 1986); therefore large changes in uptake, even with increasing N uptake, are not likely to account for significant changes in retention. As SO_4-S inputs have decreased to WS4, we may be seeing release of S in recent years due to lower concentrations in deposition, as hypothesized by Rochelle and Church (1987) and Reuss and Johnson (1986). Sulfate adsorption can be induced by increasing SO_4 concentration and decreasing pH. Because SO_4 adsorption capacity is concentration dependent, increasing concentration results in further adsorption until a new equilibrium is reached. Conversely, decreased inputs could lead to SO_4 desorption and increased leaching from the soil as a new equilibrium is established.

Some of the apparent retention of S by these watersheds may also be related to stream channel characteristics and hydrology. The watersheds in part may have net storage because the stream channels are intercepting less water during storms and higher base flows than the other watersheds, and exporting less S. Net S budgets are not strongly related to annual discharge, except when streamflows are unusually high, such as 1996, a year of record annual streamflow (P.J. Edwards, unpublished data).

4. CALCIUM CYCLING

4.1 Inputs

Calcium concentrations in wet deposition have declined considerably over the last 25 years, representing fluxes ranging from a high about 3.5 kg Ca ha^{-1} yr^{-1} to around 1.5 kg Ca ha^{-1} yr^{-1} currently. This decline is attributed to improved scrubber technology on power plants, which has not only significantly reduced S emissions (see above), but also has reduced emissions of ash and particulates, which often included constituents composed of basic components, e.g., Ca and Mg (Hedin et al. 1994). Calcium inputs to WS3 and WS4, as measured in bulk deposition, averaged less than 3.5 kg Ca ha^{-1} yr^{-1} over the period of study.

4.2 Outputs

Ca exports in stream water increased on WS3 from an average of 6 kg ha^{-1} yr^{-1} to an average of 13.4 kg ha^{-1} yr^{-1} after treatment began in 1989. Increasing exports were also observed in WS4, from 7.5 kg ha^{-1} yr^{-1} to about 10.5 kg ha^{-1} yr^{-1}, although the rate of increase was not as steep as for WS3.

4.3 Budgets

Inputs, exports and net losses of Ca are shown in Figure 7-8. Note that for both WS3 and WS4, exports of Ca exceeded inputs prior to initiation of the study. Net losses on WS3 (inputs minus outputs) ranged from 3 to 25 kg Ca ha^{-1} yr^{-1}, and net losses from WS4 ranged from 3 to about 15 kg Ca ha^{-1} yr^{-1}. While exports were greatest during the wettest years (1996, record annual streamflow) increases in stream Ca concentrations after treatment began were also observed (see Chapter 4), suggesting that these changes reflect treatment effects, not just changes in flow volumes. Between 1989 and 2002, 188 kg Ca ha^{-1} was exported from WS3, and 147 kg Ca ha^{-1} from WS4 over the same period.

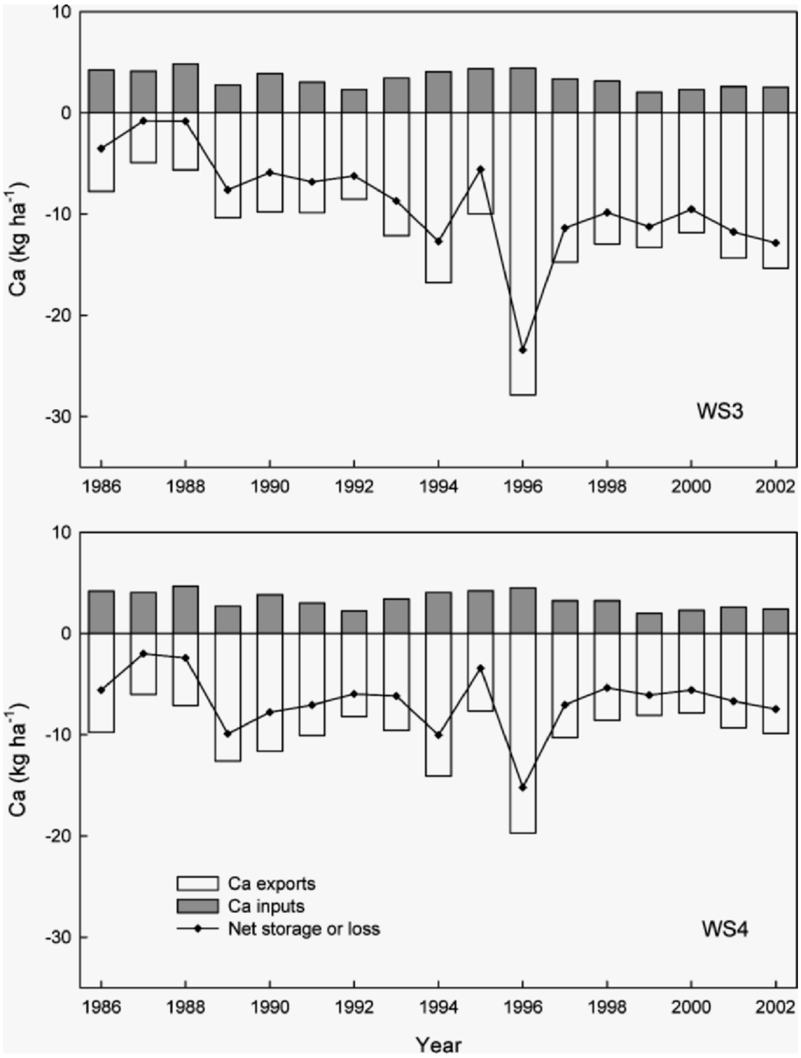

Figure 7-8. Inputs, exports and storage of Ca from WS3 and WS4. Treatments were initiated in 1989.

4.4 Internal Cycling

Important Ca cycling processes in forest ecosystems include plant uptake, litterfall and decomposition, weathering from primary minerals, soil exchange processes, and leaching via soil solution to stream water and groundwater. Some of these processes, notably weathering, have not been quantified for this study. However, we can make some observations.

Because Ca is not retranslocated from the leaves to other parts of the tree, foliar Ca levels can provide us with information about uptake by the vegetation. Foliar Ca concentrations on WS3 were lower than those on WS7 for sweet birch, yellow-poplar, and red maple in 1992 (Fig. 7-9). Concentrations of Ca in the tree boles of sweet birch, black cherry and red maple did not differ between the two watersheds, but significantly higher concentrations of Ca were detected in the bolewood of yellow-poplar on WS7 (Adams et al. 1995). These results suggest greater uptake of Ca by vegetation on WS7 relative to WS3. This could be due to greater availability of Ca on WS7 or to decreased availability on WS3.

The stands on WS3 and WS7 are of the same age, originating with the growing season of 1970 as natural regeneration. However, portions of WS7 were maintained barren of vegetation for 2 to 5 years through the use of herbicides (see Chapter 2). As a result, the litter layer quickly decomposed, and soil organic matter decreased in the upper horizons of the soil (Troendle et al. 1974). In addition to increased decomposition of the litter layer, large amounts of dead wood and slash were left on the site, and were available for rapid decomposition. This could have resulted in greater mineralization of nutrients stored in organic matter and down wood, therefore greater availability of nutrients in the medium term. This is reflected in greater soil exchangeable Ca in WS7 (1677 kg Ca ha^{-1}) than WS3 (905 kg Ca ha^{-1}) and WS4 (428 kg Ca ha^{-1}), as measured in 1991 (Adams et al. 1995). Aboveground Ca content was also greater on WS7 (169 kg Ca ha^{-1}) than on WS3 (155 kg Ca ha^{-1}), despite greater average aboveground biomass on WS3 (Adams et al. 1995).

Lower Ca contents on WS3 could also be due to decreased uptake. As soil acidification proceeds, base cations such as Ca are stripped from soil exchange sites, and leached from the soil to streams and groundwater, resulting in decreased availability over time. Soil solution data (Chapter 4) suggest such a mobilization and depletion of Ca from soil exchange sites. Dendrochemistry data also show this pattern (Chapter 5). Because

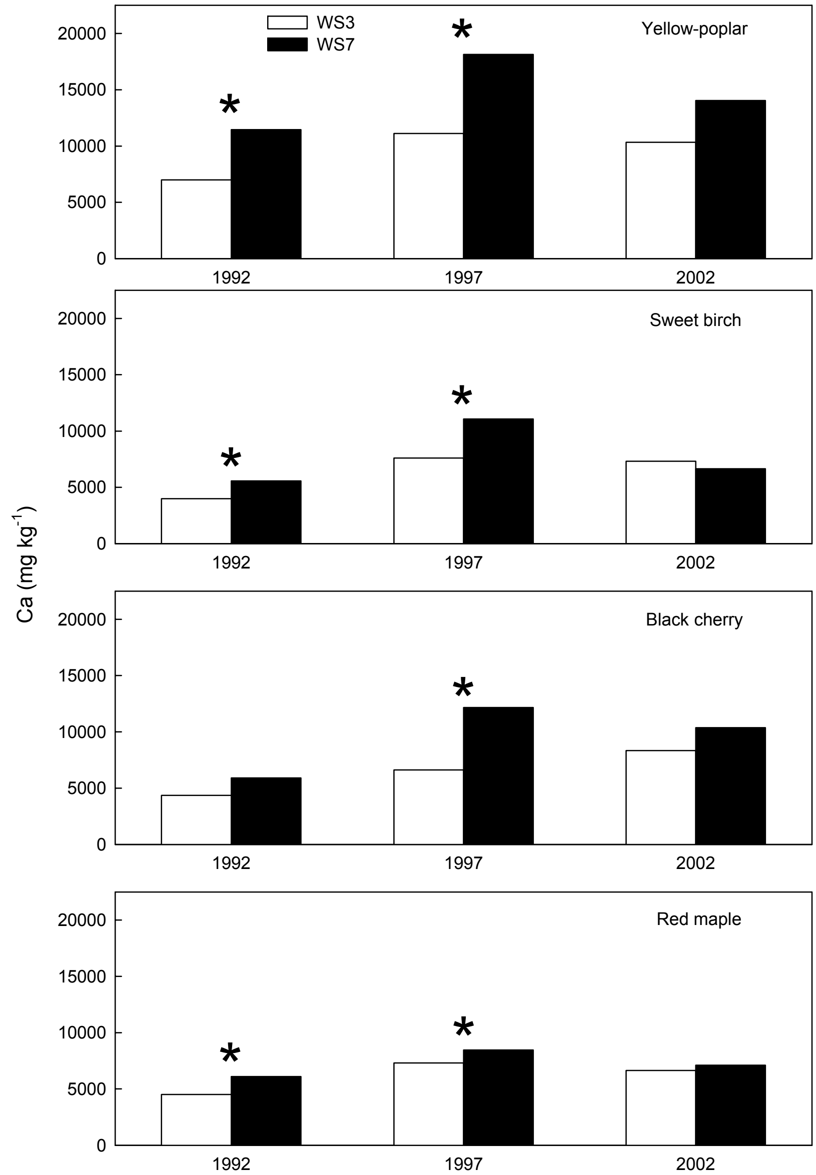

Figure 7-9. Mean foliar Ca concentrations for four tree species on WS3 and WS7 over time. * indicates statistically significant differences between watersheds ($p < 0.10$).

yellow poplar is a Ca-demanding tree species (Raynal et al. 1992), and because Ca is not retranslocated within an individual tree, this difference in bolewood concentration, along with significantly lower concentrations of Ca in foliage of yellow-poplar from WS3 supports the hypothesis that less Ca may be available for tree uptake on WS3, at least for yellow-poplar. Such a decrease in exchangeable soil Ca is not clearly indicated for WS3, however (Chapter 3).

As soil acidifies (pH decreases), soil aluminum (Al) becomes more available and may compete with Ca at the soil-root interface, inhibiting uptake of Ca (Schaberg et al. 2001). Such interactions between soil Ca and Al have been identified as a concern for root growth and aboveground productivity of some trees (Lawrence et al. 1995, Cronan and Grigal 1996), therefore, Al should also be considered when considering Ca cycling. For example, Lux and Cumming (1999) demonstrated that yellow-poplar seedlings were very sensitive to high Al concentrations in soil solution. The authors also reported that soil solution Al concentrations from WS3 were significantly greater than those from WS4 (107 uM vs. 26 uM, respectively); these high levels were considered to be toxic to yellow-poplar (Lux 1999). Foliar Al concentrations did not differ significantly between WS3 and WS7 in 1992, but bolewood Al concentrations were significantly lower for black cherry and yellow-poplar on WS7 relative to WS3 (Adams et al. 1995). However, foliar Al concentrations were significantly greater in 1997 and 2002 for black cherry and red maple on WS3. White et al. (1999) reported a similar pattern of decreases in foliar Ca and increases in foliar Al for the similarly treated West Bear Brook watershed in Maine. Thus, for some tree species on WS3, soil Al levels may be affecting Ca uptake and cycling.

Weathering rates of primary minerals are difficult to estimate (Laudelout and Robert 1994, Bailey et al. 2003), and weathering rates have not been determined for the FEF soils. However, reported rates of Ca weathering range from 2 to 5 kg Ca ha^{-1} yr^{-1} (Laudelout and Robert 1994, Bailey et al. 2003), approximately equal to or slightly less than deposition inputs. Total Ca pools in high elevation forest soils in West Virginia derived from acid sandstone and shale ranged from 400 to 1096 kg Ca ha^{-1}, with corresponding exchangeable values from 156 to 350 kg Ca ha^{-1} (Jenkins et al. 1998). Bailey et al. (2003) hypothesized that sources of Ca which have been previously unstudied in most forest ecosystems, such as calcium oxalate, may contribute significant amounts of Ca to an ecosystem, particularly in response to disturbance. Yanai et al. (2005) presented evidence that apatite provides a previously unappreciated Ca source in some forest ecosystems. Finally, Grigal and Ohmann (2005) demonstrated that diffusion from deep sources provides a plausible mechanism to replenish Ca levels in near-surface zones. Thus determining accurate weathering/mineralization rates could do much to improve our budgets and address concerns about Ca depletion of soils.

