

CHEMICAL INTERACTIONS BETWEEN RAINFALL AND
NORTHERN RED OAK (QUERCUS RUBRA L.) FOLIAGE.

by

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Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Plant Pathology, Physiology, and Weed Science

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(ABSTRACT)

Nutrient ion exchange was examined between simulated acid rain solutions and northern red oak (Quercus rubra L.) leaves of trees growing in fertile, limestone-derived soil and less fertile, sandstone/shale-derived soil. Leaves harvested from trees growing on the fertile site had greater concentrations of total N, P, K, Ca, and Mn but less total Mg than leaves of trees on the less fertile site. Cation losses from leaves of both sites were similar when exposed to simulated rain solutions of pH 5.6, 4.3, and 3.0. Simulated rain solutions of pH 3.0 leached the greatest amount of total cations from leaves of both sites. Differences in acidity between leachates and starting rain solutions increased as the acidity of starting solutions contacting leaves of either site increased. Differences in leaf nutrient status between sites typically did not affect leachate acidity. Hydrogen ion exchange, believed to be the main mechanism of cation loss from leaves of both sites, accounted for 30 to 44% of all cations leached from leaves of both sites.

Concentrations of inorganic ions were measured in bulk rainfall and bulk throughfall collected beneath northern red

oak trees growing on the fertile and less fertile sites. Rainfall passing through crowns at both sites was enriched with SO_4^{2-} , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , and Fe^{2+} , but lost NH_4^+ to the crowns. There was little difference in the inorganic chemistry of incident rainfall between sites. Large-particle dryfall ionic concentrations, rainfall volume, and leaf area were all larger at the fertile than at the less fertile site. Higher concentrations of Ca^{2+} , Mg^{2+} , NH_4^+ , Mn^{2+} , and SO_4^{2-} in throughfall at the fertile site compared to that of the less fertile site are likely due to the combination of these three factors.

Historical northern red oak crown areas were estimated for the fertile and less fertile sites by a two step procedure using annual growth ring chronologies and published regression equations. These equations related total crown area to total crown dry weight. The usefulness of crown area estimates in throughfall studies was demonstrated by applying nutrient ion exchange data, collected beneath northern red oak crowns in 1984, to 1982 and 1930 crown area estimates. Smaller nutrient ion exchange estimates in 1930 were due to smaller crown area estimates.

ACKNOWLEDGEMENTS

I thank the members of my graduate committee for their help and encouragement during the research and writing of this dissertation. Thanks to Dr. George Lacy for filling in at my dissertation defense on such short notice, and for his helpful critique of this dissertation. I especially thank my committee chairman, Dr. William E. Winner, for his unflagging support and encouragement during field and laboratory work, writing, and editing.

I am grateful to students and staff of the Laboratory for Air Pollution Impact to Agriculture and Forestry for their help in the field collecting increment cores. They

. Thanks also to _____ of the Forestry Department for collecting increment cores, and to _____ for help in the field and for measuring leaf areas. I am grateful to _____ for his computer programming expertise. And, a special thank-you to _____ for all her assistance with the day to day functioning of my work at the Laboratory.

I am indebted to _____ of the Shenandoah National Park and _____ of the Fernow Experimental Forest without whose help this research would not have been accomplished. I am also indebted to _____ and

of the Shenandoah National Park, and
of the Fernow Experimental Forest
for collecting water samples in the field.

I am grateful to
of the Virginia Tech Biology Department for allowing me the
use of their labs and equipment.

Thanks also to of the U. S. Forest
Service, Pacific Southwest Forest and Range Experiment
Station, Riverside, California for graciously providing
access to facilities of the Statewide Air Pollution Research
Center of the University of California at Riverside. His
contribution aided the completion of this dissertation.

I am most thankful for my wife, , and her loving
support through my graduate student career and beyond.
Finally, I am thankful to be father, and
to know her love and joyfulness.

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INTRODUCTION

Background. Terms such as acid rain, acid precipitation, and acid deposition have become commonplace in our society. In their broadest sense they refer to the deposition of acids and acidified chemical constituents from the atmosphere onto terrestrial and aquatic ecosystems. More accurately they refer to deposition of acid compounds in the environment resulting from man-made industrial and urban pollution. It is generally agreed that industrial emissions of sulfur and nitrogen oxides are the major precursors of acid compounds in the atmosphere (National Research Council 1981), although the evidence linking acid deposition to industrial emissions is stronger for sulfur oxides than nitrogen oxides (National Research Council 1986). Chemical processes of oxidation and reduction reactions transform sulfur and nitrogen oxides into sulfate and nitrate associated with free protons. Thus, anthropogenic pollutants emitted into the atmosphere can result in precipitation acidity in excess of that which might be expected if only "natural" acidification processes were at work in the atmosphere. "Natural" acidifying processes have been described, and expected ranges of precipitation acidity have been estimated for the non-polluted atmosphere (Charlson and Rodhe 1982, Galloway et al. 1982).

Acid deposition can occur through meteorological activity (e.g. rain, snow, fog, etc.) or as dryfall not involving

precipitation. Acid inputs to ecosystems of the eastern United States measured in wet-only precipitation and bulk precipitation have been increasing over the past 25 years (Likens et al. 1972; Cogbill and Likens 1974; Likens and Butler 1981). This increase has led to concern and questions about whether terrestrial ecosystems are becoming acidified in response to long-term anthropogenic acid inputs. Various scenarios have been described for general air pollution effects on forest ecosystems. These range from undetectable or stimulatory ecosystem effects of some pollutants at low doses, to alterations of species composition or community structure, impaired energy flow and biogeochemical nutrient cycling, and changes in hydrology and erosion at intermediate and high pollutant doses (Smith 1981, 1984). Although conclusive evidence has yet to be provided indicating a shift in forest species composition due to acid deposition, there are examples of tree decline and mortality correlated with acid deposition both in Europe (Roberts 1983) and in the eastern United States (Johnson and Siccama 1983, 1984).

In order to demonstrate any of these scenarios involving acid deposition, it is necessary to examine the fate of protons and their associated anions in wet and dry deposition within forest ecosystems. One response that has been studied in particular is the ability, or lack thereof, of

ecosystems to buffer acid deposition at some point in the plant-soil continuum. Buffering is the ability of a system to maintain an almost constant pH value during the acidification process (Paces 1985). One mechanism that decreases incident rainfall acidity is hydrogen ion exchange which occurs at leaf cuticle and cell wall surfaces. This phenomenon, which involves reactions with base cations, possibly including foliar leaching (Tukey 1980; Cronan and Reiners 1983), accounts for the partial neutralization of incident rainfall acidity. Acid/base reactions occurring when wet deposition interacts with dry deposited aerosols, gases, and particulates also accounts for some acid neutralization.

The partial neutralization of rainfall acidity by leaves can be seen by comparing the pH of bulk rainfall to the pH of bulk throughfall collected beneath northern red oak crowns (Table 1). These data were collected at two research sites which will be described in detail in the following chapters. All bulk rainfall below pH 5.6 at the Fernow Experimental Forest (FEF) and at the Shenandoah National Park (SNP) became less acidic following contact with northern red oak crowns. The more alkaline bulk rainfalls at the SNP (those above pH 6.1) were slightly acidified by northern red oak crowns. This suggests a true buffering mechanism, and that the range of rainfall pH values will be

Table 1. Weekly, wet-only rainfall (Rain) pH values ranked from most acidic to least acidic with associated weekly bulk throughfall (Tfall) pH values, and the difference in acidity (R-T) between rainfall and throughfall collected at the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va.

Rank	SNP			FEF		
	Rain	Tfall	R-T	Rain	Tfall	R-T
	$-\log[H^+]$		$\mu\text{eq/L}$	$-\log[H^+]$		$\mu\text{eq/L}$
1	3.81	4.72	136	3.82	5.89	150
2	3.95	6.27	111	3.88	4.66	110
3	4.08	5.21	77	3.89	6.13	128
4	4.12	5.26	71	3.90	5.18	119
5	4.18	5.90	65	3.94	4.20	52
6	4.41	5.59	36	3.95	4.79	96
7	4.48	5.03	24	3.98	5.06	96
8	4.57	5.87	26	4.00	4.41	61
9	5.57	5.54	0	4.11	5.09	70
10	6.10	5.51	- 2	4.20	4.39	22
11	6.26	5.55	- 2	4.22	4.80	44
12	6.34	4.96	-11	4.25	4.71	37
13	6.34	5.68	- 2	4.26	4.79	39
14	-	-	-	4.28	5.57	49

NOTE: Wet-only rainfall data is from NADP/NTN sites nearest the SNP and FEF sites.

broader than the range of throughfall pH values.

Throughfall pH values higher or comparable to those in incident rain were reported for an oak-hickory forest in eastern Tennessee (Lindberg et al. 1979). This occurrence was attributed to the temporary loss in ability of the canopy to remove protons from incident rain. The phenomenon did not coincide with the leaching of base cations. These workers concluded that some process other than ion exchange was involved, and that protons, once at exchange sites, were not retained by leaves (Lindberg et al. 1982). This explanation may not be complete, but it indicates the complexity of the chemical reactions that occur as incident rain passes through vegetative layers of terrestrial ecosystems. It also indicates the need for more research leading to a greater understanding of these processes.

Base cation leaching from forest soils also has been attributed to acid precipitation (Cronan 1980a; Mollitor and Raynal 1982). Increases in base cation leaching from foliage and soils as a result of acid deposition to forest ecosystems has been discussed for specific ecosystems and laboratory microcosms (Johnson et al. 1985; Wood and Bormann 1977; Lee and Weber 1982; Foster 1985; Cronan 1980b; Richter et al. 1983), and in a more general way (Smith 1984; Vitousek 1983), as causing alterations in nutrient cycling. Hypothetically, such alterations could affect

forest productivity if there is a decrease in nutrient use efficiency or an increase in energy cost of nutrient uptake within the system. Even if nutrients are only displaced within the plant-soil system, lost from leaves and then recovered by roots, energy will have been expended. The plant expends more energy in order to maintain a healthy nutrient status. In order for this hypothesis to be substantiated however, it must be determined that nutrients lost from leaves were needed for normal physiology and metabolism, and that loss rates exceed nutrient resupply rates. Nutrients lost from within leaf cells are likely to be important to plant productivity, whereas the consequences of ionic leaching from cell walls and cuticles are unknown.

Research questions and approach. In spite of extensive studies completed and currently underway in the area of assessing chemical inputs and outputs of forests, several critical questions remain. They are as follows: 1) Does foliar leaching really occur or are chemical differences between rainfall and throughfall (Table 1) attributable to washing of dry deposition? 2) What ions account for pH differences and buffering observed in rainfall and throughfall collected in forests (Table 1)? 3) Since throughfall chemistry is different from rainfall chemistry (Table 1) and of great ecological importance, are there ways to predict the chemical composition of throughfall? 4) If nutrient

exchange processes between foliage and rain are important to forest productivity, are there ways to predict how various acid deposition scenarios might affect nutrient uptake and loss rates for a tree over its lifetime?

To better understand the importance of chemical alterations to incident rain by tree crowns, and address the questions above, specific research questions were formulated and studies developed at two Eastern hardwood forest sites. The sites chosen for study had mature northern red oak in the overstory, and different levels of soil fertility. The link between soil fertility, foliar nutrient levels, and leachability of foliar nutrients by acid deposition was assessed at each site. Three specific research objectives were as follows: 1) to determine in the laboratory whether nutrient ion leaching from leaves was affected by leaf nutrient status; 2) to determine whether tree crown nutrient status affected bulk throughfall nutrient ion concentrations, and 3) to develop a means of estimating past nutrient ion exchange in tree crowns. These objectives, taken together, were developed to further the understanding of how acid deposition may alter nutrient cycling processes in forests, and to explore the possibility of using historical air pollution data and dendrochronological techniques for modeling changes in nutrient cycling due to air pollution emissions.