5. MAGNESIUM CYCLING

5.1 Inputs

Magnesium inputs are low, ranging from 0.1 kg ha^{-1} yr^{-1} to about 0.5 kg ha^{-1} yr^{-1} at the most, and deposition has declined since the 1970s. Deposition has remained consistently low since the mid 1980s, similar to the pattern observed for Ca, and for the same reasons (Hedin et al. 1994).

5.2 Outputs

Magnesium exports from WS3 have increased during the course of the experiment from about 4 kg ha^{-1} yr^{-1} to an average of 7 kg ha^{-1} yr^{-1}, similar to the pattern of Ca exports. Exports of Mg in WS4 stream water have increased from pretreatment levels of 3.9 kg ha^{-1} yr^{-1} to 5.0 kg ha^{-1} yr^{-1}.

5.3 Budgets

Annual exports of Mg from WS3 and WS4 exceed inputs, by as much as a factor of 10 (Fig. 7-10). Both watersheds show a significant net loss of Mg over the period of study. Between 1989 and 2002, nearly 100 kg Mg ha^{-1} was exported from WS3 and 70 kg Mg ha^{-1} from WS4. Over this same period of time, total inputs were around 6.7 kg Mg ha^{-1}.

5.4 Internal Cycling

The cycling of Mg within forest ecosystems is similar to that of Ca. Plant uptake, litterfall and decomposition, weathering and soil cation exchange are important processes. Foliar Mg for sweet birch and black cherry were at the lower end of the regional mean (Northeastern Ecosystem Research Cooperative 2004), but did not differ significantly between watersheds for most of the species and sampling dates. This suggests that Mg uptake has, for the most part, not been affected by the acidification treatment. There are exceptions: In 1992, foliar Mg concentrations were significantly less on WS3 for yellow-poplar relative to WS7 mean values, and were also significantly less for red maple on WS3 in the 1997 sampling (see Chapter 5). Also, soil exchangeable Mg levels are relatively low in all the watersheds, and did not differ between watersheds. Although we cannot rule out changes in Mg cycling due to the acidification treatment, the magnitude of the effect is sufficiently less than for Ca to be undetectable. More information on weathering and mineralization of Mg from organic matter is needed to better understand the importance of Mg on these forested watersheds.

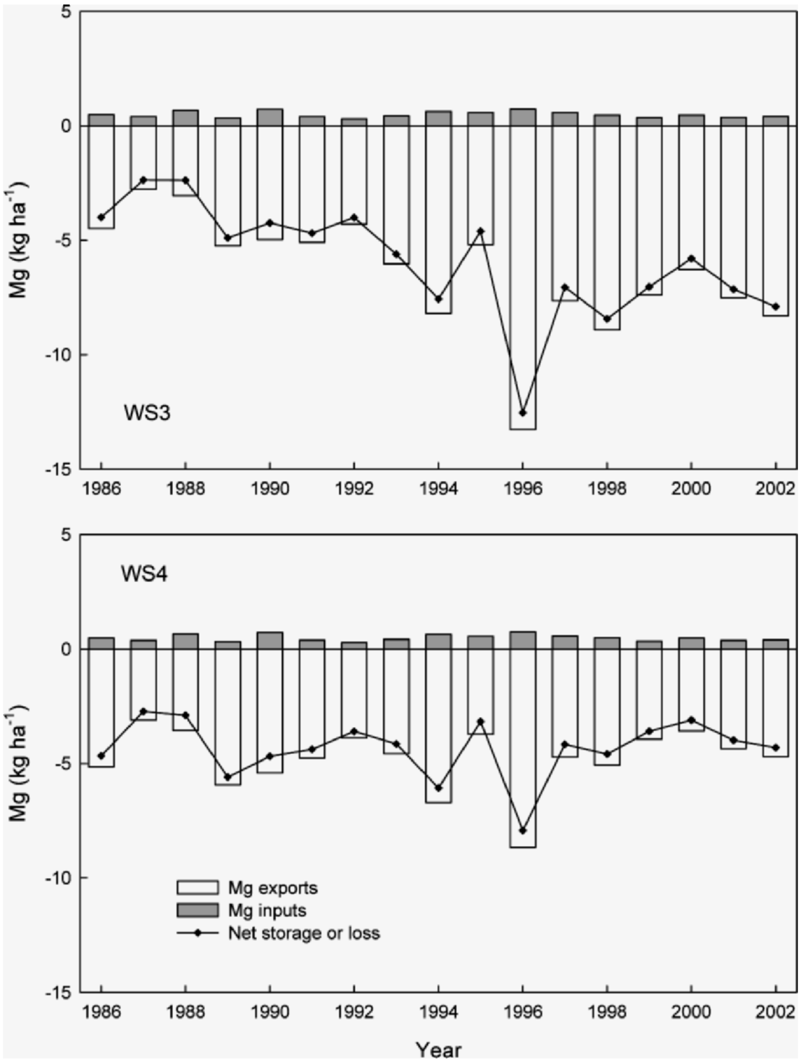

Figure 7-10. Inputs, exports and storage of Mg from WS3 and WS4. Treatments were initiated in 1989.

6. POTASSIUM CYCLING

6.1 Inputs

Measured in bulk deposition, annual K inputs ranged from less than 1 kg ha^{-1} yr^{-1} to a high of about 4.5 kg ha^{-1} yr^{-1} . Interannual variability is related to variability in annual precipitation amount. Wet deposition of K decreased from 1978 to 1988 and has remained relatively constant at around 0.2 to 0.4 kg ha^{-1} yr^{-1} since that time.

6.2 Outputs

Pretreatment exports of K in WS3 steamwater averaged 4 kg ha^{-1} yr^{-1}, and 6 kg ha^{-1} yr^{-1} during treatments. Average exports from WS4 during the same time periods were 3.5 and 4.5 kg ha^{-1} yr^{-1}. Initially exports from the two watersheds were identical, but in later years, exports increased from WS3.

6.3 Budgets

There were no immediate obvious effects of the fertilizer on K cycling (Fig. 7-11) and WS3 exports slightly exceeded inputs for a net loss of ~3 kg ha^{-1} yr^{-1}. However, WS3 K exports have increased significantly relative to those of WS4, starting in about 1993 (Fig. 7-12). Average net K export from WS3 during 1993-2002 was almost 4 kg ha^{-1} yr^{-1}. A similar increase in K concentrations in soil solution, and to a lesser extent in stream water, around 1991 is also documented in Chapter 4.

6.4 Internal Cycling

Most K available to plants comes from weathering of K containing minerals, and is found in soil solution and exchange sites. K^+ is a highly mobile cation, and there is evidence of active uptake by plants (Mengel and Kirby 1982). There are no obvious effects of the acidification treatment on nutrient uptake, based on foliar K concentrations, but there do appear to be effects on soil concentrations. Exchangeable K concentrations in the O horizon increased almost threefold between 1994 and 2002 (Chapter 3). Soil solution concentrations also increased after about 6 years of treatment (Chapter 4). The cause of this increased availability of K in soil solution is unknown, and requires further investigation.

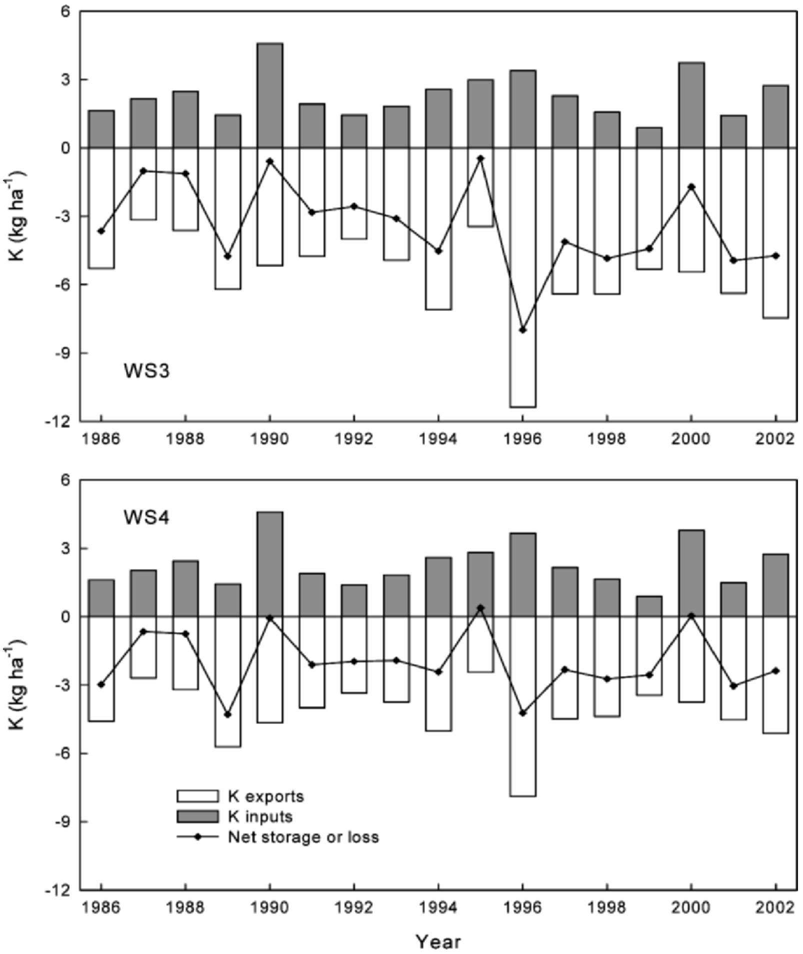

Figure 7-11. Inputs, exports and storage of K from WS3 and WS4. Treatments were initiated in 1989.

7. CONCLUSIONS

We have documented a number of significant effects of elevated N and S deposition on nutrient cycling within forested watersheds on the FEF. We have the most detailed information on N and have observed elevated stream water exports of N from the system, apparent short-term increases in plant uptake of N, and increased gaseous fluxes of N. Nitrogen mineralization and nitrification rates appear unaffected by the additional N, although that may be due in part to already high N processing rates prior to treatment. We also have documented considerable spatial variability in N cycling among, as well as within, watersheds. Some of this small-scale spatial variability may be linked to vegetation (Peterjohn et al. 1999, Gilliam et al. 2001a, b), while variability across larger scales may be due to bedrock geology (Williard et al. 2003).

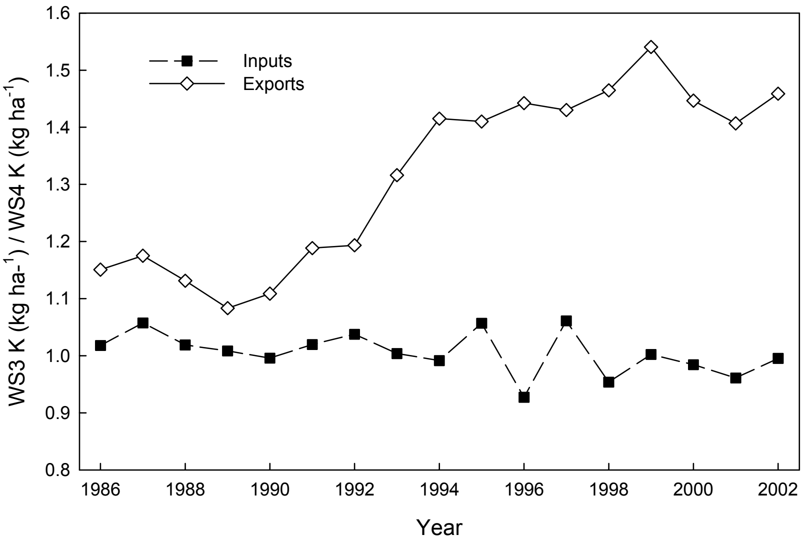

Figure 7-12. WS3:WS4 K ratio for inputs and exports over time. Treatments were initiated in 1989.

Stoddard (1994) described WS4 as being at Stage II of nitrogen saturation. Since then, a number of publications have explored the symptoms of N saturation, as described by Aber et al. (1998), on the FEF (Peterjohn et al. 1996, Fenn et al. 1998, Fernandez and Adams 2000). Additional research at FEF has focused on the possible effects of N saturation on plants (Gilliam et al. 2001a, Christ et al. 2002) and soils (Peterjohn et al. 1998; 1999; Gilliam et al. 2001a, b) of these hardwood stands. These studies have provided compelling evidence to corroborate Stoddard's earlier conclusions based on stream chemistry from WS4 — some of the forest stands of FEF are demonstrating symptoms of N saturation, including WS3 and possibly WS7. The implications of N saturation for other nutrients are further considered below. However, retention of N is still almost 70% of inputs, despite many years of elevated N inputs.

Sulfate export appears to be increasing from most of the gaged watersheds on the FEF, not just those receiving fertilizer additions. The rate of SO_4 retention by WS3 has decreased over time, suggesting a significant treatment effect. Thus, while the acidification treatment appears to have accelerated SO_4 leaching from WS3, changes in ambient deposition are also occurring which are probably contributing to the changes observed in WS4 and WS7.