References

- Charlson, R. J. and H. Rodhe. 1982. Factors controlling the acidity of natural rainwater. *Nature* 295:683-685.
- Cogbill, C. V., and G. E. Likens. 1974. Acid precipitation in the northeastern United States. *Water Resources Res.* 10:1133-1137.
- Cronan, C. S. 1980a. Controls on leaching from coniferous forest floor microcosms. *Plant Soil* 56:301-322.
- Cronan, C. S. 1980b. Solution chemistry of a New Hampshire subalpine ecosystem: a biogeochemical analysis. *Oikos* 34:272-281.
- Cronan, C. S. and W. A. Reiners. 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. *Oecologia* 59:216-223.
- Galloway, J. N., G. E. Likens, W. C. Keene, and J. M. Miller. 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res.* 11:8771-8786.
- Foster, N. W. 1985. Acid precipitation and soil solution chemistry within a maple-birch forest in Canada. *For. Ecol. Manage.* 12:215-231.
- Johnson, A. H., and T. J. Siccama. 1983. Acid deposition and forest decline. *Environ. Sci. Tech.* 17:294-305.
- Johnson, A. H., and T. J. Siccama. 1984. Decline of red spruce in the northern Appalachians: assessing the possible role of acid precipitation. *TAPPI J.* 67:68-72.
- Johnson, D. W., D. D. Richter, G. M. Lovett, and S. E. Lindberg. 1985. The effects of atmospheric deposition on potassium, calcium, and magnesium cycling in two deciduous forests. *Can. J. For. Res.* 15:773-782.
- Lee, J. J., and D. E. Weber. 1982. Effects of sulfuric acid rain on major cation and sulfate concentrations of water percolating through two model hardwood forests. *J. Environ. Qual.* 11:57-64.
- Likens, G. E., Bormann, F. H., and N. M. Johnson. 1972. Acid rain. *Environment* 14:33-40.
- Likens, G. E., and T. J. Butler. 1981. Recent acidification of precipitation in North America. *Atmos. Environ.* 15:1103-1109.
- Lindberg, S. E., D. S. Shriner, and W. A. Hoffman, Jr. 1982. The interaction of wet and dry deposition with the forest canopy. pp. 385-409. In *Acid precipitation effects on ecological systems*. Edited by Frank M. D'itri. Ann Arbor Science, Ann Arbor, Michigan.
- Lindberg, S. E., R. C. Harris, R. R. Turner, D. S. Shriner, and D. D. Huff. 1979. Mechanisms and rates of atmospheric deposition of selected trace elements and sulfate to a deciduous forest watershed. ORNL/TM-6674. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Mollitor, A. V. and D. J. Raynal. 1982. Acid precipitation

- and ionic movements in Adirondack forest soils. *Soil Sci. Soc. J.* 46:137-141.
- National Research Council. 1981. *Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion*. National Academy Press, Washington, D. C.
- National Research Council. 1986. *Acid Deposition Long Term Trends*. National Academy Press, Washington, D. C.
- Paces, T. 1985. Acidification in central Europe and Scandinavia: a competition between anthropogenic, geochemical and biochemical processes. *Ambio* 14:354-356.
- Richter, D. D., D. W. Johnson, and D. E. Todd. 1983. Atmospheric sulfur deposition, neutralization, and ion leaching in two deciduous forest ecosystems. *J. Environ. Qual.* 12:263-270.
- Roberts, L. 1983. Is acid deposition killing West German forests? *Bioscience* 33:302-305.
- Smith, W. H. 1981. *Air Pollution and Forests, Interactions between Air Contaminants and Forest Ecosystems*. Springer-Verlag, New York. 379 pp.
- Smith, W. H. 1984. Ecosystem pathology: a new perspective for phytopathology. *For. Ecol. Manage.* 9:193-219.
- Tukey, H. B., Jr. 1980. Some effects of rain and mist on plants, with implications for acid precipitation. *In* *Effects of Acid Precipitation on Terrestrial Ecosystems*. Edited by T. C. Hutchinson and M. Havas. Plenum Press, N. Y. pp. 141-150.
- Vitousek, P. M. 1983. Mechanisms of ion leaching in natural and managed ecosystems, pp. 129-144. *In* *Disturbance and Ecosystems: Components of Response*. Springer-Verlag, NY, 292 pp.
- Wood, T., and F. H. Bormann. 1977. Short-term effects of simulated acid rain upon the growth and nutrient relations of *Pinus strobus*, L. *Water, Air, and Soil Pollut.* 7:479-488.

Nutrient ion exchanges between simulated acid rain solutions and Quercus rubra L. leaves differing in nutrient status.

Abstract

Nutrient ion exchange was examined between simulated acid rain solutions and northern red oak (Quercus rubra L.) leaves of trees growing in soils of different fertility. Leaves harvested from trees growing on a fertile soil had greater concentrations of total N, P, K, Ca, and Mn but less total Mg than leaves of trees on a less fertile soil. Cation losses from leaves of both the fertile and less fertile sites were similar when exposed for 2 h to simulated rain solutions of pH 5.6, 4.3, and 3.0, except for Mg at pH 3.0. Simulated rain solutions of pH 3.0 leached 1) more Mg from leaves of the less fertile (versus fertile) site, and 2) the greatest amount of total cations from leaves of both sites. Differences in acidity between leachates and starting rain solutions increased as the acidity of starting solutions contacting leaves of either site increased. Differences in leaf nutrient status between sites typically did not affect leachate acidity. Calcium ion, K^+ , and Mn^{2+} losses increased when leaves were exposed to pH 3.0 rain solutions for an additional 5 hours. Leaching of PO_4^{3-} , as well as the leaf retention of SO_4^{2-} , NO_3^- , and NH_4^+ also was observed. Hydrogen ion exchange, believed to be the main mechanism of cation loss from leaves of both sites, accounted for 30 to 44% of all cations leached from leaves of both sites. It is not clear, however, whether these

cation losses would have been metabolically important to the leaves.

Introduction

A starting point for discerning an effect of acid precipitation on forest ecosystems is the forest canopy, the initial point of contact between precipitation and closed-canopy forests. Forest canopies can alter the chemical content of precipitation (Tamm 1951; Patterson 1975; Cronan and Reiners 1983) through the process of nutrient and metabolite leaching and/or retention by leaf tissue. Precipitation chemistry also can be altered when aerosols and particulates deposited from the atmosphere are washed from leaves. Acid precipitation associated with industrial emissions in the eastern United States contains about six times the amount of SO_4^{2-} , NO_3^- , and H^+ as rain collected in remote areas of the world (Galloway 1984). These pollutants have the potential to alter the chemical processes that occur in forest canopies.

Nutrient cations can be leached from plants by two passive processes: hydrogen ion exchange at cuticle and cell wall exchange sites, and diffusion of ions directly from the translocation stream within foliage through areas devoid of cuticle (Mecklenburg et al. 1966). Organic metabolites and inorganic ions are not leached from within cells, but from materials in transit to areas of utilization (Tukey 1980).

Thus foliar leaching has the effect of competing with cellular metabolism for exchangeable cations and metabolites in the translocation stream. The hydrogen ion exchange mechanism of cation leaching is of particular interest since increases in precipitation acidity in recent times (Likens and Butler 1981) would tend to increase nutrient losses from vegetation. If the neutralization of precipitation acidity by forest canopies corresponds to accelerated cation leaching, forest productivity may be adversely affected (Likens et al. 1981).

Base cation leaching from woody and non-woody plant species along with increases in leachate pH over simulated rain solution pH was reported previously (Wood and Bormann 1975; Scherbatskoy and Klein 1983). Craker and Bernstein (1984) reported increases in solution pH following contact with leaf tissue of several crop species, but did not chemically analyze the leachate. Leaching and retention of anions by leaves of forest tree species also has been documented (Scherbatskoy and Klein 1983; Skeffington and Roberts 1985; Haines et al. 1985).

This research was designed to simulate and measure inorganic nutrient ion exchanges that occur when rainwater contacts leaves. This was done by examining nutrient ion loss and retention by Quercus rubra L. leaves exposed to simulated acid rain solutions. One objective was to

determine the effect of two levels of leaf nutrient status on nutrient ion exchanges between leaves and simulated acid rain solutions. Secondly, the effect of three levels of simulated rain solution acidity on nutrient ion exchanges between solutions and leaves was examined. Finally, estimates were made of cation losses caused by proton exchange when leaves were exposed to rain solutions.

Materials and Methods

Site descriptions. Northern red oak leaves used in this study were collected from two forested sites chosen on the basis of their different soil nutrient element concentrations. One site is located in the Shenandoah National Park (SNP), Greene Co., Va. (38° 21' North latitude, 78° 32' West longitude). It supports an upland oak community which includes: chestnut oak (Quercus prinus L.), white oak (Q. alba L.), black oak (Q. velutina Lam.), yellow-poplar (Liriodendron tulipifera L.), eastern white pine (Pinus strobus L.), and pitch pine (P. rigida Mill.). Mean annual precipitation at this site is 109 cm. Mean elevation of the site is 615 m, and it is located on the WSW-facing side of a ridge with an average slope of 50%. Soils at this site are classified as either loamy-skeletal, mixed, mesic ruptic-alfic (Catoctin series), or loamy-skeletal, mixed, mesic typic (Parker series) dystrochrepts (USDA 1980, 1986). They are derived from sandstone/shale parent material of the

Swift Run and Pedlar geologic formations (Gathright 1976). Northern red oak site index was calculated to be 16.4 m (base age 50 years) using age and height measurements, and a published site index equation (Hahn and Carmean 1982). Northern red oak occupies 12% of the total canopy area (Chapter 4, Table 9).

The second site is in the Fernow Experimental Forest (FEF), Tucker Co., W. Va. ($39^{\circ} 3'$ North latitude, $79^{\circ} 40'$ West longitude), and supports a northern hardwood forest. Common tree species include: yellow-poplar, chestnut oak, sugar maple (Acer saccharum Marsh), red maple (A. rubrum L.), white ash (Fraxinus americana L.), black cherry (Prunus serotina Ehrh.), and American beech (Fagus grandifolia Ehrh.). The FEF site receives 147 cm of mean annual precipitation. Mean elevation of the site is 725 m, and it has a NNE aspect with an average slope of 30%. The soil is a fine-loamy, mixed, mesic typic hapludalf of the Belmont soil series (USDA 1980). It is derived from calcareous shale, sandstone, and limestone parent material (Auchmoody 1972). Northern red oak site index at base age 50 years is 25.9 m (Yawney 1964). Northern red oak accounts for 4% of the total canopy area (Chapter 4, Table 9). Northern red oak trees are dominant or codominant within the canopies of both sites.

Soil sampling procedure. A total of eight soil samples were

collected from each site using a 2.5-cm punch-tube. Soil was sampled to a depth of 20 cm. Soil samples were composited from four subsamples spaced equidistantly around the base, and between the bole and crown drip line of each sample tree. Soil was sampled at the SNP beneath four eastern white pine and four northern red oak trees toward the end of the 1982 growing season. At the FEF, soil was sampled at the start of the 1983 growing season beneath four black cherry and four northern red oak trees. All trees beneath which soils were sampled were in dominant or codominant crown classes. Prior to chemical analysis, soils were air dried and passed through a 2-mm screen.

Leaf collection and leaching procedure. Leaves were collected from the crowns of three codominant northern red oak trees at each site three times during the 1984 growing season. The same three trees at each site were used for sampling leaves throughout the growing season. Crown leaf harvest dates were June 25, August 6, and September 26 at the SNP, and June 26, August 7, and September 27 at the FEF. Leaves were collected from lower and middle portions of crowns by climbing trees and cutting branches with a pole pruner. Branches were placed in plastic bags and stored on ice in an insulated cooler for no more than 48 h while in transit from the field to the laboratory. Care was taken to minimize cold damage and bruising during the trip to the

laboratory. In the laboratory, branches were stored in a refrigerator for an additional 48 to 72 h prior to experimental treatment. Leaves remained on branches until just before experimental treatments to insure realistic conditions as much as possible. Leaf areas were measured with a Li-Cor model Li-3000 portable leaf area meter.

Whole, undamaged leaves were selected for experimentation from among all leaves collected from the three sample trees at each site. Leaves were blotted with paper towels to remove water that condensed in the storage bags. Blotting may also have removed some ions and particles solubilized or suspended in condensed leaf surface water. This was done to avoid interpreting leaf surface deposits as leachates. Incomplete removal of all leaf surface chemicals from leaves by blotting would result in overestimates of leaching, and would be similar for all leaves from both sites. After blotting, leaves were then bisected along the midrib. Chemical analyses were performed on each leaf half. However, one half was subjected to a two h treatment in a simulated rain solution prior to chemical analyses. This was done to examine the nutrient content of leaves before and after exposure to simulated acid rain solutions. Any leakage of nutrients from severed vasculature into rain solutions would be similar for all leaves, and would tend to overestimate leaching losses. To examine the affect of an extended

leaf-solution contact time on nutrient leaching, additional leaves harvested in June were exposed to rain solutions for 7 hours.

An average of eight fresh leaf halves, with a combined weight of approximately 6 g, were placed in 17.8 x 20.3 cm clear, plastic-zippered bags containing 250 ml of simulated rain solution. The plastic bags were washed previously with deionized water to remove possible chemical contaminants. Air was forced from the bags before they were sealed with leaves and simulated rain solutions. Leaves from each of three trees on each site were exposed to simulated rain solutions of pH 3.0, 4.3, and 5.6 following the June, August, and September harvests. Simulated rain solutions contained inorganic ions in proportions measured in rains occurring in Southwestern Virginia (Chevone et al. 1984). A stock rain solution of pH 4.3 was mixed to contain 1.00 ppm Ca^{2+} , 0.10 ppm Mg^{2+} , 0.55 ppm Na^{+} , 0.22 ppm K^{+} , 0.48 ppm NH_4^{+} , 0.46 ppm Cl^{-} , 2.70 ppm NO_3^{-} , 5.50 ppm SO_4^{2-} , and 0.01 ppm PO_4^{3-} . Solutions of pH 3.0 were attained by adding several drops of a 1 M H_2SO_4 , 0.5 M HNO_3 solution to the stock solution. Solutions of pH 5.6 were made by adding several drops of 1 M NaOH solution to the stock solution. Actual pH was brought within 0.02 units of the target pH.

To determine the effect of the bag on rain chemistry, simulated rain solutions of the three acidities were placed

in bags without leaves. All bags were laid flat on a table at room temperature under fluorescent room lighting. In the beginning, and halfway through the 2 or 7 h treatment periods, the bags were agitated gently to mix their contents. Following the treatment period, leaf halves were removed from the bags and prepared for chemical analysis. Solution pH was measured before contact with leaves, and immediately after leaves were removed from the bags.

Soil, foliar and simulated rain chemical analyses. Double acid extraction and a Jarrell-Ash Model 955 Atom Comp argon plasma emission spectrometer were used to determine concentrations of extractable P, K, Ca, Mg, Mn, Zn, and Al in soil. Total nitrogen was determined by the macro-Kjeldahl procedure. A glass pH electrode and reference electrode were used to determine soil pH in a 1:1 mixture of soil and distilled water. Percent organic matter in soil was determined by wet oxidation with potassium dichromate.

Nutrient element concentrations in crown leaves harvested in June and August were determined at the Soil Testing and Plant Analysis Laboratory at Virginia Tech, Blacksburg, Va. Concentrations of total Ca, Mg, Mn, Zn, Cu, and Fe were determined by atomic absorption spectrophotometry. Leaf total P and total B were determined colorimetrically, and total K was determined by flame photometry. Nutrient element concentrations of leaves harvested in September,

were determined at the University of Georgia Soil Testing and Plant Analysis Laboratory by a Jarrell-Ash Model 750 arc spark emission spectrometer. Both labs used micro-Kjeldahl techniques to measure leaf total N, and a Leco sulfur determinator to quantify leaf total S. Concentrations of nutrient elements in 10 duplicate samples sent to each lab following the last harvest did not differ (t-tests, $P < 0.05$).

Concentrations of total P, K, Ca, Mg, Na, and Mn, in simulated rain solutions and leachates were determined by a Jarrell-Ash Model 955 Atom Comp inductively coupled argon plasma (ICAP) emission spectrometer. Concentrations of NH_4^+ and NO_3^- (following reduction to NH_4^+) were determined by distillation of basic NH_4^+ and titration to an endpoint. Analysis of SO_4^{2-} concentrations in simulated rain solutions were determined by the turbidimetric method (Anonymous 1983), using a model 900-3 Klett-Summerson photoelectric colorimeter. Solution pH was measured using a Beckman combination pH electrode with a Ag/AgCl reference element.

Data analysis. Our data provided two records of chemical movement between leaves and simulated acid rain solutions:

1) chemical differences between leached and unleached leaves, and 2) chemical differences between starting rain solutions and leachates. Hypothetically, these two sets of data should be comparable. Analysis of variance with a 2 (sites) x 3 (trees/site) factorial design was used to

compare mean concentrations of 11 nutrient elements in leaves of individual trees before and after contacting rain solutions. Nutrient element concentrations of leaves before and after contact with rain solutions were so small that they were neither statistically significant ($P \leq 0.05$) nor biologically significant. It was determined that the analytical methods used to measure leaf nutrient element concentrations could not resolve the small changes in leaf chemistry occurring in these experiments. Consequently, leaf nutrient element concentration data were pooled and used to infer the influence of soil fertility at the two sites on leaf nutrient status.

Leachate data were used to determine the influence of leaf nutrient element concentrations and rain solution pH on chemical exchanges occurring between leaves and solutions. Proton and nutrient ion movement between leaves and solutions was determined by subtracting concentrations in rain solutions from concentrations in leachates. These values were expressed as milliequivalents per square meter of leaf surface area (single side). Chemical equivalents were based on the most common inorganic ion forms of nutrient elements in leaf-rain solution interactions. A 2 (sites) x 3 (rain solution acidities) factorial analysis of variance procedure was used to identify significant changes in cation and anion concentrations. This same approach was

used to compare differences in ion exchange between 2 and 7 h leaf-solution interactions.

Results

Site characterizations.

The SNP and FEF sites were characterized by 1) soil fertility, and 2) nutrient element concentrations in northern red oak leaves. Soils and foliage of the FEF site had higher nutrient element concentrations than those of the SNP. This enabled an examination of the relationship between leaf nutrient status and leaf leachate chemistry.

Soil fertility. Soils of the FEF had higher concentrations of most nutrient elements and organic matter (Table 2). For example, the concentration of extractable Ca is 12 times greater and extractable Mg nearly 4 times greater in FEF soil than in SNP soil. Concentrations of extractable P and Al, and soil solution pH were statistically the same for both sites.

Leaf nutrient element concentrations. Leaves of FEF trees had greater concentrations of total S, N, P, K, Ca, B, Zn, Mn, and Cu but less total Mg and Fe than leaves of SNP trees (Table 3). All differences in nutrient element concentrations between sites were significant ($P \leq 0.05$) for leaves collected during June. Nutrient element concentrations in leaves collected during August were similar to those of the June collections except that foliar S and Fe did not differ

Table 2. A comparison of surface soil horizon chemistry for Shenandoah National Park (SNP), Greene Co., Va. and Fernow Experimental Forest (FEF), Tucker Co., W. Va.

<u>Variable^a</u>	<u>SNP</u>	<u>FEF</u>	
	<u>ppm</u>		
N	0.07	0.21	* ^b
P	3.50	5.00	ns
K	37.38	56.00	*
Ca	12.00	138.00	*
Mg	5.88	22.00	*
Zn	1.13	2.38	*
Mn	7.75	79.25	*
Al	379.75	301.75	ns
	<u>%</u>		
Org. Matter	7.45	10.20	*
	<u>-log [H⁺]</u>		
pH	4.48	4.38	ns

a. Total N, extractable P, K, Ca, Mg, Zn, Mn and Al.

b. Significance of Student's t-test results; * indicates a significant site difference at $P < 0.05$, ns indicates no site difference.

Table 3. Leaf areas and average concentrations of eleven nutrient elements in northern red oak leaves collected three times during the 1984 growing season at Shenandoah National Park (SNP), Greene Co., Va. and Fernow Experimental Forest (FEF), Tucker Co., W. Va.

Nutrient ^a element	June 25-26			August 6-7			Sept. 26-27		
	SNP	FEF		SNP	FEF		SNP	FEF	
	%								
S	0.12	0.16	* ^b	0.13	0.14		0.13	0.14	ns
N	2.45	2.86	*	2.32	2.71	*	2.34	2.43	*
P	0.13	0.18	*	0.19	0.23	*	0.22	0.22	ns
K	1.44	1.71	*	1.15	1.33	*	0.92	1.07	*
Ca	0.56	0.67	*	0.78	0.90	*	0.80	0.84	*
Mg	0.19	0.13	*	0.20	0.14	*	0.20	0.13	*
	ppm								
B	18	22	*	16	22	*	36	53	*
Zn	24	28	*	27	31	*	32	31	ns
Mn	637	808	*	782	1075	*	684	754	*
Cu	9	12	*	4	7	*	6	7	ns
Fe	56	49	*	58	57	ns	62	58	ns

a. Nutrient elements are in total forms.

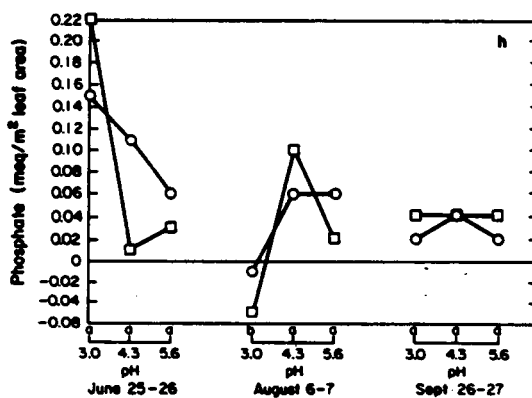
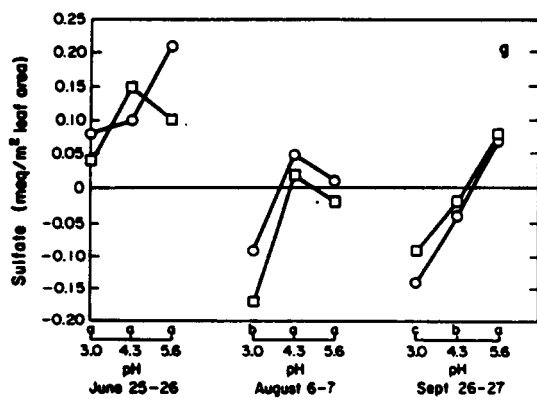
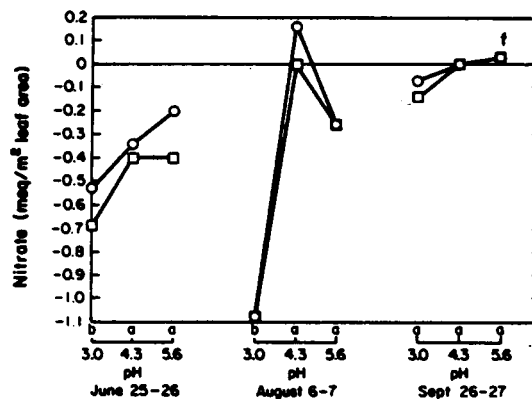
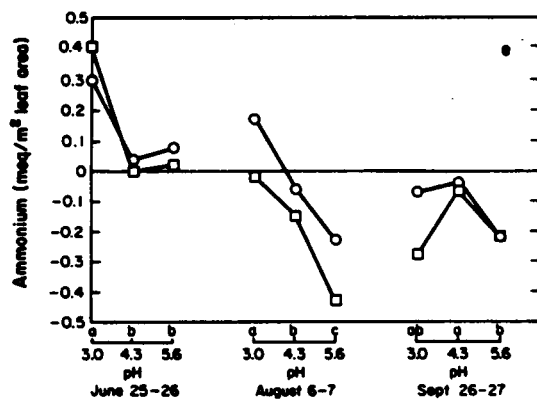
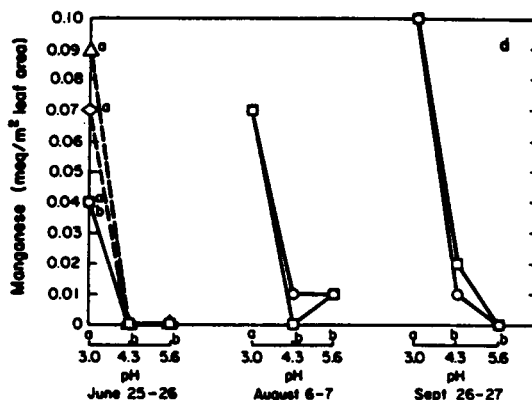
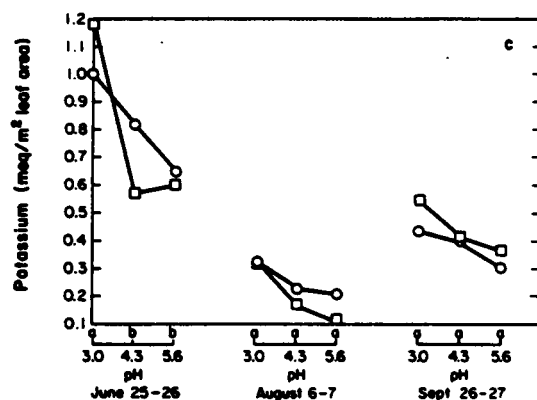
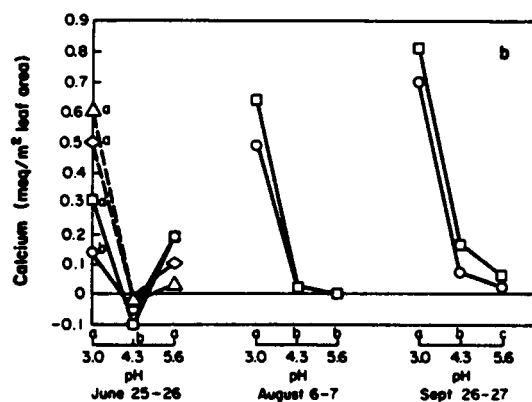
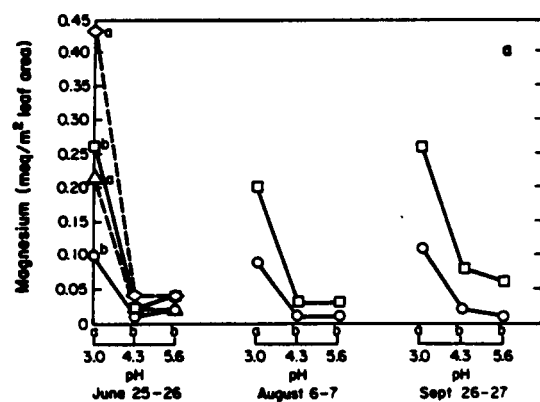
b. Significant site differences at $P \leq 0.05$ are indicated by *, ns indicates no site difference.

significantly between sites. Again, during September leaves collected from FEF trees had higher concentrations of nutrient elements than SNP leaves except for Mg, Zn, and Fe. However, differences between sites for S, P, Zn, Cu, and Fe were not significant. Leaves of the SNP site contained more Mg ($P \leq 0.05$) than leaves of the FEF site for all three leaf collection periods. Concentrations of individual nutrient elements in leaves of both sites exhibited similar growing season trends. Nitrogen and potassium concentrations were greatest in leaves harvested early in the growing season, and decreased as the season progressed. Concentrations of P, Ca, Fe, Zn and Mn increased from June to August and then either decreased (Mn), or remained about the same through September (P, Ca, Fe, and Zn). Magnesium and sulfur concentrations in leaves of both sites changed little over the growing season. Copper concentrations decreased from June to September, while foliar B doubled during the same period.