Cycling of Ca, Mg, and K also have been affected by the acidification treatment on WS3. It is significant to note that both WS3 and WS4 export more Ca, Mg and K on an annual basis than is delivered in deposition. Unmeasured fluxes, such as weathering and decomposition of organic matter, no doubt provide some of the balance, but it also seems probable that base cations are being depleted from the soils of WS3 and WS4, although we could not detect such a change on soil exchangeable cation concentrations. WS7 has slightly higher Ca levels, perhaps due to a different treatment history, and thus may have more buffering capacity than WS3 and WS4. Further work is needed to quantify additional base cation cycling processes within these watersheds, and better address the question of base cation depletion.

Some effects of the acidification treatment were immediately obvious – N appeared to have an effect very early on – while the effects on other elements were more subtle or appeared later as acidification of the watershed progressed. We know that foliar nutrient concentrations have increased in some tree species, but not in all species, nor across all sampling periods, suggesting that uptake of some nutrients has been altered by acidification processes for some tree species. The acidification treatment has resulted in increased exports of N, S, Ca, Mg and K from WS3, and may be contributing to changes in Al availability as well. While we conceptually understand many of these nutrient cycling processes, we were only able to detect a few changes with any degree of certainty. Part of this difficulty is due to the problems of large spatial and temporal variability: in tree species composition and their differential sensitivity to acidification, and in nutrient cycling processes. The difficulty of sampling, with sufficiently rigorous techniques to detect differences within this large variability, also contribute to this uncertainty.

There are still important questions to be answered about the cycling of these nutrients and others in forest ecosystems and their responses to acidification and other chronic disturbances. At the Fernow the most intriguing of these are related to the high retention of N in a supposedly “saturated” watershed, and the cycling of base cations, in particular weathering and other sources of these cations.

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Chapter 8

IMPLICATIONS FOR FOREST ECOSYSTEM SUSTAINABILITY AND RESILIENCY

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1. INTRODUCTION

Large scale watershed acidification experiments such as the Fernow Watershed Acidification Study help us understand how forest ecosystem functions will be affected by high, chronic levels of acidic deposition. As anthropogenic inputs of atmospheric deposition have increased over the decades, it has been difficult to predict how these changes will affect long term forest health and productivity. To predict the effects of long term acidification on forest ecosystem structure and function requires experimental manipulations such as the Fernow Watershed Acidification Study, in association with predictive ecosystem modeling to extend the treatments into the future. Ecosystem process modeling can also provide estimates of how the current deposition loads and predicted future trends may affect forest ecosystem sustainability and resiliency in the future. The CAAA have decreased SO_4 and H^+ deposition significantly since implementation (see Chapter 4), but N deposition has remained more or less consistent, showing limited change during the 1990s for much of the eastern United States (Lynch et al. 1996, 2000). This leads us to ask questions about the future: Will N leaching from forested watersheds increase under current levels of N deposition? What will happen to the productivity of forest ecosystems under current or increased N loading? What areas have high deposition and are sensitive to leaching? Are certain forest types more sensitive to leaching? Will the current CAAA regulations be effective over time to maintain forest productivity and ecosystem functioning?

The purpose of this chapter is to address some of these questions and to investigate how forest sustainability and resiliency will change under different N deposition scenarios. To do this, we will use a scalable ecosystem

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process model to extrapolate from the watershed to the region, and will predict the possible outcomes of N deposition over time by assessing the impacts of N deposition at multiple scales, which will include the Fernow Experimental Forest (FEF), the Monongahela National Forest proclamation area (MNF), and forested lands in the state of West Virginia (WV). We will compare our predictions with field results from the Fernow Watershed Acidification Study. The modeling will provide a decision support tool to assess how forest ecosystem productivity and sustainability will change and how resilient these forest ecosystems are to long term N deposition.

2. METHODS

2.1 Model Description: Focus on N Deposition

Nitrogen fixation from anthropogenic sources has exceeded the background N fixation by biological sources (Vitousek 1994, Vitousek et al. 1997). Nitrogen from fossil fuel use and volatilized from agricultural applications (as nitrate (NO_3) and ammonium (NH_4)), are regionally dispersed as N deposition in wet (National Acid Deposition Program 2004) and dry forms (Harding ESE 2002). The role of N in increasing plant productivity is well documented. Forests are typically limited by N, especially in coniferous forest ecosystems. Elevated inputs of atmospheric N deposition through acidic precipitation and dry deposition may lead to N saturation in sensitive forest systems (Peterjohn et al. 1996, Fenn et al. 1998), and declines in growth rates for high elevation spruce-fir (McNulty et al. 1996).

In this analysis, we are using an established forest ecosystem process model, PnET-CN (Aber et al. 1997, Aber and Driscoll 1997), to evaluate the impacts of N deposition on forest productivity, N leaching losses and N retention. PnET-CN is a lumped-parameter model of carbon and water dynamics for forest ecosystems. The core relationships in the model are a linear response of maximum net photosynthetic rate to foliar N concentration (Field and Mooney 1986, Reich et al. 1995). Conductance varies linearly with photosynthesis, and transpiration is a function of CO_2 gain and atmospheric vapor pressure deficit. The soil water holding capacity interacts with plant water utilization and allocation to determine water yield. These algorithms result in very specific and direct links between N status, carbon gain, and water use.

PnET-CN was developed for northeastern U.S. watersheds and simulates the carbon, N and water cycles of forest ecosystems for New England and the mid-Atlantic, and has been extensively validated for these regions (Aber et al. 1995, Pan et al. 2004a, 2004b). The model contains the processes of the complete N cycle to estimate inorganic N loading and retention under chronic increases of atmospheric N deposition.

The model description (Aber and Driscoll 1997, Aber et al. 1997, Ollinger et al. 2002) assumes that atmospheric N deposition enters forest ecosystems and collects in the soil N pools. The N available for tissue formation is determined by plant N uptake from the available N soil pools and the ratios of carbon to N in the plant tissues. Nitrogen leaching loss from a forest stand is directly proportional to the NO_3 remaining in the soil solution after plant uptake and to the soil drainage rate. Therefore, N leaching loss is indirectly related to several variables that affect N soil solution and drainage rate such as the leaf photosynthesis rate, available N pools, plant N uptake, and soil water-holding capacity.

Watershed acidification resulting from chronic inputs of S and N also may affect forest health and biomass growth through the loss of nutrients through cation depletion and changes in toxic soil conditions due to Al mobilization. Recently, the rate and extent of recovery of eastern U.S. watershed chemical and water quality indicators has been modeled under different emission reduction scenarios (Driscoll et al. 2001) using a biogeochemistry model, PnET-BGC. Currently, the acidification effects of cation depletion/Al toxicity in the stream and soil as predicted by the biochemistry model PnET-BGC, have not yet been linked with the forest productivity modeling in PnET-CN. Therefore, our modeling analysis will focus mainly on the effects of current and future N deposition scenarios on forest net primary productivity (NPP), N leaching loss, and forest N retention, and will not address the effects of acidification on other soil nutrients (i.e., S, H, Ca, Al), and subsequent growth effects.

2.2 Nitrogen Deposition Scenarios

The NO_3 and NH_4 deposition scenarios selected for these analyses were based on 10-year averages from 1990 to 1999 at 1-km^2 resolution, generated from wet deposition data and calculating dry deposition as a ratio of wet deposition for the region (Meyers et al. 2000, Valigura et al. 2000). The high resolution interpolation maps of N deposition are based on concentration data collected at National Atmospheric Deposition Project/National Trends Network monitoring sites, and precipitation data from a denser network of weather stations from the National Oceanic and Atmospheric Administration (Fig. 8-1, Sheeder et al. 2002, Grimm and Lynch 2004).

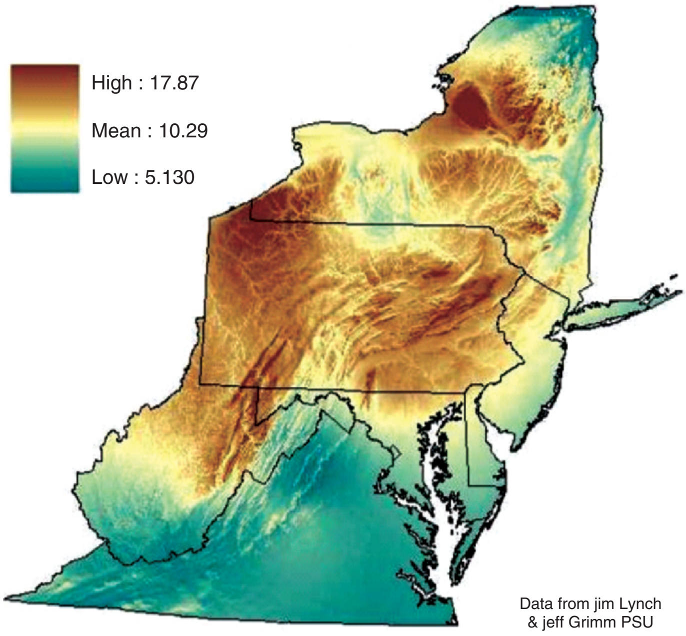

Figure 8-1. Total wet and dry nitrogen deposition: NO_3 and NH_4, (averaged from 1990-1999 NADP/NTN data) for the mid-Atlantic region.

The N deposition scenarios used in this study follow those of Pan et al. (2004a, 2004b), used for studying the impacts of rising N deposition at current and 2X current levels in the mid-Atlantic region. We have enhanced that analysis by including an N regulation scenario that mirrors the effects of the CAAA on N deposition, which shows no significant change in total N deposition after the implementation of the 1990 CAAA (Lynch et al. 1996, 2000, Nilles and Conley 2001).

Extending the analysis that current CAAA regulations will level off N deposition for another 100 years (at year 2000 levels), until the year 2100, will allow us to predict long term effects under realistic levels of N deposition. It should be noted that the most recent EPA trends show that reductions of N deposition and wet NO_3 concentrations have occurred in the northeastern and mid-Atlantic regions in the last few years (http://www.epa.gov/airmarkets/cmprpt/arp03/summary.html).

For the scenarios with increasing N deposition, we assumed that N deposition before 1930 was approximately 20% of the current average level, which is consistent with the rate of additional anthropogenic N in terrestrial ecosystems from pre-industrial time (Galloway et al. 1995). The ambient N scenario (1XN) is ramped up to current levels (year 2000) over 70 years (1930 to 2000) to approximate the historic buildup of acidic deposition. The twice ambient N deposition scenario (2XN) essentially is double the ambient N input for the same 70 year period, and the N deposition regulation scenario (N Dep Reg) holds constant the total N deposition set at the year 2000 levels after the implementation of the 1990 CAAA (Lynch et al. 2000, Nilles and Conley 2001) for an additional 100 years. Atmospheric CO_2 was held constant at pre-industrial levels of 280 ppmv in all the nitrogen scenarios (VEMAP 1995, Fig. 8-2).

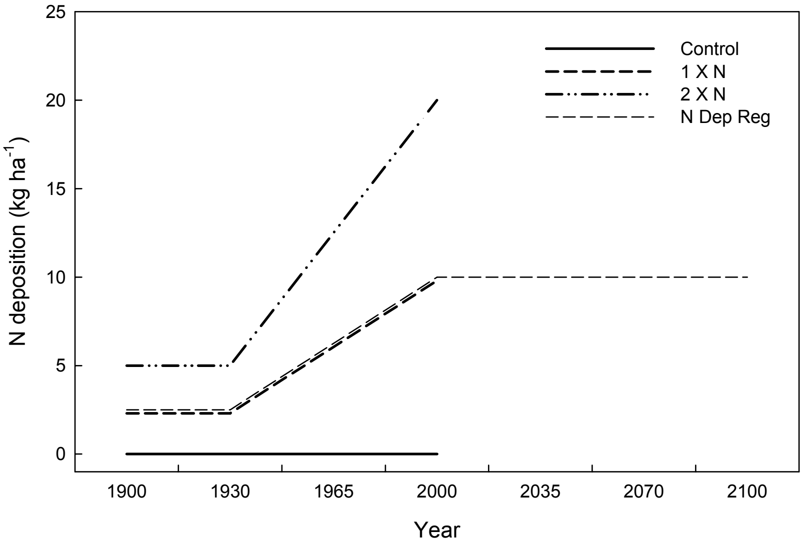

Figure 8-2. Nitrogen deposition treatments scenarios and pre-conditions used for model predictions: no deposition (control), ambient nitrogen deposition (1XN) ramped from 1930 to 2000 levels, twice ambient (2XN) ramped from 1930 to 2000, and N regulated with 1XN level held constant at year 2000 levels for 100 years (N Dep Reg). CO_2 fixed at 280 ppmv.

The model uses four nitrogen scenarios treatments:

1. ***Model Control***: No N input (0.0 kg ha^{-1}). Fixed CO_2, 280 ppmv 1800–2000 (Fig. 8-2). Drivers such as climate and CO_2 are held constant. (VEMAP 1995).
2. ***Ambient N Deposition* (1XN)**: Averaged N deposition (1991-2000, Fig. 8-1) as the level for 2000, ramped from 1930 to 2000. Fixed CO_2, 280 ppmv 1800-2000. Assumed that N deposition before 1930 was approximately 20% of the current level (Fig. 8-2). This is comparable to the loading on the Fernow reference WS4.