Leaf-rain solution processes.

Leaf nutrient status and nutrient ion exchange. With the exception of Mg^{2+} , differences in leaf nutrient element concentrations between the FEF and SNP sites did not affect cation and anion leaching or retention by leaves previously exposed to ambient rain conditions (Figs. 1a-h). Significantly more Mg^{2+} ($P \leq 0.05$) was lost from SNP leaves than FEF

FIG. 1. The effect of three acidities on the exchange of 8 nutrient ions (meq m^{-2} leaf area) between simulated rain solutions and northern red oak leaves harvested three times during the 1984 growing season at the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va. \bigcirc = FEF, 2 h exposure; \square = SNP, 2 h exposure; \triangle = FEF, 7 h exposure; \diamond = SNP, 7 h exposure. Different lower case letters along the x-axis indicate significant differences between mean nutrient ion exchanges from leaves of the FEF and SNP sites as determined by Duncan's multiple range test, $P \leq 0.05$. Different lower case letters along the y-axis indicate differences between mean nutrient ion exchanges within site and between 2 and 7 h exposures for leaves treated with pH 3.0 simulated rains where: $P \leq 0.05$ for Mg; $P \leq 0.10$ for Ca; and $P \leq 0.08$ for Mn.



leaves at all three harvest times (Fig. 1a). A Duncan's multiple range test indicated that site differences were due to Mg^{2+} lost from leaves exposed to pH 3.0 rain solutions ($P \leq 0.05$).

Cation losses from leaves and total nutrient element content of leaves may be related. The contrast in Mg concentrations in leaves and leachates between the sites throughout the growing season is an example. Also, Mg levels in leaves remained constant through time as did Mg^{2+} leaching levels. Leaf Ca and K increase over time as do Ca^{2+} and K^+ leaching. However, Mn in leaves of both sites is greater in August than in June or September, yet Mn^{2+} leaching increases steadily from June to September.

Despite differences in preconditioning of leaf surfaces by ambient rain at the sites, the loss or retention of cations and anions by leaves did not differ between sites, except for Mg. The amount of rainfall occurring seven days prior to leaf harvests was six times greater in June at the FEF (4.72 cm) compared to the SNP (0.79 cm). Rainfall was about equal at the FEF (4.42 cm) and SNP (4.93 cm) during August. There was no rain at either site in the week prior to the September harvest. Bulk throughfall at the FEF contained greater amounts of Ca^{2+} , Mg^{2+} , NH_4^+ , Mn^{2+} , and SO_4^{2-} than that of the SNP (Chapter 3, Table 7). Thus, precipitation and throughfall data suggest that most of the dry deposition

was removed from leaves prior to experimentation.

Rain solution acidity and nutrient ion exchange. The pH of starting rain solutions affected ionic concentrations of leachates following leaf contact. Leaves typically lost cations to simulated rain solutions, and the largest concentrations of cations were leached from leaves in solutions of pH 3.0. For all three harvests, more Mg^{2+} , Ca^{2+} , and Mn^{2+} were leached from leaves in solutions of pH 3.0 ($P \leq 0.05$) than solutions of pH 4.3 or 5.6 (Figs. 1a, b, and d). However, there was no difference between Ca^{2+} concentrations in leachates resulting from leaves harvested in June being placed in solutions of pH 3.0 and 5.6. Leaves harvested in June lost more K^+ and NH_4^+ (Figs. 1c and e) in solutions of pH 3.0 than those of pH 4.3 or 5.6 ($P \leq 0.05$). In August, leaves retained more NH_4^+ in solutions of pH 5.6 than those of pH 4.3 ($P \leq 0.05$). Leaves of the SNP harvested in August retained more NH_4^+ in pH 4.3 than pH 3.0 ($P \leq 0.05$); while for FEF leaves, amounts of NH_4^+ retained in pH 4.3 were significantly different ($P \leq 0.05$) from NH_4^+ leached at pH 3.0. In September, concentrations of Mg^{2+} leached from SNP leaves were greater than those leached from FEF leaves in solutions of all acidities ($P \leq 0.05$).

More potassium was leached from SNP and FEF leaves than any other cation (Fig. 1). Potassium was leached from

leaves in solutions of pH 4.3 and 5.6 when few other cations, and small concentrations of those cations, were leached. Leaves retained Ca^{2+} and NH_4^+ (Figs. 1b and 1e). Concentrations of these cations were smaller in leachates following contact with leaves than in solutions prior to leaf contact. The retention of Ca^{2+} was small (about 0.1 meq m^{-2}), and no well defined trend was apparent. Ammonium retention was larger ($0.2\text{-}0.4 \text{ meq m}^{-2}$), and appeared in August and September but not in June. In August, NH_4^+ retention decreased as solution acidity increased.

Nitrate and sulfate were generally retained by leaves, whereas phosphate was typically leached from leaves (Figs. 1f, g, and h). Nitrate and sulfate retention were larger ($P \leq 0.05$) following contact with solutions of pH 3.0 than solutions of pH 4.3 and 5.6. Nitrate was retained by leaves in rain solutions of all three acidities throughout the growing season, with the exception of pH 4.3 in August, and pH 4.3 and 5.6 in September. Under these conditions nitrate either was leached slightly from leaves, or was not exchanged at all (Fig. 1f). Sulfate was leached from leaves collected in June at both sites. Leaves collected in August and September retained sulfate when exposed to pH 3.0 rain solutions. Leaves either lost or retained sulfate when exposed to rains of pH 4.3 or 5.6. This suggests that less acidic treatments do not affect sulfate movement at leaf

surfaces one way of the other. Phosphate leaching from leaves exposed to rains of all three acidities across the growing season (Fig. 1h) showed no clear pH related trends.

Ion exchange between leaves and rain solutions also was measurable as a change in acidity of solutions (Table 4). In August, FEF leaves altered the initial pH of simulated rain solutions more than did SNP leaves ($P \leq 0.05$). Leaves from both sites, however, altered the acidity of pH 3.0 solutions more than pH 4.3 solutions. The acidity of pH 4.3 solutions was altered more than the acidity of pH 5.6 solutions by SNP and FEF leaves. This occurred for all treatment periods and harvests. Rain solutions of pH 4.3 showed the largest change in pH after leaf contact. However, changes in proton concentrations (meq L^{-1}) were greatest in solutions that began at pH 3.0. The interaction of solution acidity and leaf nutrient status was significant ($P < 0.05$) for August and September.

Time mediated ion exchange. Leaves from both sites that contacted simulated rain solutions for seven rather than two hours lost from 40% to 75% more Mg^{2+} , Ca^{2+} , or Mn^{2+} to pH 3.0 solutions. This time mediated loss of nutrient ions from leaves was significant for: Mg^{2+} ($P < 0.05$) from SNP and FEF leaves, and Ca^{2+} and Mn^{2+} ($P < 0.10$) from FEF leaves (Figs. 1a,b and d). The exchange of nutrient ions between leaves and solutions of pH 4.3 and 5.6 was no different

Table 4. Change in simulated rain solution acidity following contact with northern red oak leaves harvested three times during the 1984 growing season at Shenandoah National Park (SNP), Greene Co., Va. and Fernow Experimental Forest (FEF), Tucker Co. W. Va. Positive and negative values indicate increases and decreases, respectively, in pH compared to starting rain solution acidities.

Harvest	Site	Solution pH			Ave. ^a	
		3.0	4.3	5.6		
June 25-26	7h	SNP	0.16	0.52	-0.04	0.21 a a
		FEF	0.17	0.82	-0.03	0.32 a A
		Ave. ^a	0.165 b	0.67 a	-0.035 c	
	2h	SNP	0.09	0.21	-0.19	0.04 a b
		FEF	0.08	0.44	-0.17	0.12 a B
		Ave.	0.085 b	0.32 a	-0.18 c	
August 6-7	2h	SNP	0.03 b	0.26 a	-0.24 c	0.02 b
		FEF	0.03 b	0.48 a	-0.21 c	0.10 a
Sept. 26-27	2h	SNP	0.08	0.72	-0.17	0.21 a
		FEF	0.13	0.46	0.00	0.20 a
		Ave.	0.105 b	0.59 a	0.085 c	

a. Means followed by the same lower case letter for between pH treatment comparisons, between site comparisons within the same exposure time (2 and 7 h) , and within site comparisons between exposure times (2h vs. 7h) are not significantly different, $P < 0.05$. Means followed by the same upper case letter for within site comparisons between exposure times (2h vs. 7h) are not significantly different, $P < 0.06$.

between 2 and 7 hours of solution-leaf contact. Average proton exchange between solutions of all acidities and leaves from the same site was different (SNP, $P \leq 0.05$; FEF, $P = 0.06$) for 2 and 7 h rain solution exposures (Table 4).

Rates of magnesium and calcium leaching from SNP leaves exposed to pH 3.0 solutions for 2 hours was four times that of the following 5 hours. Magnesium leached twice as fast from FEF leaves in two hours as it did in the next 5 hours. Manganese also leached twice as fast from SNP and FEF leaves during the two hour exposure compared to the seven hour exposure. Potassium, a small cation that is more readily leached than other cations, did not increase in leachate during the additional 5 hours.

The hydrogen ion exchange mechanism. The hypothesis was tested that all cations lost from leaf surfaces were displaced by hydrogen ion exchange. An estimate of nutrient cation displacement from leaf surfaces was made by dividing the amount of H^+ leaves retained by the amount of total cations leached from leaves. This percentage, along with the magnitude and direction of total proton, cation, and anion movement within the leaf-solution system, were determined (Table 5).

Percentages of proton mediated cation exchange are similar for SNP and FEF leaves through the growing season. Nutrient cation losses from SNP leaves harvested in August and

Table 5. Ion movement between simulated rains of three acidities and northern red oak leaves harvested three times in 1984 from trees in the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W.Va. The vertical bar represents a leaf surface; arrows pointing toward and away from the bar indicate retention and loss, respectively, of cations, protons, and anions by leaf surfaces.

Solution pH		Harvest Time					
		June 25-26		August 6-7		Sept. 26-27	
		SNP	FEF	SNP	FEF	SNP	FEF
5.6	C ⁺ a	1.31 < >	1.12	0.29 > <	0.02	0.26 < >	0.08
	H ⁺ b	0.01 < >	0.01	0.02 < >	0.01	0.01 <	0.00
	A ⁻ c	0.27 > <	0.07	0.26 > <	0.18	0.15 < >	0.09
	% H ⁺ d	0	0	0	0	0	0
4.3	C ⁺	0.75 < >	0.97	0.07 < >	0.23	0.63 < >	0.46
	H ⁺	0.10 > <	0.13	0.13 > <	0.16	0.18 > <	0.13
	A ⁻	0.24 > <	0.13	0.12 < >	0.27	0.02 <	0.00
	% H ⁺	13	13	186	70	28	28
3.0	C ⁺	2.27 < >	1.58	1.06 < >	1.06	1.51 < >	1.29
	H ⁺	0.91 > <	0.71	0.33 > <	0.35	1.09 > <	1.45
	A ⁻	0.43 > <	0.30	1.30 > <	1.16	0.19 > <	0.19
	% H ⁺	40	45	31	33	72	112

a. Net cation movement (C⁺) = meq m⁻² leaf area of K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Na⁺, and NH₄⁺ in leachate minus meq m⁻² of same in rain solutions.

NOTE: Sodium exchange was not presented previously because Na⁺ generally is not a plant nutrient. Sodium retention and leaching occurred between leaves and rain solutions, and are important to net cation movement.

b. Net proton movement (H⁺) = meq m⁻² leaf area of H⁺ in leachate minus meq m⁻² of H⁺ in rain solutions.

c. Net anion movement (A⁻) = meq m⁻² leaf area PO₄³⁻, SO₄²⁻, and NO₃⁻ in leachate minus meq m⁻² of same in rain solutions.

d. Percent H⁺ exchange (%H⁺) = (net proton movement/net cation movement) x 100.

exposed to rain solutions of pH 4.3 were less than proton retention. The same was true for FEF leaves harvested in September and exposed to pH 3.0 rain solutions. Thus, percent H^+ exchanges were greater than 100. Excluding these two interactions, the average estimate of proton mediated cation loss from leaves is 30% of total cation losses in solutions of pH 4.3 throughout the growing season. This estimate increased to 44% of total cation losses in solutions of pH 3.0. In rains of pH 5.6, none of the nutrient cation loss was caused by proton exchange since proton retention by leaves did not occur.

The direction of anion movement, in all but two instances, opposes that of cation movement. Anions and cations were leached from leaves harvested in September and exposed to pH 5.6 solutions. They were also leached from leaves harvested in August and exposed to pH 4.3 solutions. In these instances cation leaching may be associated solely with anion leaching. The adsorption of cations by August leaves in pH 5.6 solutions may be associated with anion adsorption.

Discussion

Site characterizations: Soils and Foliage.

Concentrations of total N, P, K, Ca, Mg, Mn, and Fe in northern red oak leaves measured in the present study and in an earlier study (Auchmoody 1975) are in agreement. Differences in nutrient element concentrations between SNP

and FEF leaves reflect differences in soil nutrient element concentrations between the sites. Differences in soil chemistry at the sites are affected primarily by differences in parent material. Contrasts in fertility between the two sites also may be due to contrasts in precipitation and soil texture. The FEF receives 26% more mean annual precipitation than the SNP. The FEF soil has more clay, being a silty clay loam, compared to the loam of the SNP. Thus, many site factors including: more fertile soil, greater soil moisture, and finer soil texture could lead to greater availability of most nutrients for plant uptake in FEF soil.

Total magnesium concentrations were higher in leaves collected from SNP than FEF. This was true throughout the growing season. Increased foliar Mg at SNP occurred even though the extractable Mg concentration in SNP surface soil was one fourth that of FEF surface soil. Low levels of Mg in FEF leaves may be due to a high ratio of extractable calcium to extractable magnesium (6.3:1) in FEF soil. The Ca/Mg ratio of FEF soil was similar to that of leaves (6.0:1) over the growing season. The Ca/Mg ratio in SNP soil was 2.0:1, and in SNP leaves was 3.6:1. High levels of extractable Ca in soil inhibit the absorption of extractable Mg by plant roots (Epstein 1972; Barber 1984). As the central atom of chlorophyll, magnesium is important

to photosynthesis. Insufficient Mg supply in soil coupled with Mg leaching from foliage has been associated with Norway spruce decline in Germany (Huetttl 1986).

Leaf-rain solution processes.

Forest canopy leaves may alter the chemistry of ambient precipitation in two ways. Inorganic ions, carbohydrates, and other metabolites can be leached when water contacts leaves. Tukey (1971) describes an exchangeable pool of nutrients accumulated in excess of requirements which can be leached quickly and easily until a certain level of nutrient concentration is reached within a plant. Proton displacement of cations from cuticle and cell wall exchange sites may make up part of this leaching. Cations located on exchange sites may or may not originate in cell sap. Leaves can also serve as surfaces from which aerosols and particulates, deposited from the atmosphere, can be washed. The chemical enrichment of precipitation passing through a forest canopy is probably due to the combination of these two mechanisms (Parker 1983).

Leaf nutrient status and nutrient ion exchange. The nutrient rich leaves of the FEF might be expected to lose more cations than the less nutrient rich SNP leaves if cations on exchange sites are regularly supplied from within cells. Differences in leaf nutrient status and cation leaching, contrasts in the alteration of rain acidity, and

similarities in percentages of cations displaced by protons from leaves of both sites provide evidence to the contrary. This information suggests that there is a specific and similar number of exchange sites, and/or a similar amount of cations in the exchangeable pool within northern red oak leaves at both sites. The difference in overall nutrient status between leaves of the two sites is apparently due to nutrient elements in cell sap and fixed in cell walls which are not readily subject to leaching.

Rain solution acidity and nutrient ion exchange. Distinct pH related trends in cation leaching from leaves, and greater neutralization of H^+ in solutions of pH 3.0 than pH 4.3 or 5.6, indicate proton displacement of cations from exchange sites. The total amounts of Ca^{2+} , Mg^{2+} , and Mn^{2+} leached from leaves in solutions of pH 3.0 increased with additional leaf-rain contact time (+ 5h). This suggests that cation leaching continues as long as leaves are wet, and ion exchange sites contain leachable cations. Cations in general were not being removed from within cells. If cellular nutrient pools were the sources of ions in leachate solutions, leach rates should be constant over time until nutrient pools are depleted. The leaching treatments did not alter nutrient pool sizes by detectable amounts.

In order for cations to leach from within cells, they must move across the cell membrane, the cell wall, and finally

the cuticle. Well developed, undamaged plant cuticles are formidable barriers separating plant cells from the ambient environment. Cuticles are naturally hydrophobic and chemically resistant to degradation by strong acids (Martin and Juniper 1970; Berg 1985). Cations may move through cuticles, perhaps via pores (Schönherr 1976; McFarlane and Berry 1974), but the mechanism is poorly understood. In addition, the cuticle may become eroded or broken as it ages and eventually lose its effectiveness as a barrier.

It is not clear why more sulfate and nitrate were retained by leaves or were leached less from leaves in rain solutions of greater acidity. However, more sulfate and nitrate was available for retention in solutions of pH 3.0 since simulated rains were made by adding sulfuric and nitric acids to a stock solution of pH 4.3. It is possible that nitrate was assimilated and reduced by the excised leaves, or by microbes on leaf surfaces.

Ionic exchanges in the leaf-rain solution system do not balance (Table 5). Organic compounds not measured in these experiments may account for some charge imbalances. Acid/base reactions and reactions with dry deposits also would influence solution chemistry. Although an attempt was made to remove leaf surface deposits, it is likely that some remained. Some nutrient ions also may have originated in severed vasculature. These amounts, however, are likely to

be small due to the small ratio of severed vasculature area to total leaf area. Thus, proton exchange was probably not the only mechanism at work in the leaf-rain solution interaction. Cation losses from leaves probably involved H^+ exchange on cell walls and cuticular exchange sites, dissolution of material deposited on leaves, and direct washing from severed vasculature. The loss of anions from leaves probably involved dissolution of dry deposited material, and direct washing from severed vasculature.

The hydrogen ion exchange mechanism. The loss of nutrient cations from leaves via the H^+ exchange mechanism is of concern in light of increasing acidity in ambient precipitation (Likens and Butler 1981; Galloway 1984). High concentrations of protons in precipitation causing the loss of cations needed for cell metabolism, could lead to energy and productivity losses in trees. Leaves of both sites gave up protons to simulated rains of pH 5.6, the calculated pH of ambient rain in a non-polluted atmosphere. In simulated rains of pH 4.3, representative of ambient rains at both sites (Chapter 3, Table 6), leaves retained an average of 25 meq^{-1} of protons, thereby contributing to cation leaching from leaves. Proton exchange accounted for 30% of cations leached from leaves in pH 4.3 rain solutions, and 44% of cation losses in pH 3.0 solutions. These values are similar to measurements of H^+ displacement of cations from forest

canopies determined in ecosystem studies (Eaton et al. 1973; Hoffman et al. 1980; Richter et al. 1983). More research is needed to determine the potential for metabolically important ions to be lost from leaves. This is important since cation leaching, and Mg in particular, has been suggested as a possible cause of regional declines in forest health, and since the ionic strength of precipitation is, in part, defined by anthropogenic pollutant emissions.

References

- Anonymous. 1983. Methods of chemical analysis of water and wastes. Environmental Monitoring and Support Laboratory. Office of Research and Development. U. S. Environmental Protection Agency, Cincinnati, Ohio. 430 pp.
- Auchmoody, L. R. 1972. Nutrient properties of five West Virginia forest soils. USDA For. Serv. Res. Note NE-145. 4 pp.
- Auchmoody, L. R. and K. P. Hammack. 1975. Foliar nutrient variation in four species of upland oaks. USDA For. Ser. Res. Pap. NE-331. 16 pp.
- Barber, S. A. 1984. Soil Nutrient Availability: A Mechanistic Approach. John Wiley and Sons, New York. 398 pp.
- Berg, V. S. 1985. Plant cuticle as a barrier to acid rain penetration. In Proceedings of the Advanced NATO Research Workshop, Effects of Acidic Deposition on Forests, Wetlands, and Agricultural Ecosystems. Edited by T. C. Hutchinson. May 13-17, 1985, Toronto, Canada.
- Chevone, B. I., Y. S. Yang, W. E. Winner, I. Storcks-Cotter, and J. S. Long. 1984. A rainfall simulator for laboratory use in acidic precipitation studies. J. Air Pollut. Contr. Assoc. 31:355-359.
- Craker, L. E., and D. Bernstein. 1984. Buffering of acid rain by leaf tissue of selected crop plants. Environ. Pollut. 36:375-381.
- Cronan, C. S., and W. A. Reiners. 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. Oecologia 59:216-223.
- Eaton, J. S., G. E. Likens, and F. H. Bormann. 1973. Throughfall and stemflow chemistry in a northern hardwood forest. J. Ecol. 61:495-508.
- Epstein, E. 1972. Mineral Nutrition of Plants: Principles and Perspectives. John Wiley and Sons, New York. 412 pp.
- Galloway, J. N., G. E. Likens, and M. E. Hawley. 1984. Acid precipitation: Natural versus anthropogenic components. Science 226:829-831.
- Gathright, T. M., II. 1976. Geology of the Shenandoah National Park, Virginia. Dept. of Conservation and Economics Development, Division of Mineral Resources, Bull. #86, 93 pp.
- Hahn, J. T. and W. H. Carmean. 1982. Lake states site index curves formulated. USDA For. Serv. Gen. Tech. Rep. NC-88. 5 pp.
- Haines, B., J. Chapman, and C. D. Monk. 1985. Rates of mineral element leaching from leaves of nine plant species from a southern Appalachian forest succession subjected to simulated acid rain. Bull. Torrey Bot. Club 112:258-264.
- Huettl, R. F. 1986. Research methods and preliminary results in the Black Forest of Germany. In Proceedings of the

- Mid-South Symposium on Acid Deposition, April 20-21, 1986, Little Rock, Arkansas.
- Hoffman, W. A., Jr., S. E. Lindberg, and R. R. Turner. 1980. Precipitation acidity: the role of the forest canopy in acid exchange. *J. Environ. Qual.* 9:95-100.
- Likens, G. E., F. H. Bormann, and N. M. Johnson. 1981. Interactions between major biogeochemical cycles in terrestrial ecosystems. In *Some Perspectives of the Major Biogeochemical Cycles*. Edited by G. E. Likens. John Wiley and Sons, New York. pp. 93-112.
- Likens, G. E., and T. J. Butler. 1981. Recent acidification of precipitation in North America. *Atmos. Environ.* 15:1103-1109.
- Martin, J. T., and Juniper, B. E. 1970. *The Cuticles of Plants*. Edward Arnold Ltd. 347 pp.
- McFarlane, J. C., and W. L. Berry. 1974. Cation penetration through isolated leaf cuticles. *Plant Physiol.* 53:723-727.
- Mecklenburg, R. A., H. B. Tukey, Jr., and J. V. Morgan. 1966. A mechanism for the leaching of calcium from foliage. *Plant Physiol.* 41:610-613.
- Parker, G. G. 1983. Throughfall and stemflow in the forest nutrient cycle. *Adv. Ecol. Res.* 13:57-133.
- Patterson, D. T. 1975. Nutrient return in the stemflow and throughfall in individual trees in the piedmont deciduous forest. In *Mineral Cycling in Southeastern Ecosystems*. Edited by F. G. Howell, J. B. Gentry, and M. H. Smith. U.S. ERDA Symp. Ser. 36, Washington, D. C. pp. 800-812.
- Richter, D. D., D. W. Johnson, and D. E. Todd. 1983. Atmospheric sulfur deposition, neutralization, and ion leaching in two deciduous forest ecosystems. *J. Environ. Qual.* 12:263-270.
- Scherbatskoy, T., and R. M. Klein. 1983. Responses of spruce and birch foliage to leaching by acidic mist. *J. Environ. Qual.* 12:189-195.
- Schönherr, J. 1976. Water permeability of isolated cuticular membranes: the effect of pH and cations on diffusion, hydrodynamic permeability and size of polar pores in the cutin matrix. *Planta* 128:113-126.
- Skeffington, R. A., and T. M. Roberts. 1985. The effects of ozone and acid mist on Scots pine saplings. *Oecologia* 65:201-206.
- Tamm, C. O. 1951. Removal of plant nutrients from tree crowns by rain. *Physiol. Plant.* 4:184-188.
- Tukey, H. B., Jr. 1971. Leaching of Substances from Plants. In *Ecology of Leaf Surface Micro-organisms*. Edited by T. F. Preece and C. H. Dickinson. Academic Press, N.Y. pp. 67-80.
- Tukey, H. B. Jr. 1971. Leaching of substances from plants. In *Ecology of Leaf Surface Micro-organisms*. Edited by T. F. Preece and C. H. Dickinson. Academic Press, London.