3. ***Doubled ambient N deposition*** **(2XN)**: Twice average N deposition (1991-2000, Fig. 8-1) ramped from 1930 to 2000. Fixed CO_2, 280 ppmv 1800-2000. Assumed that N deposition before 1930 was approximately 20% of 2XN at current level (Fig. 8-2). Because the modeling was based on existing 2XN model runs for the mid-Atlantic (Pan et al. 2004a), no 3X modeling scenarios were available to directly compare with the 3XN addition treatment levels used at the FEF.
4. ***Nitrogen deposition regulated*** **(N Dep Reg)**: Averaged N deposition (1991-2000, Fig. 8-1) as the level for 2000, ramped from 1930-2000, then leveled off for 100 years, to 2100. Fixed CO_2, 280 ppmv 1800-2100. Assumed that N deposition before 1930 was approximately 20% of the current level (Fig. 8-2).

Information about the land-use history is required for the model simulation and was based on a generalized land-use history for the mid-Atlantic and was not parameterized for a particular study site such as the Fernow. Forests in the mid-Atlantic region were established primarily from abandoned farmlands in the 18th century, and the current forests are recovering from extensive harvesting of secondary forests that occurred in the early 1930s. The model was run for 200 years to incorporate the impacts of the agriculture and harvesting on forest ecosystems. These factors and additional parameters used in the model are described in detail by Pan et al. (2004a), Aber and Driscoll (1997), and Ollinger et al. (2002).

Geospatially referenced data are required to run the model. Essential data layers include forest types (Fig. 8-3), monthly minimum and maximum temperature, monthly precipitation, monthly solar radiation, and soil water-holding capacity (Fig. 8-4). A scaling approach was used to extrapolate from the watershed to the region to determine how applicable the results from the Fernow watershed studies were to other forested regions in the state. The spatial resolution of the model simulation was scaled to 1 km^2, which was the resolution of available data, for the number of forested pixels in the FEF (19), the MNF (6,164), and WV (44,578) (Widmann and Griffith 2004).

Forest Service forest cover type maps derived from AVHRR data at 1-km^2 resolution (Zhu and Evans, 1994) were cross-walked to the functional forest types used in PnET-CN to produce reclassified forest type maps for northern hardwoods, spruce-fir, pine, oak-hickory, and oak-pine (Fig. 8-3). The operational spatial resolution of this modeling study at 1 km^2 precluded individual treatment watersheds (0.24-0.39 km^2) at the FEF from being parameterized with watershed specific data.

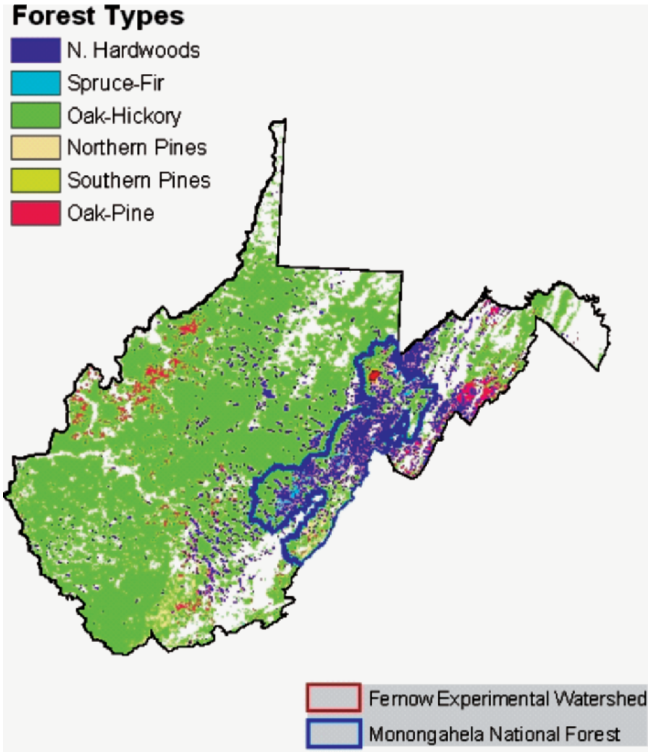

Figure 8-3. Functional forest types used in PnET-CN model.

3. RESULTS

3.1 N Deposition Modeling and Mapping

The average annual N deposition, including both wet and dry components, interpolated for the state of West Virginia was approximately 10.0 kg N ha^{-1} (Fig. 8-1, Grimm and Lynch 2004). Nitrogen deposition varied across the region because of complex landscape features. Generally, greater wet N deposition occurred in the higher elevations, such as the Appalachians, as a result of higher concentrations of NH_3 and NO_3 and higher precipitation at the higher elevations (Gilliam and Adams 1996). The N deposition rate increased to 10.9 kg N ha^{-1} for the MNF, and reached 13.0 kg N ha^{-1} for the FEF (Fig. 8-4) using high resolution modeling of wet N deposition and adding dry N deposition as a ratio to wet deposition.

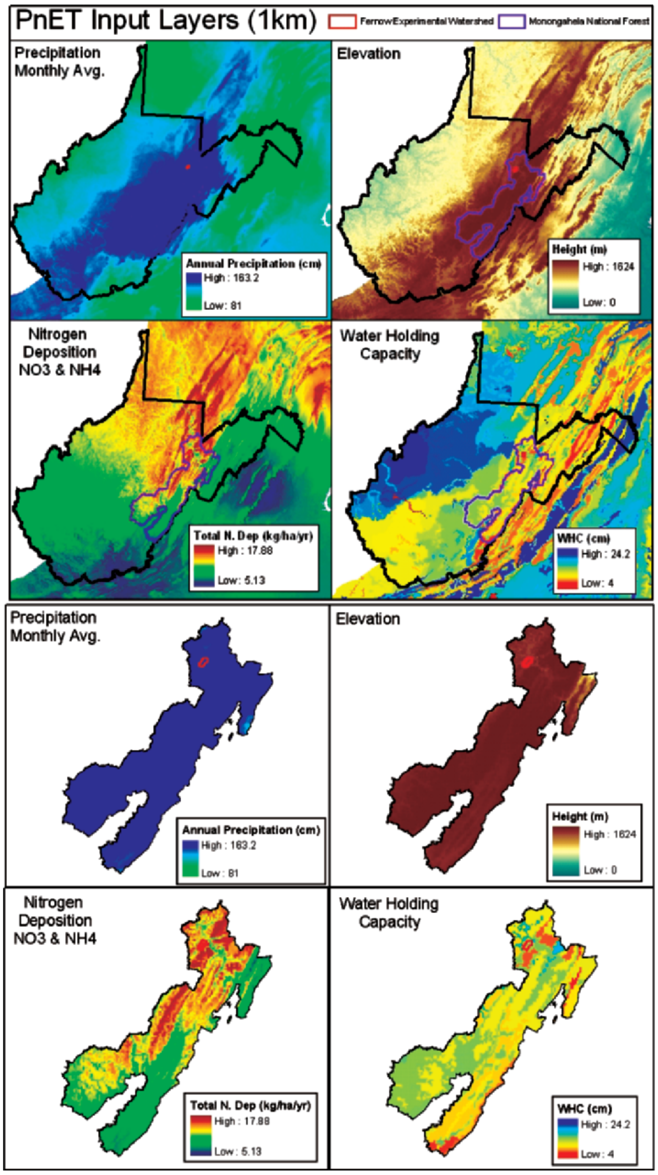

Figure 8-4. Input data layers for driving PnET-CN. (a) precipitation, (b) digital elevation map, (c) total nitrogen deposition, and (d) soil water holding capacity for West Virginia, Monongahela National Forest, and Fernow Experimental Forest at 1-km^2 resolution. The three sites demonstrate the model results at different scales, from West Virginia with the largest area to the Fernow with the smallest area.

3.2 Net Primary Productivity, NPP

Net primary productivity is defined as the annual net organic matter production by plants after accounting for respiration losses. The modeling results consistently show greater NPP with 1XN over the model control, ranging from 1072-1198 g m^{-2} yr^{-1}. NPP leveled off at 2XN for all sites, reaching up to 1146-1269 g m^{-2} yr^{-1}. Extending the N deposition for another 100 years at 2000 levels (N Dep Reg) did not increase NPP substantially, leveling out at 1134-1287 g m^{-2} yr^{-1}. Highest NPP across all treatments was found at the FEF site, followed by MNF, and WV (Fig. 8-5, Table 8-1). It appears that the increased N deposition had an initial fertilizer enhancement effect (see Chapter 5), but the system cannot increase NPP beyond that with 2XN. Adding lower, ambient levels of deposition for a longer period (N Dep Reg) resulted in a similar limitation to increased productivity.

3.3 Water Yield

Water yield consistently decreased with increasing N deposition (Table 8-1, Fig. 8-6) indicating that as NPP increases, water use by the vegetation will increase, and therefore water yield decreases. Water yield averaged between 49-77 cm yr^{-1}, with the highest water yield found in the steep topography of the MNF, followed by FEF and WV.

3.4 Current Forest N Leaching Losses and Retention

Under the model control scenario, with no N input from the atmosphere, N leaching losses are close to zero, as expected. This indicates a conservative N cycling in these forest ecosystems. Slight N leaching losses from high elevation coniferous forests, even with no N input, suggest that sites with spruce-fir and pine species components (MNF and WV) are less conservative in retaining N (Fig. 8-3, Table 8-1). Nitrogen leaching increases with increasing N deposition, being highest in the MNF for 1XN and 2XN, despite higher deposition loads at the FEF. The leaching losses for WV were less than the other sites. Both N leaching and water yield increased in regions with steep topography (Figs. 8-4, 8-6, 8-7). Areas that are most sensitive to N leaching are the high elevation, steep slopes found in the Appalachian Mountain regions, including the MNF and the FEF.

Although total N leaching losses were higher with 2XN than 1XN, the N retention rate stayed the same, indicating that the forest was maintaining high N retention rates (84-92%) for these sites. The lowest retention rate was from the MNF with 14% conifer cover, followed by FEF, and WV with 7% conifer cover. With long term inputs under the N Dep Reg scenario, an apparent threshold was reached resulting in increased N leaching loss and a consequent large drop in N retention to 65-73% (Fig. 8-7), with FEF exhibiting the lowest retention.

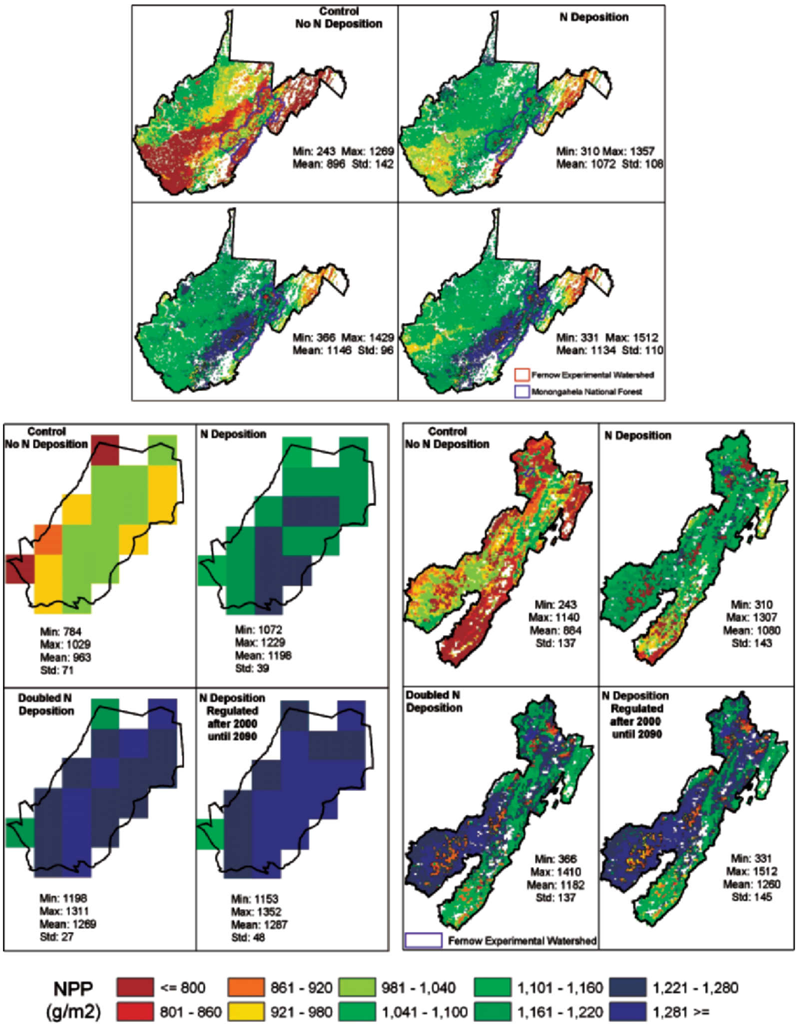

Figure 8-5. Predictions of net primary productivity, NPP, for forested lands in West Virginia, the Monongahela National Forest, and Fernow Experimental Forest under no deposition (control), ambient nitrogen deposition (1XN), twice ambient (2XN), and N regulated with 1XN level held constant at year 2000 levels for 100 years (N Dep Reg) at 1-km^2 resolution. The model results are shown at different scales, from West Virginia with the largest area to the Fernow with the smallest area.

Table 8-1. Summary table of field and model data.