- Tukey, H. B., Jr. 1980. Some effects of rain and mist on plants, with implications for acid precipitation. In Effects of Acid Precipitation on Terrestrial Ecosystems. Edited by T. C. Hutchinson and M. Havas. Plenum Press, N. Y. pp. 141-150.
- United States Department of Agriculture. 1980. Classification of Soil Series of the United States, Puerto Rico, and the Virgin Islands. USDA, Soil Conservation Service.
- United States Department of Agriculture. 1986. Soil Survey of Greene County, Virginia. USDA, Soil Conservation Service, Richmond, Virginia. In press.
- Wood, T., and Bormann, F. H. 1975. Increases in foliar leaching caused by acidification of an artificial mist. Ambio 4:169-171.
- Yawney, H. W. 1964. Oak site index on Belmont limestone soils in the Allegheny mountains of West Virginia. USDA For. Serv. Res. Pap. NE-30. 16 pp.

Throughfall chemistry beneath Quercus rubra L. crowns: atmospheric, foliar, and soil chemistry considerations.

Abstract

Concentrations of inorganic ions were measured in bulk rainfall and bulk throughfall collected beneath northern red oak (Quercus rubra L.) trees growing in fertile, limestone-derived soil and less fertile sandstone/shale-derived soil. Rainfall passing through the crowns at both sites was enriched with SO_4^{2-} , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , and Fe^{2+} , but lost NH_4^+ to the crowns. Concentrations of Na^+ and H^+ in incident rainfall were higher at the less fertile site. There was no difference in ionic leaching from red oak crown leaves exposed to simulated acid rain solutions three times during the rain collection period. Large-particle dryfall ionic concentrations, rainfall volume, and leaf area were all larger at the fertile rather than less fertile site. Concentrations of Ca^{2+} , Mg^{2+} , NH_4^+ , Mn^{2+} , and SO_4^{2-} measured in throughfall at the fertile site were higher than those of the less fertile site. These differences in throughfall chemistry are likely due to site differences in i) the ability of tree crowns to capture dry deposition, ii) dry deposition chemistry and occurrence, and iii) rainfall volume.

Introduction

The forest canopy is the initial point of contact between rain influenced by air pollutants and forest ecosystems. Although the chemical composition of throughfall differs from rainfall, the degree of change is variable. Throughfall from hardwood and coniferous forests is generally higher in potassium, calcium, and magnesium content, and may be higher or lower in nitrate and sulfate content than incident precipitation (Eaton et al. 1973; Killingbeck and Wali 1978; Cronan 1980; Cronan and Reiners 1983; Mollitor and Raynal 1983; Lindberg et al. 1986). Hardwood throughfall during the growing season usually has higher pH than rain, whereas conifer throughfall is generally more acidic than rain (Nihlgard 1970; Hart and Parent 1974; Ulrich 1979; Mollitor and Raynal 1983; Cronan and Reiners 1983). Incident rain falling on a leafless Quercus prinus canopy, however, had a higher pH than that of throughfall (Hoffman et al. 1980). Factors such as stand structure (Olson et al. 1981) and canopy structure (Reiners and Olson 1984; Olson et al. 1985) also influence throughfall chemistry.

Washing of large-particle dryfall and leaching of substances from leaves are probably the dominant processes in throughfall chemical enrichment (Parker 1983). Foliar absorption of nutrients in low supply (e.g. N) may also

occur. Foliar nutrient status has been increased with fertilizers and found to affect throughfall enrichment (Mahendrappa and Ogden 1973; Yawney et al. 1978; Khanna and Ulrich 1981). Other studies suggest that foliar nutrient status is a useful indicator of throughfall enhancement (Eaton et al. 1973; Henderson et al. 1977).

In this study, the influence of foliar nutrient status on inorganic ion concentrations of throughfall was examined. Northern red oak (Quercus rubra L.) growing on sites with either low or high soil fertility were used to test this relationship. Rainfall and throughfall at each site were collected and chemically analyzed. Northern red oak leaves were treated with simulated acid rain solutions to determine differences in ion leaching between sites. Thus, the study was designed to determine whether the capacity of soils to buffer acidic inputs is projected above the forest floor and into the forest canopy.

Materials and Methods

Study sites. Two forested sites were chosen on the basis of their different soil nutrient status. One site was located in the Shenandoah National Park (SNP), Greene Co., Va. (38° 21' North latitude, 78° 32' West longitude). Soils of the SNP are classified as either loamy-skeletal, mixed, mesic ruptic-alfic (Catoctin series), or loamy-skeletal, mixed, mesic typic (Parker series) dystrochrepts (USDA 1980, 1986).

These soils are derived from sandstone and shale parent material of the Swift Run and Pedlar geologic formations (Gathright 1976). The site supports an upland oak community including: northern red oak, chestnut oak (Quercus prinus L.), black oak (Q. velutina Lam.), white oak (Q. alba L.), yellow-poplar (Liriodendron tulipifera L.), eastern white pine (Pinus strobus L.), and pitch pine (P. rigida Mill.). The SNP site is on the WSW-facing side of a ridge with an average slope of 50%. Its mean elevation is 615 m, and it receives an average of 109 cm of precipitation annually. Northern red oak site index was calculated to be 16.4 m (base age 50 years) using age and height measurements, and a published site index equation (Hahn and Carmean 1982). Northern red oak occupies 12% of the total canopy area (Chapter 4, Table 9).

The second site was located in the Fernow Experimental Forest (FEF), Tucker Co., W. Va., (39° 3' North latitude, 79° 40' West longitude) on a fine-loamy, mixed, mesic typic hapludalf of the Belmont soil series (USDA 1980). This soil is derived from calcareous shale, sandstone, and limestone parent material (Auchmoody 1972). The FEF site supports northern hardwood forest species including: northern red oak, chestnut oak, yellow-poplar, sugar maple (Acer saccharum Marsh), red maple (A. rubrum L.), white ash (Fraxinus americana L.), black cherry (Prunus serotina

Ehrh.), and American beech (Fagus grandifolia Ehrh.). The site faces NNE, has an average slope of 30%, mean elevation is 725 m, and it receives 147 cm of mean annual precipitation. Northern red oak site index at base age 50 years is 25.9 m (Yawney 1964). Northern red oak accounts for 4% of the total canopy area (Chapter 4, Table 9).

Soil sampling method. Soil was sampled at the SNP beneath four eastern white pine and four northern red oak trees during the 1982 growing season. Samples of FEF soil were collected during the 1983 growing season beneath four black cherry and four northern red oak trees. All sample trees were dominant or codominant in the main tree canopy. A total of eight soil samples were collected from each site using a 2.5-cm punchtube. Soil was sampled to a depth of 20 cm. Soil samples were composited from four subsamples spaced equidistant around the base and between the bole and crown drip line of each sample tree. Prior to chemical analysis, soils were dried at room temperature and passed through a 2-mm screen.

Leaf collection and leaching methods. Northern red oak crown leaves were sampled from three codominant trees on each site, at three six-week intervals beginning on June 25, 1984. The same three trees on each site were used throughout the growing season, and were also the trees beneath which throughfall was collected. Trees were climbed, and

with the aid of a pole pruner, branches with leaves were removed from the lower to middle portions of the crown. Branches were kept in plastic bags, on ice, in an insulated cooler for no longer than 48 h while being transported to the laboratory. In the laboratory, branches were stored in a refrigerator for an additional 48-72 h prior to chemical analysis. Leaves remained on branches until just prior to experimental treatments to insure realistic conditions as much as possible. Leaf areas were measured with a Li Cor model Li-3000 portable leaf area meter.

Leaves from each site were exposed to simulated rain solutions of pH 3.0, 4.3, and 5.6 following the three harvests. Simulated rain solutions contained inorganic ions in proportions measured in rains occurring in Southwestern Virginia (Chevone et al. 1984). A stock rain solution of pH 4.3 was mixed to contain 1.00 ppm Ca^{2+} , 0.10 ppm Mg^{2+} , 0.55 ppm Na^{+} , 0.22 ppm K^{+} , 0.48 ppm NH_4^{+} , 0.46 ppm Cl^{-} , 2.70 ppm NO_3^{-} , 5.50 ppm SO_4^{2-} , and 0.01 ppm PO_4^{3-} . Solutions of pH 3.0 and 5.6 were attained by adjusting the acidity of the stock solution. Approximately 6 g of fresh leaves were placed in 17.8 x 20.3-cm clear, plastic-zippered bags containing 250 ml of simulated rain solution. Leaves were bisected along the midrib, and were blotted with paper towels to remove water and dry deposits from leaf surfaces (Chapter 2, pp.16-17). To determine the effect of the bag

on rain chemistry, simulated rain solutions of the three acidities were placed in bags without leaves. Following a two hour treatment period, leaves were removed from the bags and prepared for chemical analysis. Solution pH was measured before contact with leaves, and immediately after leaves were removed from the bags. Inorganic ion concentrations were measured in control and treatment rain solutions. In preparation for chemical analysis leaves were dried in an oven at 70° C for 24 h, and ground to pass a 1-mm screen.

Atmospheric deposition sampling methods. Bulk throughfall and rainfall were collected as weekly samples for 16 weeks beginning June 5 and ending September 25, 1984. Bulk rainfall and throughfall collectors consisted of a 20-cm diameter polyethylene funnel and a 250-ml polyethylene bottle connected by 75 cm of clear tygon tubing. Collectors were mounted 1.8 m above the ground on metal posts. Bulk rainfall collectors were placed in a clearing near each site. Bulk throughfall collectors were placed beneath three randomly selected northern red oak trees on each site. Glass wool, rinsed in deionized water to remove trace elements, was placed in the neck of each funnel to exclude contaminants. Each week the collectors were cleaned with deionized water and new glass wool was placed in the funnels.

Inorganic ion concentrations in SNP and FEF rainfall were compared to similar data of National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites near the FEF and SNP. Rainfall at the SNP, FEF, and NADP/NTN sites was collected during the same time period. The NADP/NTN sampler WV 18 is about 5 km from the FEF site; NADP/NTN sampler VA 28 is about 24 km from the SNP site. Large-particle dryfall data also were obtained from NADP/NTN sites WV 18 and VA 28. Dry bucket collectors are exposed to the atmosphere during periods of no precipitation for two months at a time. Data from NADP/NTN WV 18 were collected from May 17 to July 12, 1983. Data from NADP/NTN VA 28 were collected from July 12 to September 6, 1983. These data were the best available data corresponding to the approximate period of rain collection at the two sites.

Chemical analyses. A double acid extraction procedure was used to determine concentrations of P, K, Ca, Mg, Mn, Zn, and Al in soil. Soil extracts were analyzed by a Jarrell-Ash Model 955 Atom Comp argon plasma emission spectrometer. Total nitrogen was determined by the macro-Kjeldahl procedure. A glass pH electrode and reference electrode were used to determine soil pH in a continuously stirred 1:1 mixture of soil and deionized water. Percent organic matter in soil was determined by wet oxidation with potassium dichromate.

Nutrient element concentrations of leaves collected in June and August were analyzed by the Virginia Tech Soil Testing and Plant Analysis Laboratory, Blacksburg, Va. Concentrations of total Ca, Mg, Mn, Zn, Cu, and Fe were measured by atomic absorption spectrophotometry. Leaf total P and total B were determined colorimetrically, and total K was determined by flame photometry. Nutrient element concentrations of leaves harvested in September, were determined by a Jarrell-Ash Model 750 arc spark emission spectrograph, at the University of Georgia Soil Testing and Plant Analysis Laboratory, Athens, Ga. Both labs used a micro-Kjeldahl technique to measure leaf total N, and a Leco sulfur analyzer to measure leaf total S. There were no differences (t-tests, $P \leq 0.05$) in the chemical analyses of 10 duplicate samples sent to each lab.

Concentrations of total P, K, Ca, Mg, Mn, Zn, Fe, B, Mo, and Na, in rainfall and throughfall samples were determined by a Jarrell-Ash Model 955 Atom Comp argon plasma emission spectrograph. Concentrations of ammonium and nitrate (following reduction to ammonium) were determined by distillation of basic ammonium and titration to an end-point. Sulfate concentrations were determined by the turbidimetric method (Anonymous 1983) using a model 900-3 Klett-Summerson photoelectric colorimeter. Rainfall and throughfall pH were determined using a Beckman combination

pH electrode with a Ag/AgCl reference element. Electrical conductivity of rainfall and throughfall were measured using a Thomas Model 275 linear conductance/resistance meter.

Data analysis. Student's t-tests were used to compare nutrient element concentrations in soil surface horizons, rainfall samples, and NADP/NTN rainfall between sites. Concentrations of 11 nutrients in leaves were compared between sites using analysis of variance and a 2 (sites) x 3 (trees/site) factorial design. A one-way analysis of variance procedure was used to determine whether within each site chemical concentrations in rainfall differed from those in throughfall. Chemical concentrations in throughfall were compared between sites using nested analysis of covariance and a 2x3 factorial design. Rainfall chemical concentrations served as covariates on an ion by ion basis. All comparisons of rainfall and throughfall chemistry use data from weeks in which wet deposition occurred. No measurable rainfall occurred during weeks 1 and 14 at the SNP site or week 1 at the FEF site, thereby reducing sample sizes for statistical comparison to 14 and 15, respectively. When rainfall or throughfall samples overflowed collection bottles, the maximum volume of 510 ml was used to calculate volume-weighted means. Comparisons of rainfall and throughfall acidity were the same regardless of whether acidity was expressed as pH or meq^{-1} .

Results

Site characterization comparisons.

Surface soil chemistry, leaf nutrient status, leaf size, and atmospheric deposition chemistry were characterized at the SNP and FEF sites. These baseline data facilitated an examination of factors associated with northern red oak crowns which enable the alteration of rain chemistry.

Soil chemistry. The soil surface horizon of the FEF had greater concentrations of total N, extractable P, K, Ca, Mg, Mn, Zn, and greater percent organic matter than that of the SNP (Chapter 2, Table 2). Ratios (FEF:SNP) of concentrations were about 3:1 for total N, 12:1 for extractable Ca, 4:1 for extractable Mg, and 10:1 for extractable Mn. Concentrations of extractable P, K, Zn, and percent organic matter in soil were about 1.5 times greater at the FEF than SNP. Aluminum concentrations and soil solution pH of the two soils were not significantly different.

Northern red oak crowns. Chemical and physical characteristics of red oak crowns differed between the two sites. Concentrations of total N, P, K, Ca, Mn, and Zn were greater in FEF leaves than in SNP leaves (Chapter 2, Table 3). However, SNP leaves had higher concentrations of Mg than FEF leaves despite greater concentrations of extractable Mg in FEF soils. In addition, leaves of the FEF had greater concentrations of S, B, and Cu, but less Fe than leaves of

the SNP. Differences in N, K, Ca, Mg, B, and Mn concentrations of leaves between sites were significant ($P \leq 0.05$) at all three harvest times. During the same time FEF leaves (129 cm^2) were an average 20% larger than SNP leaves (107 cm^2)).

The magnitude and direction of nutrient ion exchange were similar between red oak leaves with high (FEF) and low (SNP) nutrient element concentrations when exposed to simulated rain solutions of pH 4.3 (Table 6). Similar results occurred when leaves were treated with simulated rain solutions of pH 5.6 and 3.0.

Rain chemistry. Average concentrations of Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , PO_4^{3-} , $\text{B}(\text{OH})_4^-$, Zn^{2+} , Mn^{2+} , Fe^{2+} , MoO_4^- , and electrical conductivity measured in rainfall were not significantly different between the FEF and SNP sites (Table 7). The average concentration of Na^+ in rain at SNP was more than twice that of rain at FEF ($P < 0.05$). Rainfall pH at the FEF (pH 4.69) was lower than that of the SNP (pH 5.57). Potassium concentrations were nearly 6 times greater ($P \leq 0.05$) and NH_4^+ was nearly 3 times greater ($P \leq 0.05$) in rain collected at NADP/NTN sampler VA 28 (SNP) compared to NADP/NTN WV 18 (FEF) (Table 8). The acidity of rainfall was greater ($P \leq 0.05$) at the FEF than the SNP (Table 8).

Dry deposition. Substantial differences in large-particle dryfall ion concentrations were apparent between NADP/NTN

Table 6. Exchange of eight nutrient ions (meq m⁻² leaf area) between simulated rain solutions of pH 4.3 and northern red oak leaves harvested three times during the 1984 growing season at the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va.

Nutrient Variable	June 25-26		August 6-7		Sept. 26-27	
	SNP	FEF	SNP	FEF	SNP	FEF
Ca ²⁺	-0.10	-0.05	0.02	0.02	0.16	0.07
Mg ²⁺	0.02	0.01	0.03	0.01	0.08	0.02
K ⁺	0.57	0.82	0.17	0.23	0.42	0.40
NH ₄ ⁺	0.00	0.04	-0.15	-0.06	-0.07	-0.04
Mn ²⁺	0.00	0.00	0.00	0.01	0.02	0.01
PO ₄ ³⁻	0.01	0.11	0.10	0.06	0.04	0.04
SO ₄ ²⁻	0.15	0.10	0.02	0.05	-0.02	-0.04
NO ₃ ⁻	-0.40	-0.34	0.00	0.16	0.00	0.00

NOTE: Positive values indicate ions leached from leaves, negative values indicate ions retained by leaves. Site differences were all non-significant (F-tests, $P \leq 0.05$).

Table 7. Average weekly chemistry of rainfall (RF) and throughfall (TF) at the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va. from June 12 to September 25, 1984.

	Bulk rainfall			RF vs TF		Bulk throughfall			
	SNP	FEF		SNP	FEF	SNP	FEF		
	ppm								
Ca ²⁺	0.65	0.74	ns ^a	*	*	1.12 (1.04) ^b	1.39	(1.44)	**
Mg ²⁺	0.18	0.13	ns	*	*	0.28 (0.31)	0.33	(0.30)	**
K ⁺	0.51	0.20	ns	*	*	2.53 (2.46)	3.30	(3.39)	ns
Na ⁺	1.47	0.62	*	ns	ns	1.02 (1.31)	1.17	(1.27)	ns
NH ₄ ⁺	0.73	0.48	ns	ns	ns	0.40 (0.39)	0.46	(0.46)	*
Zn ²⁺	0.05	0.03	ns	ns	ns	0.04 (0.04)	0.03	(0.03)	ns
Mn ²⁺	0.00	0.01	ns	*	*	0.06 (0.05)	0.10	(0.11)	**
Fe ²⁺	0.01	0.01	ns	*	*	0.02 (0.02)	0.02	(0.02)	ns
PO ₄ ³⁻	0.09	0.06	ns	ns	*	0.15 (0.15)	0.18	(0.18)	ns
SO ₄ ²⁻	4.09	4.19	ns	ns	*	4.36 (4.13)	6.79	(6.83)	**
NO ₃ ⁻	0.32	0.44	ns	ns	ns	0.42 (0.36)	0.39	(0.44)	ns
B(OH) ₄ ⁻	0.73	0.58	ns	ns	ns	0.66 (0.66)	0.80	(0.73)	*
MoO ₄ ⁻	0.03	0.02	ns	*	*	0.02 (0.02)	0.00	(0.00)	ns
	-log[H ⁺]								
pH	5.57	4.69	**	ns	*	5.21 (5.46)	5.30	(5.07)	ns
	μhos/cm								
Cond	28.1	32.3	ns	ns	ns	29.7 (28.6)	34.7	(35.8)	*

a. Variable means were compared by F-tests; ns indicates no site difference; * and ** indicate site differences at $P \leq 0.05$ and $P \leq 0.01$, respectively.

b. Analysis of covariance (ANCOVA) means, the ANCOVA procedure used the natural log of adjusted means. Values in parentheses are non-ANCOVA, volume-weighted mean concentrations among three replicate samplers.

Table 8. A comparison of rainfall and large-particle dryfall chemistry collected at NADP/NTN sites near the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va. sites.

Chemical variable	Rainfall		Dryfall	
	SNP	FEF	SNP	FEF
		ppm		
Ca ²⁺	0.38	0.29 ns ^a	1.04	8.24
Mg ²⁺	0.10	0.06 ns	0.24	0.64
K ⁺	0.23	0.04 *	0.64	1.60
Na ⁺	0.15	0.08 ns	0.08	0.40
NH ₄ ⁺	1.03	0.37 *	1.04	0.48
NO ₃ ⁻	1.95	2.34 ns	0.64	4.24
Cl ₂	0.35	0.19 ns	0.08	0.48
SO ₄ ²⁻	5.48	4.82 ns	7.84	19.12
PO ₄ ³⁻	0.11	0.00 ns	1.04	0.00
		-log[H ⁺]		
pH(lab)	4.26	4.02 *	4.77	6.81
		μhos/cm		
Cond	39.45	47.57 ns	29.12	64.48

a. Significant site differences (Student's t-tests, $P \leq 0.05$) are indicated by *, ns indicates no site difference.

NOTE: NADP/NTN rainfall was collected from June 5 to September 25, 1984. Dryfall was collected at the SNP from July 12 to September 6, 1983, and at the FEF from May 17 to July 12, 1983. Dryfall concentrations were determined by standard NADP/NTN techniques.

sites (Table 8). The data were not sufficient, however, to test differences between the SNP and FEF. Data coinciding with the time period of our study were not available. The data are indicative of large-particle dryfall ion concentrations at both sites. All cation and anion concentrations, except NH_4^+ and PO_4^{3-} , were larger at the FEF site than at the SNP site. Ion concentration ratios (FEF:SNP) of large-particle dry deposition ranged from 2.5:1 for sulfate to nearly 8:1 for calcium.

Site process comparisons.

Rainfall to throughfall transformation. Higher concentrations of Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , and Fe^{2+} were measured in throughfall than in rainfall at SNP (Table 7). Throughfall at the FEF had greater concentrations of Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , Fe^{2+} , SO_4^{2-} , and PO_4^{3-} than rainfall. Concentrations of MoO_4^- were higher in rainfall than in throughfall at the SNP and FEF. The pH of bulk throughfall (pH 5.30) was higher than that of rainfall (pH 4.69) at the FEF. There was no statistical difference in pH (or meq^{-1}L of H^+) between throughfall (pH 5.21) and bulk rainfall (pH 5.57) at SNP. These data indicate that acid buffering may be occurring at leaf surfaces (Chapter 1, p.3). There were no significant differences in electrical conductivity and concentrations of NH_4^+ , Na^+ , Zn^{2+} , NO_3^- , and B(OH)_4^- between rainfall and throughfall at both sites, or SO_4^{2-} and PO_4^{3-} at the SNP.

Throughfall chemistry. Differences in throughfall chemistry exist between the two sites. Data for each chemical variable were tested for normality and were found to be skewed. Natural log transformations of chemical variable data resulted in normal distributions. All of the chemical variables measured in rainfall served as significant covariates in the analysis of throughfall for transformed data. These analyses indicated significantly greater concentrations of Ca^{2+} , Mg^{2+} , Mn^{2+} , NH_4^+ , SO_4^{2-} , $\text{B}(\text{OH})_4^-$, and electrical conductivity in FEF throughfall than SNP throughfall (Table 7). There was 30% more K^+ in FEF throughfall than SNP throughfall, but this difference was not statistically significant due to high variability in the data. There was no significant difference in pH between sites.

Ternary plot analysis. Ratios of Ca:Mg:K concentrations, on a meq L^{-1} basis, were calculated for throughfall and the factors analyzed in this study which might affect throughfall chemistry. The ratios (SNP, FEF) are as follows: 1) rainfall (54:24:22, 70:20:10), 2) throughfall (37:18:45, 39:14:47), 3) NADP/NTN rainfall (45:23:32, 71:24:5), 4) NADP/NTN large-particle dryfall (60:22:18, 81:11:8), 5) foliage (44:20:36, 47:13:40), 6) surface horizon soil (29:24:47, 68:18:14), and 7) leachate (28:15:57, 25:6:69) resulting from treating leaves with simulated acid rain

solutions of pH 4.3. Plots of the Ca:Mg:K ratios (Fig. 2) show calcium decreasing, potassium increasing, and magnesium differing slightly from atmospheric variables to throughfall and leaf leachate. Ratios for northern red oak foliage at both sites fall between atmospheric variables, and throughfall and leaf leachate.

Discussion

There are three possible sources of chemical input at each site that could account for the difference in throughfall chemistry between the SNP and FEF. First, the chemistry of rain falling on the two sites could be different. Second, amounts of leachable nutrients and metabolites within canopy leaves could be different. Lastly, there could be differences in amounts and composition of dry material deposited onto the canopy from local and regional sources. Data that characterized the sites were important in determining which factors contributed to differences in throughfall chemistry between sites.

Site characterization.