	Field data			Modeled inputs and outputs		
Study area	WS3 34 ha	WS4 39 ha	WS7 24 ha	FEF 19 km^2	MNF 6164 km^2	WV 44758 km^2
Nitrogen inputs, kg ha^{-1}						
Pre-treatment ambient reference level (1988) [a]	8.2	8				
Acidification Treatment (1989-1995) [b]	44.6	9.26				
Model Control, no deposition [c]				0	0	0
Model Ambient Deposition, 1XN [d]				13	10.9	10
Model Twice Ambient, 2XN [e]				26	21.8	20
Model N Deposition regulated at year 2000 level [f]				13	10.9	10
Water Yield, cm yr^{-1}						
Fernow Experimental Watersheds (1993-2003) [g]	67.4	68.6	84.3			
Model Control, no deposition [c]				77	86	65
Model Ambient Deposition, 1XN [d]				69	77	56
Model Twice Ambient, 2XN [e]				64	72	51
Model N Deposition regulated at year 2000 level [f]				57	69	49
NPP, g m^{-2} yr^{-1}						
Calculated from aboveground whole tree biomass [h]	1276.8	1052.4	1081.2			
Model Control, no deposition [c]				963	884	896
Model Ambient Deposition, 1XN [d]				1198	1080	1072
Model Twice Ambient, 2XN [e]				1269	1182	1429
Model N Deposition regulated at year 2000 level [f]				1287	1260	1512
N Outputs, kg ha^{-1}						
Pre-treatment (1988) [a]	4.2	3.5				
Acidification Treatment (1989-1995) [b]	9.5	5.5				
Model Control, no deposition [c]				0	0.46	0.28
Model Ambient Deposition, 1XN [d]				1.36	1.57	0.89
Model Twice Ambient, 2XN [e]				2.10	3.48	1.87
Model N Deposition regulated at year 2000 level [f]				4.54	3.68	2.71

*Table 8-1 (*continued). Summary table of field and model data.

	Field data			Modeled inputs and outputs		
Study area	WS3	WS4	WS5	FEF	MNF	WV
N Retention, %						
Pre-treatment (1988) [a]	57.3	47.5				
Acidification Treatment (1989-1995) [b]	78.3	41.5				
Model Control, no deposition [c]						
Model Ambient Deposition, 1XN [d]				89.6	85.5	90.1
Model Twice Ambient, 2XN [e]				91.9	83.9	90.4
Model N Deposition regulated at year 2000 level [f]				65.1	66.1	72.8
Biomass, Mt ha^{-1}						
Aboveground whole tree biomass [i]	203.4	310.4	157.5			
Model Control, no deposition [c]				269	321	251
Model Ambient Deposition, 1XN [d]				302	257	277
Model Twice Ambient, 2XN [e]				308	269	285
Model N Deposition regulated at year 2000 level [f]				326	286	302

[a] Fernandez and Adams 2000

[b] Fernandez and Adams 2000

[c] No N input (0.0 kg ha^{-1}). Fixed CO_2, 280 ppmv 1800-2000

[d] Averaged N deposition (1991-2000) as the level for 2000, ramped from 1930 to 2000. Fixed CO_2, 280 ppmv 1800-2000

[e] Doubled N deposition level of 2000, ramped from 1930 to 2000. Fixed CO_2, 280 ppmv 1800-2000

[f] Same as 1XN ramped from 1930-2000, then leveled off for 100 year. Fixed CO_2, 280 ppmv 1800-2000

[g] Frederica Wood, 2005 per. comm

[h] Aboveground whole tree biomass yrs^{-1} (Adams et al. 2004, Frederica Wood, 2005 per. comm.) + coarse and fine roots allocation (Pan et al. 2005)

[i] Brenneman et al. 1978, Frederica Wood, 2005 per. comm. WS3 (1991-2004), WS4 (1995-1999), WS7 (1992-2004)

The spatial mapping in Figure 8-7 shows long term changes in N leaching with the N regulation scenario, with greater retention in areas with low deposition loads and greater losses in areas receiving high N deposition. This would indicate that rapid increases at 2XN ambient N deposition levels do not produce the same pattern of leaching as the long term chronic additions at ambient levels (1XN).

Generally, our results show that deciduous forests have greater N retention than coniferous forests, which is consistent with studies that find

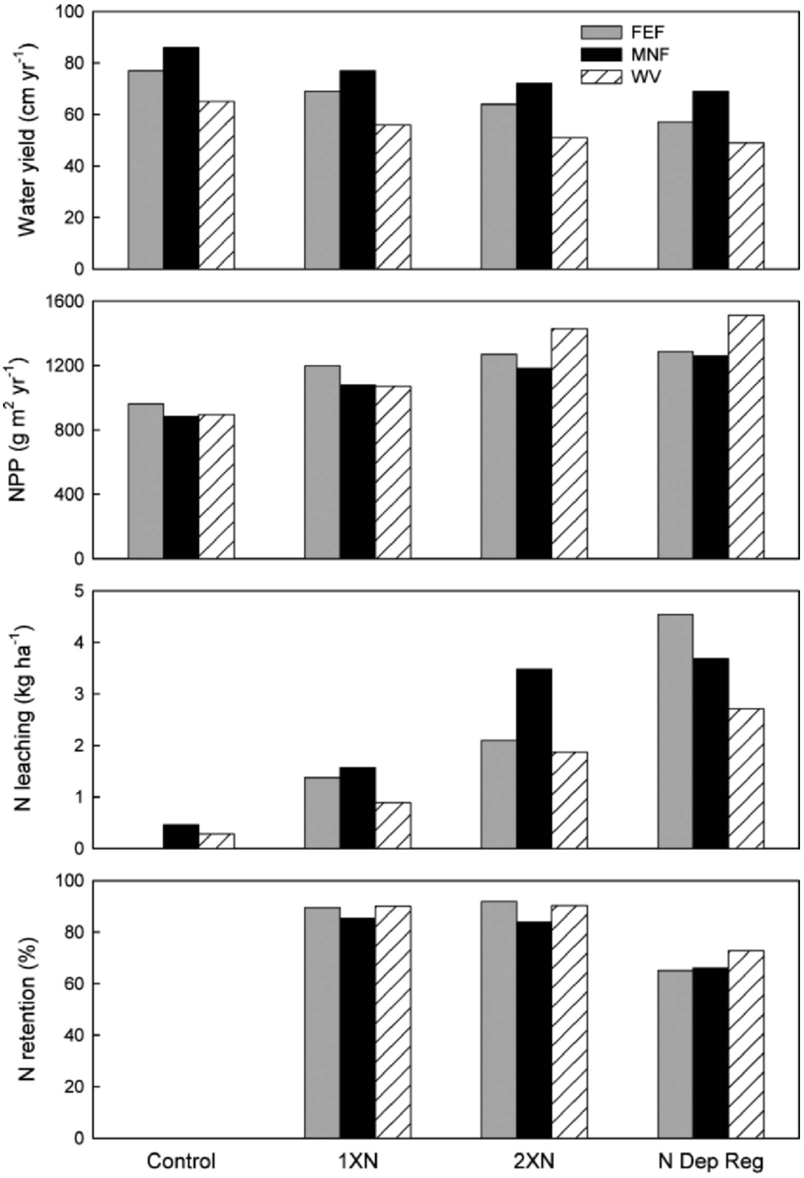

Figure 8-6. Predictions of water yield (a), net primary productivity (b), nitrogen leaching (c), and nitrogen retention (d) for forested lands in West Virginia, the Monongahela National Forest, and Fernow Experimental Forest under no deposition (control), ambient nitrogen deposition (1XN), twice ambient (2XN), and N regulated with 1XN level held constant at year 2000 levels for 100 years (N Dep Reg) at 1-km^2 resolution.

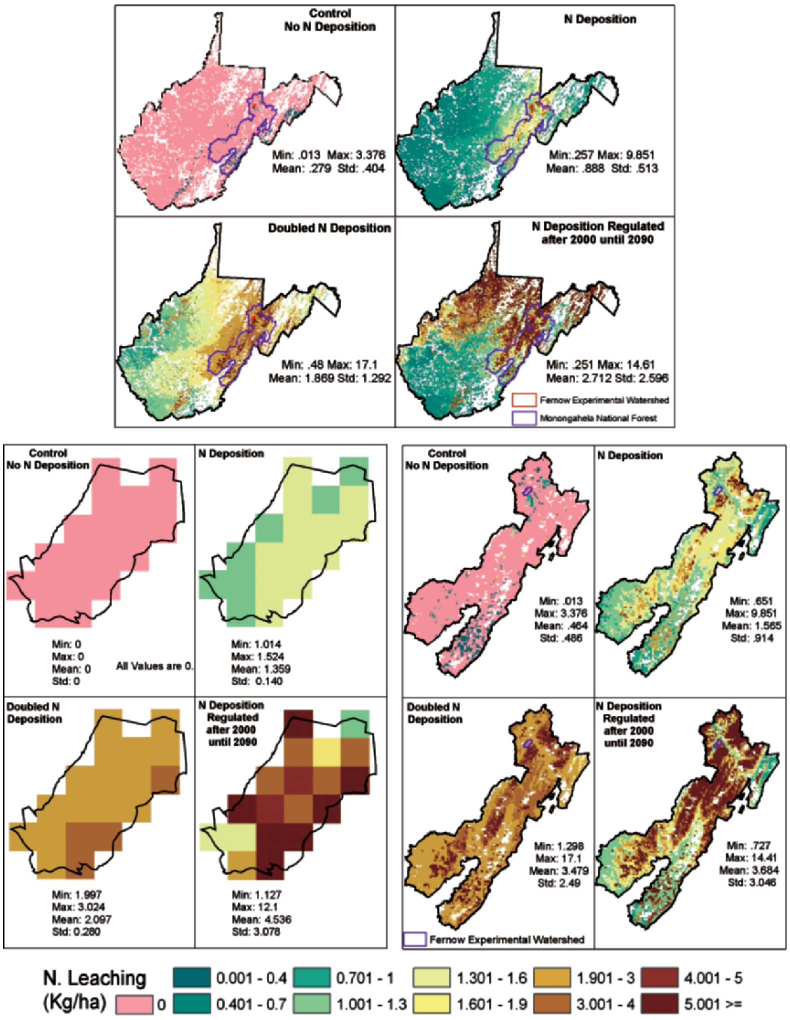

Figure 8-7. Predictions of nitrogen leaching losses (kg N ha^{-1}) for forested lands in West Virginia, the Monongahela National Forest, and Fernow Experimental Forest under no deposition (control), ambient nitrogen deposition (1XN), twice ambient (2XN), and N regulated with 1XN level held constant at year 2000 levels for 100 years (N Dep Reg) at 1-km^2 resolution. The model results are shown at different scales, from West Virginia with the largest area to the Fernow with the smallest area.

deciduous forests have tighter N cycling (Ollinger et al. 2002, Aber et al. 2003). The spruce-fir and northern pine forests have the lowest N retention rate, while oak-hickory and northern hardwood forests have the highest (Fig. 8-8). Lower retention rates in coniferous forests may be related to site conditions characterized by high drainage, high N leaching rates found at high elevation sites, and soils with low water holding capacity.

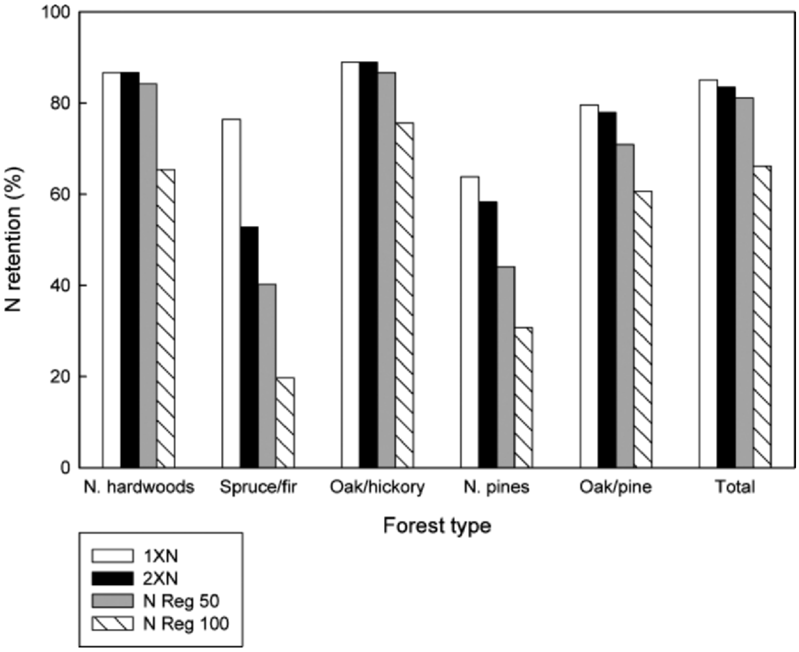

Figure 8-8. Predictions of nitrogen retention by forest type under prior nitrogen deposition treatments scenarios of ambient (1XN), twice ambient (2XN), and N deposition regulated at year 2000 level for an additional 50 (N Reg 50) and 100 years (N Reg 100) for the Monongahela National Forest.

As the duration of N deposition increased, spruce-fir forests decreased in N retention rate from 74% to 14%, and showed symptoms of N saturation (Fig. 8-8). This result is consistent with experimental studies that indicate particularly severe N saturation symptoms in high-altitude spruce-fir ecosystems in the Appalachian Mountains (Fenn et al. 1998).

The PnET-CN model has been used to predict N leaching losses from forest ecosystems in the mid-Atlantic regions with reasonable accuracy (Pan et al. 2004a, Pan et al. 2005). Our study shows that the capacity of forests to retain N could quickly decline if N deposition continues to rise. Our results also indicate that N retention by forests changes as forest ecosystems approach N saturation, a likely situation in these watersheds (Peterjohn et al. 1996). The process based model PnET-CN has shown the ability to predict potential changes of N cycling in watersheds under different levels of atmospheric N deposition.

3.5 Comparison with Field Data

The ambient N deposition in the model (1XN) is roughly equivalent to that received in WS4 as the acidification treatment reference control (Table 8-1). The addition of N at WS3 (ambient deposition + 35 kg N ha^{-1} yr^{-1}; see Chapter 2) is roughly equivalent to 3XN, and considerably more than that used in any of our available N modeling scenarios (Pan et al. 2004a).

The modeled N deposition for the FEF overestimated the measurements from the Parsons NADP/ NTN and CASTNet monitoring stations, 13 kg N ha^{-1} vs. 8 kg N ha^{-1} (WV18, PAR107, Table 8-1). This may be due to overestimating the ratio of dry deposition for this area (~50 % for modeled dry N deposition vs. <30% from CASTNet, Chapter 7), and greater variability in modeling N deposition in steep terrain.

The PnET-CN model could not predict the low N retention of WS3 and WS4 (47.5-57.3%) prior to the acidification treatment. This was not a complete surprise, as the input data layers were not parameterized for a particular watershed nor did they match the deposition used in the acidification treatments. It would have been difficult to model the initial conditions, given the non-compliant nature of N cycling at this research site. Surprisingly, the net rates of mineralization and nitrification in soils at the FEF do not appear to increase in response to treatment (Gilliam, et al. 1996). Contrary to our current understanding, this large increase in biotic immobilization can be induced simply by providing more NO_3 to the soil (Chapter 4).

Retention in WS3 prior to treatment was 57%, yet retention of N substantially increased to 78% after 7 years of N additions at 3X ambient levels, compared to 42% retention for the WS4 control (Fernandez and Adams, 2000). It is not apparent how NO_3 is retained in WS3, and this topic deserves further study (see Chapter 7, Peterjohn et al.1996, Fernandez and Adams 2000).

Surprisingly, the model showed good agreement with the treatment field data, showing enhanced growth with increased N deposition, initially maintaining high N retention with increased N deposition, but showing greater N losses with time (100 yr vs. 50 yr, Fig. 8-8) for all forest types including the dominant deciduous forest types, northern hardwoods and oak-hickory. This indicates that forested watersheds in this region will reach a threshold of N retention ability and begin to lose this ability to retain N after about 50 years at the current deposition rates. The initial increase in retention may be caused by the N fertilizer effect, by increasing tree growth, which is consistent with the field data (Chapter 5, Table 8-1).

Water yield matched well with the field data, estimated at 69 cm yr^{-1} with the model and 67-84 cm yr^{-1} with site data. Good agreement was also reached in estimates of NPP for the model for FEF showing a range of

1198-1287 g m^{-2} yr^{-1} for the model, and 1052-1276 g m^{-2} yr^{-1} for the treatment watersheds based on allometric relations for aboveground woody biomass (Brenneman et al.1978) with allocations for coarse and fine roots. A comparison of modeled vs. measured aboveground whole tree biomass revealed reasonably accurate values, ranging from 269 to 326 Mt ha^{-1} from the modeling study and 203.4 to 310.4 Mt ha^{-1} for the treatment watersheds (Chapter 5).

Although the spatial and temporal scales are dissimilar, and the magnitude of N additions in the acidification experiment are different from our N scenarios, the PnET-CN modeling showed reasonably comparable results to those obtained for the treatment watersheds, except for our inability to model the initial pretreatment conditions for WS3 and WS4.

4. CONCLUSIONS

We proposed in this chapter to investigate how forest sustainability and resiliency might change under different N deposition scenarios using an ecosystem process model, PnET-CN. Specifically we asked the following questions:

- Will N leaching from forested watersheds to streams increase under the current levels of deposition?
- What happens to the productivity of the forest ecosystem under current or increased loading of N deposition?
- What areas have the highest N deposition and are sensitive to leaching? Are certain forest types more sensitive to leaching?
- Will the current CAAA regulations be effective over time to maintain forest productivity and ecosystem functioning?
- Are the results from the Fernow watershed studies applicable to other forested watersheds in the region?

The CAAA have decreased SO_4 and H^+ deposition significantly since implementation, but N deposition has remained more or less constant for much of the eastern United States. Forest productivity under increasing deposition will initially increase, as shown by NPP and biomass, but doubling the current N deposition will not increase forest productivity much more than N deposition at ambient levels. Areas that are most sensitive to N leaching are the high elevation, steep slopes found in the Appalachian Mountain regions of West Virginia, including the Monongahela National Forest and the Fernow Experimental Forest. Conifers appear to be the most sensitive forest types, with high elevation spruce-fir receiving the greatest N deposition loads and showing the lowest N retention. Additional N deposition will likely increase N leaching in spruce-fir, pine, and oak-pine forest types. Given the historic N deposition and the current N levels from CAAA regulation, the modeling analysis shows that the dominant deciduous forest types in the region (northern hardwoods and oak-hickory) will reach a threshold of N retention and begin to lose their ability to retain N by 2050 (Fig. 8.8), even if N deposition were to level off at the current ambient level (1XN).

We were able to predict the increased growth, and higher N retention commensurate with the initial fertilizer effect of N on NPP, as well as produce comparable estimates to the field studies for water yield, annual primary productivity, and aboveground tree biomass. However, there are limitations to our understanding of the overall N behavior in these watersheds receiving chronically high N deposition. In particular, we do not yet fully understand the complex processes of NO_3 retention on WS3, and the factors that contribute to the low initial N retention rates on both watersheds. These shortcomings in our understanding of N cycling in these non-compliant systems is also reflected in our modeling results. We could not predict the initial conditions of WS3 and WS4, both of which showed symptoms of N saturation and low N retention prior to treatment. Also, it would be difficult to predict the long term results of the Fernow Watershed Acidification Study, as the model does not currently incorporate the effects of acidification on cation depletion and mobilization of Al on tree health and productivity. Nonetheless, ecosystem process models, such as PnET-CN, provide a useful research tool to test N scenarios and predict how resilient the forested ecosystem is to continued acidification and address management and policy concerns about forest health and sustainability.

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Chapter 9

CONCLUSIONS AND RECOMMENDATIONS FROM THE FERNOW WATERSHED ACIDIFICATION STUDY

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Ecosystem acidification as a process and theories of ecosystem acidification were presented in Chapter 1. Research themes were developed around the stages of acidification, and questions and indicators were identified which we hypothesized to be sensitive to acidification and which we would use to evaluate the effects of the acidification treatments. Chapters 3 through 8 provided detailed analyses of these various indicators and processes. In this chapter, we revisit the research themes identified in Chapter 1 and identify answers to the most relevant questions, using conclusions from Chapters 3 through 8 to develop a synthesis of lessons learned. We also identify the important unanswered questions and identify research and development needs for the future.

1. NUTRIENT CATION MOBILIZATION

Theories of forest ecosystem response to atmospheric deposition all suggest that base cations, generally defined to include Ca^{2+} and Mg^{2+} and sometimes K^+ and Na^+, will be mobilized due to replacement on soil exchange sites by H^+ and NH_4^+, by Al compounds due to increased weathering in response to soil acidification, and leaching by mobile NO_3^- and SO_4^{2-} anions. Cation mobilization (see Chapter 1 for discussion of acidification theories) would appear as an early response to acidification, in Stage 2 of the Galloway et al. (1983) diagram (Fig. 1-6) and the soil strong acid

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exchanger phase described by Ulrich (1984; Fig. 1-4). According to theory, cation mobilization should be manifested in higher levels of base cations in soil solution, increases in cation concentrations in plant tissue such as leaves and bolewood, changes in exchangeable cations in soil, and eventually changes in peakflow and baseflow stream chemistries. Results of research from the Fernow Watershed Acidification Study provide clear evidence of base cation mobilization in the early stages of acidification.

Soil solution chemistry provided perhaps the best indicator of base cation mobilization for both WS3 and WS9 (Chapter 4). Mobilization in soil solution occurred on both watersheds up to 4 or 5 years after treatments began. Cations mobilized were primarily Ca on WS3, while Mg and Na were mobilized on WS9. The K mobilization response was delayed on WS3.

Mobilization of base cations was also indicated in stream chemistry at peakflows of storm events and, to a lesser extent, baseflow on both WS3 and WS9 (Chapter 4). Peak streamflow increases in base cations appeared to also reach a maximum at about 4 to 5 years after treatments began on WS3 and WS9, while baseflow levels of nutrient cations continued to increase through 2002 on WS3 and peaked just before termination of treatments on WS9 after 7 years of treatment.

Bolewood chemistry also appeared to reflect cation mobilization in some tree species, although resolution of the timing could not be resolved as accurately as with stream or soil solution sampling (Chapter 5). Bolewood sampled 4 years after treatments began on WS3 showed effects of mobilization, but only for overstory species such as black cherry and yellow-poplar. Red maple and black locust bolewood did not show cation mobilization on WS3, perhaps due to the intermediate or understory canopy position of the trees that restricted competition for available nutrients or due to other species' characteristics. Japanese larch bolewood chemistry on WS9, sampled after 7 years of treatment, showed signs of mobilization of Ca and Mg in wood formed during the first 4 to 5 years of treatment.

Foliar chemistry did not, in general, show mobilization on WS3 or WS9 (Chapter 5), perhaps because of sampling problems or the timing of sampling after initiation of treatments, or for other physiological reasons. Note that foliar chemistry on both WS3 and WS9 did show effects of base cation depletion, which is discussed later.

Comparisons of the soil base cation concentrations between WS3 and WS4 did not show clear evidence of significant differences in exchangeable base cations due to mobilization. It can be hypothesized that if mobilization occurred from the soil exchange sites without replacement by mineralization and weathering, then mobilization could result in reductions in exchangeable base cations early in the treatment. Some evidence exists for reduced exchangeable cations on WS3 compared to WS7 after 12 years of treatment, but this does not coincide with the mobilization peaks observed in solution chemistry. Soil sampling on WS9 also only indicated depletion of exchangeable cations due to treatment. Soil sampling across entire watersheds to detect small differences due to treatment was found to be problematical and the effect of mobilization on levels of soil exchangeable bases is uncertain.

2. CATION DEPLETION/ALUMINUM MOBILIZATION

After initial stages of cation mobilization and increased availability of nutrients, acidification models predict a decline in base cation availability and increasing availability of Al and other metals. We were particularly interested in questions related to changes in soil, foliar and bolewood chemistry, and whether there were shifts in solution chemistry that demonstrated cation depletion and Al mobilization.

Soil solution data again provided the strongest evidence of base cation depletion (Chapter 4). For WS3, after initial increases in soil solution Ca concentrations linked with mobilization of base cations from the soil exchange sites, concentrations decreased significantly. These decreases coincided with increasing soil solution acidity. However, WS3 soil solution Mg concentrations in the upper soil horizons decreased consistently from the beginning of the experiment, which may suggest that available Mg on the soil exchange sites was largely depleted in the upper soil horizons prior to the start of treatments, and what was observed during the study period was continued removal from the exchange sites at rates that are not offset by mineralization. Soil solution data from WS9 clearly showed increases followed by decreases, similar to what was observed for WS3, providing further support for the idea of treatment-induced base cation depletion.

Peakflow stream concentrations of Ca and Mg followed similar patterns. Depletion may have been observed in baseflow on WS9, but not in baseflow from WS3.

Bolewood chemistry data (Chapter 5) support the idea of base cation depletion following a mobilization phase, with the relative radial growth derived from tree rings also showing apparent synchrony. After 8 and 12 years of treatment, treated trees generally showed lower levels of Ca and Mg compared to control trees. Trends in Mn concentrations were essentially the opposite, with treated trees showing lower levels than controls after four years and higher levels of Mn after 8 and 12 years of treatment. Ratios of Ca:Mn were found to be good indicators of such trends: larger ratios were observed in treated trees relative to control trees after 4 years of treatment, and lower ratios after 8 and 12 years of treatment. Although the lack of pretreatment data hamper interpretations somewhat, increasing levels of bolewood Mn over time also support the idea of continuous acidification. Data from WS9 showed both lower Ca and increased Mn in bolewood of treated trees.

Foliar chemistry data from WS3 and WS7 also provide limited support for the idea of base cation depletion. Data from the first two sampling periods (1992 and 1997) showed significantly lower foliar Ca concentrations in trees from WS3 during these two time periods; these sampling periods coincide with the decrease in Ca available in soil solution for uptake by the plant. However, in the 2002 sampling, significant differences in foliar Ca between watersheds were not detected. Foliar Ca levels in WS3 generally increased from 1992 to 1997 and then leveled off, except for black cherry which continued to show increased Ca concentrations through 2002. If Ca concentrations in soil solution were diminished, then foliar levels should also decrease. Thus foliar chemistry data do not entirely support the hypothesis of base cation depletion. Foliar chemistry from WS9 also showed significantly greater Mn concentrations on the treated plots relative to the controls, and significantly reduced Mg levels. These mixed results from foliar chemistry monitoring disagree with bolewood chemistry results, and suggest that foliar and bolewood chemistry tissues respond differently to cation depletion.

Cation depletion, by definition, occurs through removal or replacement of available cations from the soil exchange sites. Thus, available soil cation levels should be lower when soil solution cation concentrations are declining, or at least lower than during the pre-acidification phase. Because of the paucity of soil chemical data from the pretreatment period, it is difficult to determine whether soil exchangeable levels have declined due to treatment over time. Soil chemistry time series data for WS3 and WS4 did not provide strong support for the idea of base cation depletion, as significant decreases in exchangeable Ca or Mg from pretreatment levels were not observed. However, mean pretreatment levels of exchangeable Ca in soil were about 400 mg kg^{-1} compared to around 150 mg kg^{-1} in 1994 and 2002, after several years of treatments. Lack of significant changes may be partly due to high spatial variability and relatively few pretreatment samples. Soil Ca levels were significantly lower in upper horizons on WS3 relative to WS7 after both 7 and 12 years of treatment (Figs. 3-12 and 3-13), corresponding with a decrease in pH (Fig. 3-11). Odenwald's (2002) data also showed significantly higher Al levels in WS3 soils after 12 years. In contrast, comparison of soil chemistry from treated and untreated plots on WS9 showed significantly lower concentrations of exchangeable Ca and Mg in the soil of the treatment plots, and significantly greater levels of Mn and Al (Table 3-4, Fig. 3-14.). Thus cation depletion was evident on WS9 but was not clearly shown by soil monitoring on WS3. Differences in pretreatment soil nutrient availability, and large amounts of variability may contribute to this apparent contradiction.

3. BIOMASS GROWTH CYCLES

Theories of forest response to atmospheric deposition suggest that biomass production (plant and animal biomass) likely would be increased by the fertilizer effect of N added to the system, the increased abundance of base cations due to mobilization, or other biogeochemical changes due to treatment (Chapter 1). Theory further suggests that, as acidification progresses, due to nutrient imbalances, soil Al toxicity, or other impacts, later growth declines could result. Our studies of salamanders showed no impacts of treatment on size or productivity. Studies of herbaceous plant species showed no changes in species composition or density due to treatment, other than a change in seasonal abundance of some species due to a decoupling from the natural N cycle by periodic ammonium sulfate treatments.

Determination of the effects of the acidification treatments on tree growth on WS3 vs. WS7 were particularly difficult to resolve due to differences between watersheds (treatment history, aspect, species composition, tree density, etc.). Analysis of data collected repeatedly from permanent growth plots suggested that stand growth on WS3 increased during the first 15 years of treatment in plots dominated by black cherry and yellow-poplar, and in the first 7 years of treatment in plots dominated by red maple and sweet birch. These data helped to evaluate growth of all species on these plots including effects of in-growth and mortality. Tree growth calculated from tree cores sampled after 12 years of treatment also showed accelerated growth of black cherry and yellow-poplar in the first 6 to 7 years of treatment, but reduced growth thereafter in these species plus red maple. The permanent growth plots also showed that plots with greater amounts of red maple and sweet birch showed no treatment effect in the later 8 years of treatment. Thus we conclude that, initially, tree growth was accelerated overall, but not all species were similarly affected. Growth declines found with tree cores in later years of treatment in three species are less certain, but the pattern of growth increases followed by growth declines followed the expected growth cycle explained above.

Treatment effects on WS9, as predicted from theory, clearly showed decreased height and diameter growth of Japanese larch within 6 years of initiating treatments. Soils were nutrient-poor on WS9 prior to treatment, and nutrient deficiencies, most particularly Mg and P, could have limited growth responses. If such were the case, additional fertilization would only exacerbate incipient deficiencies. If any initial growth acceleration occurred in the young planted larch in response to treatment, it was not detected.

Therefore we conclude that Japanese larch growth on WS9 was adversely affected by the acidification treatment. Trees on WS3 generally showed an initial positive growth response to the treatments. Tree growth declined in later years for some species, based on tree core data, and continued to increase for some tree species, based on the permanent plot data. The complex species diversity in these stands makes interpretation of growth effects difficult. No effects on tree species diversity were recorded.

4. STEADY STATES

Most models of ecosystem acidification propose several stages, with the eventual stage indicating an equilibrium or steady state condition, although that secondary equilibrium may not be at the same level as initially observed. For example, Galloway's (1983) model proposes a temporary equilibrium in SO_4 concentrations and alkalinity of stream water in response to acidic deposition, and a return to equilibrium at approximate pre-acid deposition levels, upon removal of the acidic deposition inputs (Fig. 1-6).

As another example, base cation concentrations should reach a new equilibrium when available pools have been depleted, and soil leaching equals weathering rates. This was demonstrated to some extent with soil solution Ca concentrations in the A horizon of WS3 (Fig. 4-4a). After initial increases, peaking in 1992, concentrations decreased through 1996, and then leveled off at approximately those observed immediately prior to initiation of treatments. A similar response was observed for A horizon soil water SO_4 concentrations (Fig. 4-4b), and A horizon soil solution ANC (Fig. 4-8). Such trends to equilibrium do not appear in deeper soil horizons or in WS3 baseflow concentrations, however.

Soil solution data from WS9 clearly showed responses to the acidification treatment, and the responses were similar to those for WS3. However, treatments at WS9 were discontinued in 1994, thus allowing the opportunity to evaluate the recovery response. Evaluation of soil solution concentrations of Ca and Mg suggest that recovery of Ca and Mg began occurring as ammonium sulfate inputs ceased, and that a new equilibrium concentration level has been reached. Such an equilibrium is not observed in any other soil solution analytes on WS9, however, except for pH.

Ratios of annual stream water nutrient exports for WS3 compared to WS4 are shown in Figure 9-1. From these, we can see that the system may be approaching a new equilibrium with respect to N and the base cations (Ca, Mg, K), but that SO_4 exports have not yet leveled off. Comparisons with trends in baseflow concentrations (Fig. 4-19) reveal similar conclusions, with the exception that baseflow concentrations of K also have not yet leveled off.

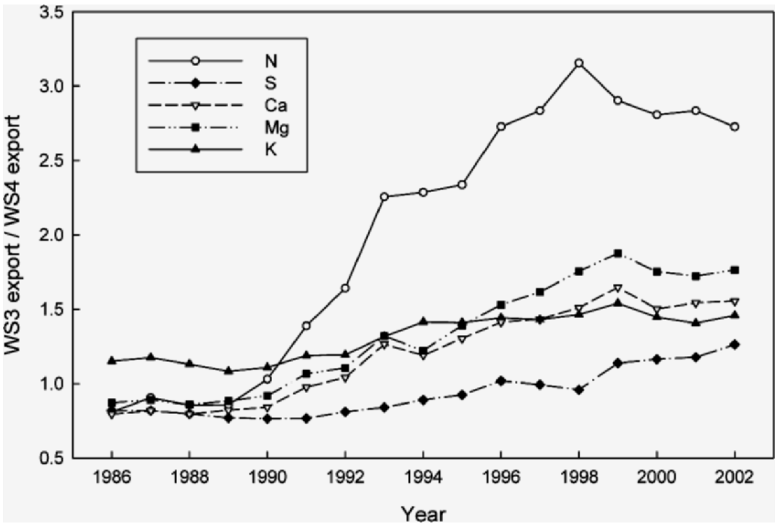

Figure 9-1. Ratios of annual stream water nutrient exports for WS3 compared to WS4.

There is no evidence of steady state in the growth plot data from WS3 and WS7, nor could we detect signs of species changes that have been hypothesized elsewhere. Some of this is due to limitations in the experimental design, but growth, particularly in the plots with a majority of black cherry and yellow-poplar, is still increasing in response to the treatments. Growth from the tree cores suggest that some of the trees (black cherry and red maple) may be approaching a steady state in basal area increment, with BAI growth less than predicted (Fig. 5-9). There are only minor differences between the dendrochemistry at years 8 and 12 after treatment, which provides some support for an equilibrium in base cation concentrations and/or availability. Thus we have some evidence that cycling of some nutrients on WS3 is approaching equilibrium, although not all nutrients showed such response and changes that did occur were not synchronous for all.

5. IMPLICATIONS FOR FOREST SUSTAINABILITY AND RESILIENCY

Modeling predictions help us understand the possible long-term implications of acidification for management and policy decisions. We could not predict the initial conditions of the Fernow WS3 and WS4 which showed symptoms of N saturation and low N retention prior to treatment. We were able to predict the increased growth, and higher N retention commensurate with the initial fertilizer effect of N on NPP. Our modeling results suggest that areas that are most sensitive to N leaching are the high elevation, steep slopes found in the Appalachian Mountain regions, including the Monongahela National Forest and the Fernow Experimental Forest. Forest productivity under increasing deposition will initially increase, as shown in the NPP and biomass, but doubling the current N deposition will not increase forest productivity much more than N deposition at ambient levels. Deposition of SO_4^{2-} and H^+ has decreased significantly since CAAA implementation in 1995, but N deposition remains more or less constant, showing limited change over the past decade for much of the eastern United States. Given the historic N deposition and the current N levels from CAAA regulation, the modeling analysis shows that if we maintain N deposition at the current ambient level (1XN), the dominant deciduous forest types, northern hardwoods and oak-hickory, will reach a threshold and begin to lose their ability to retain N by 2050-2100.

6. RESEARCH RECOMMENDATIONS

The Fernow Watershed Acidification Study has highlighted the complex dynamic and interactive responses associated with the acidification of a forested watershed as demonstrated by stream water, soil solution chemistry, and biomass changes over time. Teasing a coherent story from amongst the vast amounts of data, experimental designs, time frames, and investigator interpretations has proven challenging. Continued commitment to Fernow's long term acidification research is necessary as ecosystem responses are complex and cannot be predicted from short term studies. Also, mixed species ecosystems such as make up most of the eastern hardwood forests, are complex because of the differences in species' response to ecosystem stressors and controlling factors such as temperature, precipitation amount, etc., and long-term studies in such forests are particularly needed to understand trends in species composition, productivity and health of mixed species forests.

The variability associated with previous forest management practices on the Fernow experimental watersheds adds to the complexity of these watershed studies, yet these real-world practices are representative of the conditions found in forested watersheds in the Central Appalachian region. Research on how resilient forested ecosystems are to continued acidification and their recovery with decreased acidic deposition would address management and policy concerns about forest health and sustainability.

Soil solution chemistry appears to be a most sensitive indicator of nutrient cycling, but obtaining reliable, consistent sampling for soil solution requires considerable dedication of resources, as does refining the raw measurements into meaningful information. Other indicators/diagnostics of acidification processes need to be developed, especially indicators that can easily be used in association with forest health and productivity assessments and measurements. Indicators of system effects that can integrate and are sensitive are most valuable. Long-term stream chemistry records meet some of these criteria and are imperative for understanding effects, but other, simpler, indicators are also needed. As our understanding of ecosystem processes develops and improves, it is imperative that indicators also be developed and improved.

A better understanding of how atmospheric chemistry, soils, hydrologic processes, and vegetation interact to regulate export/retention of N and S is still needed: How and where NO_3 is retained on treated WS3? What causes the initial low retention in WS3 and WS4? How does the diverse species mix affect nutrient retention and cycling? Further research is also needed to determine growth and productivity patterns by species. Comparative studies at the watershed level should be expanded, such as WS3 vs. WS7. Mixed hardwood species composition/successional patterns/species replacement in both overstory and understory species, nutrient content and biomass need to be monitored.

Since there are concerns about effects on forest productivity, physiological studies/processes studies to measure treatment effects on tree photosynthetic capacity are recommended to see if there are treatment effects for carbon uptake and productivity. An improved knowledge of the effects on nutrient uptake and within-tree nutrient cycling would also be useful in fully understanding implications for forest health, and response to other stressors such as insects, disease, and changes in climate. Additional process-level studies also would provide the input parameters for site ecosystem modeling at higher resolution, and for individual treatment watersheds at the species level.

Continued monitoring of WS9 to evaluate apparent recovery due to termination of acidification treatments in 1994 is needed. This can help policy makers understand the implications of policies that result in decreased emissions and provide further tests of acidification theory.

This synthesis represents the first step towards a more holistic, long-term, research program at the Fernow Experimental Forest which will combine the expertise of academic and government scientists to evaluate the impacts that environmental changes may have on forest structure, function, and management. Funding we have received from various agencies over the years has been critical to achieving our current success, and the recent inclusion of the Fernow as a LTREB site by the National Science Foundation will help ensure that the long-term data records from the Fernow continue to be collected and used to address emerging ecological questions.

We remain convinced that small watersheds are useful experimental systems which should remain at the core of efforts to understand the link between long-term alterations in atmospheric chemistry and the sustainable productivity of forest ecosystems. However, the new questions identified in this synthesis indicate that a more complete understanding of acidification, and other changes, would be obtained if we expanded our focus to characterize ecosystem processes at larger spatial and temporal scales.

7. REFERENCES

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Appendix A: Common and Scientific Names

Trees

Alternate-leaved dogwood	*Cornus alternifolia* L.
American basswood	*Tilia americana* L.
American beech	*Fagus grandifolia* Ehrh.
American chestnut	*Castanea dentata* (Marsh.) Borkh.
American hornbeam	*Carpinus caroliniana* Walt.
Balsam fir	*Abies balsamea* (L.) P. Mill.
Bitternut hickory	*Carya cordiformis* (Wang) K. Koch.
Black cherry	*Prunus serotina* Ehrh.
Blackgum	*Nyssa sylvatica* Marsh.
Black locust	*Robinia pseudoacacia* L.
Black walnut	*Juglans nigra* L.
Butternutt	*Juglans cinerea* L.
Chestnut oak	*Quercus prinus* L.
Common serviceberry	*Amelanchier arborea* (Michx. f.) Fern.
Cucumber tree	*Magnolia acuminata* L.
Eastern hemlock	*Tsuga canadensis* (L.) Carr.
Eastern hophornbeam	*Ostrya virginiana* (Mill.) K. Koch.
Fire cherry	*Prunus pennsylvanica* L.
Flowering dogwood	*Cornus florida* L.
Fraser magnolia	*Magnolia fraseri* Walt.
Japanese larch	*Larix leptolepsis* Seib. and Zucc.
Northern red oak	*Quercus rubra* L.
Norway spruce	*Picea abies* L.
Paper birch	*Betula papyrifera* Marsh.
Red maple	*Acer rubrum* L.
Red pine	*Pinus resinosa* Ait.
Red spruce	*Picea rubens* Sarg.
Sassafras	*Sassafras albidum* (Nutt.) Nees.
Scots pine	*Pinus sylvestris* L.
Serviceberry	*Amelanchier arborea* (Michx f.) Fern.
Shagbark hickory	*Carya ovata* K. Koch
Sourwood	*Oxydendrum arboreum* (L.) D.C.
Striped maple	*Acer pensylvanicum* L.
Sugar maple	*Acer saccharum* Marsh.
Sweet birch	*Betula lenta* L.
White ash	*Fraxinus americana* L.
White oak	*Quercus alba* L.
White pine	*Pinus strobus* L.
Yellow birch	*Betula lutea* Michx.
Yellow-poplar	*Liriodendron tulipifera* L.

Understory Plants

Blackberry	*Rubus* spp.
Black snakeroot	*Cimicifuga racemosa* (L.) Nutt.
Blueberry	*Vaccinium* spp.
Blue cohosh	*Caulophyllum thalictroides* Michx.
Bog buckbean	*Menyanthes trifoliata* L.
Bog rosemary	*Andromeda glaucophylla* L.
Catbrier	*Smilax glauca* Walter.
Christmas fern	*Polystichum acrostrichoides* (Michx.) Schott.
Great laurel	*Rhododendron maximum* L.
Greenbrier	*Smilax rotundifolia* L.
Mountain laurel	*Kalmia latifolia* L.
Panic grass	*Panicum* spp.
Running buffalo clover	*Trifolium stoloniferum* Muhl. Ex. A. Eaton.
Shield fern	*Dryopteris marginalis* (L.) A. Gray.
Star chickweed	*Stellaria pubera* Michx.
Stinging nettle	*Laportea canadensis* L.
Violet	*Viola* spp.
White snakeroot	*Eupatorium rugosom* Houtt.

Wildlife

Allegheny mountain dusky salamander	*Desmognathus ochrophaeus*
Beaver	*Castor canadensis*
Black bear	*Ursus americanus*
Buffalo	*Bison bison*
Eastern coyote	*Canis latrans*
Elk	*Cervus elaphus*
Fisher	*Martes pennanti*
Grey wolf	*Canis lupus*
Hog	*Sus scrofa*
Indiana bat	*Myotis sodalis*
Mountain lion	*Felis concolor*
Northern dusky salamander	*Desmognathus fuscus*
Northern red salamander	*Pseudotriton r. ruber*
Northern red-backed salamander	*Plethodon cinereus*
Northern slimy salamander	*Plethodon glutinosus*
Northern spring salamander	*Gyrinophilus p. porphyriticus*
Northern two-lined salamander	*Eurycea bislineata*
Porcupine	*Erethizon dorsatum*
Red-spotted newt	*Notophthalmus v. viridescens*
Seal salamander	*Desmognathus monticola*
Spotted salamander	*Ambystoma maculatum*
White–tailed deer	*Odocoileus virginianus*
Wild turkey	*Meleagris gallopavo*
Wehrle’s salamander	*Plethodon wehrlei*

Insects and Diseases

Balsam woolly adelgid	*Adelges piceae*
Beech bark disease	*Nectaria coccinea var. faginata*
Butternut canker	*Sirococcus clavigignenti-juglandacearum*
Chestnut blight	*Cryphonectria parasitica*
Dogwood anthracnose	*Discula destructiva*
Dutch elm disease	*Ophiostoma ulmi*
Gypsy moth	*Lymantria dispar*
Hemlock woolly adelgid	*Adelges tsugae*

Apendix B: Abbreviations and Acronyms

Al	Aluminum
ANC	Acid Neutralizing Capacity
ANOVA	Analysis of Variance
BAI	Basal Area Increment
BC	Black Cherry
BBWM	Bear Brook Watersheds in Maine
Ca	Calcium
CAAA	Clean Air Act Amendments
CASTNET	Clean Air Status and Trends Network
CCC	Civilian Conservation Corps
CEC	Cation Exchange Capacity
Cl	Chloride
DON	Dissolved Organic Nitrogen
ECEC	Effective Cation Exchange Capacity
EPA	Environmental Protection Agency
FEF	Fernow Experimental Forest
HNO_3	Nitric Acid
K	Potassium
LOI	Loss on Ignition
Mg	Magnesium
Mn	Manganese
MNF	Monongahela National Forest
Na	Sodium
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NAPAP	National Acid Precipitation Assessment Program
NH_3	Ammonia
NH_4	Ammonium
NO	Nitric Oxide
NO_3	Nitrate
N_2O	Nitrous Oxide
NPP	Net Primary Productivity
P	Phosphorus
RM	Red Maple
RRG	Relative Radial Growth Rate
SB	Sweet Birch
SM	Sugar Maple
SO_4	Sulfate
$SrCl_2$	Strontium Chloride
USDA	United States Department of Agriculture
YP	Yellow-poplar

Appendix C: Contributor's Biographies

Dr. Mary Beth Adams is a research soil scientist and Project Leader with the USDA Forest Service, Northeastern Research Station in Parsons, WV. She received Bachelors and Master's degrees from Purdue University in Forestry, and a Ph.D. in Forestry and Soil Science from North Carolina State University. She joined the Forest Service after serving as a post-doctoral research associate at Oak Ridge National Laboratory in Tennessee, evaluating acidic deposition and ozone effects on loblolly pine. She has conducted research on air pollution effects on forests and forest soils, nutrient cycling in forests, effects of forest management activities on watershed processes, and long-term soil productivity. Her collaborations include researchers and graduate students from West Virginia University, University of Pittsburgh, Virginia Tech., Marshall University, University of Maine, and The Pennsylvania State University, among others.

Dr. David R. DeWalle, Professor of forest hydrology, has been with the School of Forest Resources at Penn State for over 35 years. He teaches courses in watershed management, microclimatology and snow hydrology. Dr. DeWalle is currently Director of the Pennsylvania Water Resources Research Center and Associate Director of the Penn State Institutes of the Environment. He has been involved with field research at Fernow related to the impacts of atmospheric deposition on forest ecosystems since the 1980's.

Dr. Pamela J. Edwards is a research hydrologist with the USDA Forest Service, Northeastern Research Station in Parsons, West Virginia. Over the past 24 years, Pam has conducted research in atmospheric deposition and air pollution, watershed acidification and episodic stream chemistry, forest management effects on water quality and quantity, watershed runoff processes, erosion and sedimentation, forest soil chemistry and tree growth/health, and forestry best management practices. She also serves as an adjunct faculty member at The Pennsylvania State University, Southern Illinois University, Marshall University, and West Virginia University.

Dr. Frank S. Gilliam received his Ph.D. at Duke University in 1983, after which he went on to post-doctoral research at Kansas State University and the University of Virginia, and teaching at the University of North Carolina–Greensboro. He joined the faculty at Marshall University in 1990, where he is Professor of biological sciences, teaching courses in ecology and plant ecology. His research interests lie at the interface between terrestrial plant communities and ecosystems.

Dr. John Hom has been with the Northern Global Change Research Program since 1992 as the deputy program manager. He started working for the Forest Service in 1989 as a plant physiologist for the Riverside Fire Lab, on interactive stresses to forest species. Prior to the Forest Service, he received his degrees at Stanford, San Diego State and his doctorate at the University of Alaska, where he did research on soil warming in permafrost forest ecosystems in Alaska . He served as the Biomass Program Director at San Diego State University where he established biological field stations and studied fuel reduction of chaparral for biomass energy. He is currently conducting research on large scale validation of forest productivity using remote sensing, carbon sequestration in non-forest regions of Baltimore, fire weather research in the Pine Barrens of New Jersey, and the interactive effects of elevated CO_2 and ozone at the Aspen FACE site.

James N. Kochenderfer received his undergraduate degree from West Virginia University and his M.F. from Duke University. He has been a research forester at the Timber and Watershed Laboratory since 1967. During this period he has been involved with research in various aspects of forest hydrology and silviculture. He has authored and co-authored articles in both fields.

Dr. Michael Little is presently chairperson of the Department of Integrated Science and Technology and a Professor teaching courses in the Integrated Science and Environmental Science degree programs at Marshall University. He received B.S. and M.S. degrees from Marshall University and a Ph.D. in Biology from the University of Louisville in 1983. His initial research, in collaboration with Dr. John Wiley of the East Carolina University School of Medicine, tracked the movement of mobile genetic elements through the genomes of a diploid-tetraploid species complex of treefrogs. His environmental work in collaboration with Dr. Tom Pauley of Marshall University used terrestrial and aquatic salamanders as bio-indicators of impacts from environmental acidificationand insecticide use. He has recently worked with a group of undergraduate and graduate students who have sequenced a portion of the mitochondrial genome in a rare Appalachian fish, the Cheat Minnow. Current research involves the use of GIS and digital technology to map the relationship between stream structure and distribution of Appalachian fishes.

Dr. Gary W. Miller received a B.S. (1977) and M.S. (1980) in forest management from West Virginia University, and a Ph.D. (1993) in forest management from Virginia Tech. Since 1981, he has worked as a research forester with the USDA Forest Service, Northeastern Research Station. His research covers topics in ecology and silviculture of central Appalachian hardwood forests with a specific interest in the regeneration, growth, and culture of oak-dominated forests.

Stephanie Odenwald-Clemens works for the Penn State Institutes of the Environment as the state coordinator for the Master Well Owner Network. She has an M.S. in environmental pollution control from Penn State University where her thesis research focused on the effects of watershed acidification on soil chemistry, radial growth, and bolewood chemistry of three hardwood species in West Virginia. Stephanie has also completed the Center for Watershed Stewardship Program at Penn State University. She has experience working with watershed associations, County Planning Commissions, and Municipalities on solving natural resource issues. Stephanie's professional interests are in community outreach and water resources education.

Dr. Thomas K. Pauley currently is Professor in the Department of Biology at Marshall University. He received a B.S. from Morris Harvey College (now University of Charleston) in 1962, a M.S. from Marshall University in 1966, and his Ph.D. from West Virginia University in 1977. Dr. Pauley has taught courses in herpetology, ornithology, and conservation biology, and has 40 years of university experience, and 41 years of experience as a field herpetologist. His research interests lie with the natural history of amphibians and reptiles, and he is co-author of *Amphibians and Reptiles in West Virginia*.

Dr. William Peterjohn received a B.S. in biology and mathematics from Baldwin-Wallace College in 1979, a Master's in environmental science from Miami University in 1982, and a Ph.D. in botany from Duke University in 1990. Dr. Peterjohn worked for three years at the Smithsonian Environmental Research Laboratory where he examined the effects of land-use on water quality, and he documented the important role that riparian forests can play in reducing non-point source pollution in agricultural ecosystems. Dr. Peterjohn also worked for three years at the Ecosystems Center in Woods Hole, MA, studying the effects of elevated soil temperatures on the exchange of greenhouse gases between forest soils and the atmosphere. Currently, Dr. Peterjohn is an associate professor of biology at West Virginia University where he and his students investigate three topics: 1) the effects of UV-B radiation on plant growth and ecosystem processes; 2) how management practices may affect carbon storage in forest ecosystems; and 3) how increased nitrogen deposition may affect forest ecosystem processes. The last two research activities are based at the Fernow Experimental Forest where Dr. Peterjohn has conducted federally funded research for over ten years.

Dr. William E. Sharpe is a professor of forest hydrology with a joint appointment in the School of Forest Resources and the Penn State Institutes of the Environment at The Pennsylvania State University. He has been engaged in research on the effects of acidic deposition for more than 30 years and has authored or coauthored numerous scientific and popular articles covering such subjects as acid runoff episodes, aquatic biota, drinking water quality, soils and forest health.

Dr. Mark B. Watson received B.S. and M.S. degrees from Marshall University, earned a Ph.D. in botany from the University of Georgia and studied as a Post-doctoral Fellow at The Penn State University. Dr. Watson then worked as a private consultant dealing with conservation biology of amphibians and reptiles. He currently serves as an assistant professor of biology at the University of Charleston (West Virginia) where he teaches courses in biology, botany and microbiology. His research interests center around amphibian conservation biology, specifically the effects of habitat fragmentation and invasive species on amphibians.

Dr. Karl W.J. Williard is an assistant professor of forest hydrology and watershed management in the Department of Forestry at Southern Illinois University Carbondale. He received a B.A. in biology from Lehigh University, an M.S. in environmental pollution control from Penn State University, and a Ph.D. in forest hydrology from Penn State University. Presently, Dr. Williard teaches undergraduate and graduate courses in watershed management, forest hydrology, advanced watershed hydrology and management, and forest soils. His current research interests include nitrogen, phosphorus, and sediment attenuation in riparian buffer zones; nutrient biogeochemistry in forested and agricultural watersheds; impacts of forest road construction and harvesting on erosion and sedimentation; and the ecological and water quality impacts of invasive, exotic plants. He serves as Associate Editor of Ecohydrology for the *Journal of the American Water Resources Association*.

Frederica Wood has worked for the USDA Forest Service, Northeastern Research Station in Parsons, West Virginia since 1987. As part of her duties as an information technology specialist, she serves as data manager, computer programmer, laboratory quality assurance specialist, and GIS manager. Frederica has been a co-author on 12 peer-reviewed papers covering subjects including acid deposition effects, air pollution monitoring, hydrology, and forest management effects on stream water quality.

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