Atmospheric, soil, and foliar chemistry. Average chemistry of bulk rainfall was similar for the SNP and FEF with the exception of Na^+ concentrations and pH (Table 7). Differences in pH between the FEF (4.69, 20 meq) and the SNP (5.57, 3 meq) are small in terms of chemical milliequivalents. Analyses of these rainfall data and NADP/NTN

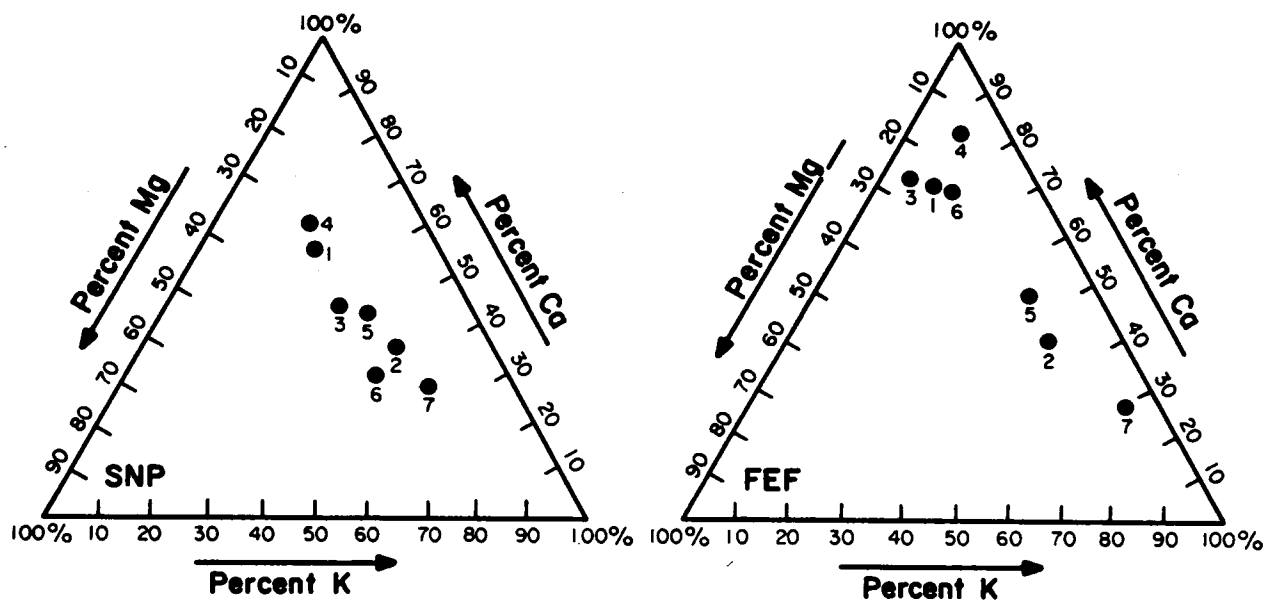


FIG 2. A comparison of the relative amount of Ca^{2+} , Mg^{2+} , and K^+ on a meq L^{-1} basis in: (1) rainfall; (2) throughfall; (3) NADP/NTN rainfall; (4) NADP/NTN large-particle dryfall; (5) foliage; (6) surface horizon soil; (7) and leaf leachate resulting from treating leaves with simulated acid rain solutions of pH 4.3 at the Shenandoah National Park (SNP), Greene Co., Va. and the Fernow Experimental Forest (FEF), Tucker Co., W. Va. sites. Coordinates of each point are determined by percent Ca, Mg, K in the sample. Percentages are determined for a given element by moving away from a point toward the axis of the desired element on a line paralleling the axis immediately clockwise to the axis of the desired element. For example, the percent K content of leachate (point 7) at the SNP is found to be 57% by moving toward the percent K axis in a line paralleling the percent Mg axis.

data both indicate few statistical differences between the SNP and FEF. Large-particle dryfall is different between sites as indicated by NADP/NTN data.

Soil fertility and site productivity are greater at the FEF due to differences in the chemical nature of soil parent material, and amounts of rainfall occurring at each site. Long-term records show that FEF receives 26% more average annual precipitation than the SNP. This would tend to increase weathering and depth of soil at the FEF. Higher clay and organic matter content in the FEF soil suggest a higher cation exchange capacity than at SNP. Greater total N in FEF indicates that biological turnover of N, and mineralization rates of nutrients in general, may be greater at the FEF.

Soil fertility was reflected above the forest floor in northern red oak leaf nutrient concentrations. Leaves from the fertile (FEF) site had higher nutrient element concentrations throughout the growing season than leaves from the less fertile (SNP) site, with the exception of Mg (Chapter 2, Table 3). Low levels of Mg^{2+} in FEF leaves may be due to a high extractable calcium to extractable magnesium ratio (6.3:1) in FEF soil. The Ca/Mg ratio of FEF soils was similar to that of leaves (6.0:1) over the growing season. The Ca/Mg ratio was 2.0:1 in SNP soil and 3.6:1 in SNP leaves. Levels of extractable Ca^{2+} in soil, that are

high relative to extractable Mg^{2+} levels, are known to inhibit the absorption of extractable Mg^{2+} by plant roots (Epstein 1972; Barber 1984). The absence of between-site differences in nutrient losses from leaves (Table 6), with the exception of Mg, despite large differences in leaf nutrient concentrations (Chapter 2, Table 3) suggests that leaf surfaces remained impermeable to simulated rain solutions. Differences in leaf nutrient concentrations may be due to nutrients in the tissue not being readily subject to leaching.

It appears that Mg leaching is related to Mg concentrations in leaves, but it is not clear why Mg, and none of the other ions, respond this way. One hypothesis is that the amount of available Mg was greater in SNP leaves even though total Mg concentrations were greater in FEF leaves. Preconditioning of leaf cation availability by ambient rain prior to harvesting leaves does not explain this phenomenon either since cations were leached in the same manner regardless of prior ambient rain conditions (Chapter 2, p.35).

Site processes.

Throughfall comparisons between sites. Rainfall was enriched chemically at both sites. This enrichment is likely due to contributions from cation leaching and washing of dryfall from leaf surfaces. Plots of Ca:Mg:K concentra-

tion ratios (Fig. 2) show Ca^{2+} concentrations decreasing, K^+ concentrations increasing, and Mg^{2+} concentrations varying slightly from atmospheric sources to throughfall and leachate. This implies that potassium in throughfall is primarily of foliar origin, calcium is primarily of atmospheric origin, while magnesium may originate from both of these sources. The importance of foliar Ca^{2+} and Mg^{2+} leaching must not be ignored since Ca:Mg:K ratios in throughfall are most similar to foliar ratios. The Ca:Mg:K ratio of foliage at both sites falls between those of atmospheric variables, and throughfall and leachate. This indicates that tree crowns play a role in combining internal and external chemical sources in altering precipitation chemistry.

Throughfall nutrient content differences between sites (Table 7), in the absence of between site leaf leaching losses, except Mg (Table 6), suggest a leaf surface phenomenon. Leaf surfaces were preconditioned in different ways at each site prior to individual rain events. First, the sequence of rain events was different between sites (Chapter 2, p.35). Secondly, the amount (Table 8) and occurrence of dry deposition at each site is likely to have been different before each rain event. This suggests the important role of leaf surface deposits in altering rain chemistry.

The relationship of soil nutrient content to leaf nutrient content is not apparent in these cation ratios, particularly for the FEF site. Similar foliar Ca:Mg:K ratios for the sites indicate that major cation apportionment within leaves may be genetically, and physiologically based even though absolute concentrations may be site dependent.

Rainfall chemistry is similar at the SNP and FEF (Tables 7 and 8). Where differences do occur (e.g. K^+ and NH_4^+ , Table 8), they are not evident in throughfall chemistry (Table 7). Thus, wet deposition is not likely to cause the differences in throughfall chemistry between the SNP and FEF. Differences in leaf nutrient concentrations (Table 3), caused no difference in the chemical alteration of simulated acid rain solutions (Table 6). Although foliar leaching of nutrients and metabolites at the SNP and FEF contribute to the chemical alteration of rainfall, they are not likely to cause differences in inorganic ion concentrations measured in throughfall. Large-particle dryfall data (Table 8) indicate that the concentrations of Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , and SO_4^{2-} deposited dry onto the FEF crowns is greater than that of SNP crowns. Although large-particle dryfall is only a small part of total dryfall (Lindberg et al. 1986; Parker 1983), the data suggest a reason for the difference in chemical enrichment of rainfall between the two sites.

The physical nature of tree crowns can play a role in

determining the chemical content of throughfall (Reiners and Olson 1984; Olson et al. 1985). The average area of green leaves used in this experiment was 20% greater at the FEF than SNP. Larger leaves at the FEF would provide a larger surface area for capturing dryfall. In addition, greater rainfall (26%) at the FEF would affect greater leaching of chemicals from leaves, since leaves need only to be wet in order for leaching to occur (Tukey 1971). Thus, differences in the ability of northern red oak crowns to capture dryfall, differences in rainfall volume, and differences in dryfall chemistry may account for differences in throughfall chemistry.

Ternary plot analysis was used to determine factors influencing throughfall chemistry of coniferous and hardwood forests in New England. Cronan and Reiners (1983) compared the Ca^{2+} , Mg^{2+} , and K^+ chemical equivalent ratios of rainfall, throughfall, dry aerosols, and foliage. They concluded that major cation enrichment in throughfall did not originate from salts contained in wet or dry deposition. Throughfall enrichment resulted from "foliar leaching or a combination of extreme foliar potassium leaching plus canopy washout of aerosols rich in magnesium and calcium". The Ca:Mg:K equivalent ratio of throughfall from their two forests was 37:15:48. Throughfall collected beneath northern red oaks at the FEF and SNP sites had a ratio of

38:16:46. This similarity in ratios suggests that processes altering the chemistry of rain falling on forests of the northeastern and western Mid-Atlantic regions of the country may be the same.

References

- Anonymous. 1983. Methods of chemical analysis of water and wastes. Environmental Monitoring and Support Laboratory. Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio. 430 pp.
- Auchmoody, L. R. 1972. Nutrient properties of five West Virginia forest soils. USDA For. Ser. Res. Note NE-145. 4 pp.
- Barber, S. A. 1984. Soil Nutrient Availability: A Mechanistic Approach. John Wiley and Sons, New York. 398 pp.
- Chevone, B. I., Y. S. Yang, W. E. Winner, I. Storks-Cotter, and J. S. Long. 1984. A rainfall simulator for laboratory use in acidic precipitation studies. J. Air Pollut. Contr. Assoc. 31:355-359.
- Cronan, C. S. 1980. Solution chemistry of a New Hampshire subalpine ecosystem: a biogeochemical analysis. Oikos 34:272-281.
- Cronan, C. S., and W. A. Reiners. 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. Oecologia 59:216-223.
- Eaton, J. S., G. E. Likens, and F. H. Bormann. 1973. Throughfall and stemflow chemistry in a northern hardwood forest. J. Ecol. 61:495-508.
- Epstein, E. 1972. Mineral Nutrition of Plants: Principles and Perspectives. John Wiley and Sons, New York. 412 pp.
- Gathright, T. M., II. 1976. Geology of the Shenandoah National Park, Virginia. Dept. of Conservation and Economic Development, Division of Mineral Resources, Bull. #86, 93 pp.
- Hahn, J. T., and W. H. Carmean. 1982. Lake states site index curves formulated. USDA Forest Serv. Gen. Tech. Rep. NC-88. 5 pp.
- Hart, G. E., and D. R. Parent. 1974. Chemistry and throughfall under douglas fir and rocky mountain juniper. Am. Midl. Nat. 92:191-201.
- Henderson, G. S., Harris, W. F., Todd, D. E., Jr. and Grizzard, T. 1977. Quality and chemistry of throughfall as influenced by forest type and season. J. Ecology 65:365-374.
- Hoffman, W. A., Jr. S. E. Lindberg, and R. R. Turner. 1980. Precipitation acidity: the role of the forest canopy in acid exchange. J. Environ. Qual. 9:95-100.
- Khanna, P. K. and B. Ulrich. 1981. Changes in the chemistry of throughfall under stands of beech (*Fagus sylvatica*) and spruce (*Picea abies*) following the addition of fertilizers. Acta Oecol. Plant 2:155-164.
- Killingbeck, K. T., and M. K. Wali. 1978. Analysis of a North Dakota gallery forest: nutrient, trace element and productivity relations. Oikos 30:29-60.

- Lindberg, S. E., G. M. Lovett, D. D. Richter, and D. W. Johnson. 1985. Atmospheric deposition and canopy interaction of major ions in a forest. *Science* 231:141-145.
- Mahendrappa, M. K. and E. O. Ogden. 1973. Effects of fertilization of a Black Spruce stand on nitrogen contents of stemflow, throughfall, and litterfall. *Can. J. For. Res.* 3:54-60.
- Mollitor, A. W., and D. J. Raynal. 1983. Atmospheric deposition and ionic input in Adirondack soils. *J. Air Pollut. Control Assn.* 33:1032-1035.
- Nihlgard, B. 1970. Precipitation, its chemical composition and effect on soil in a beech and spruce forest in south Sweden. *Oikos* 21:208-217.
- Olson, R. K., W. A. Reiners, C. S. Cronan, and G. E. Lang. 1981. The chemistry and flux of throughfall and stemflow in subalpine balsam fir forests. *Holarctic Ecology* 4:291-300.
- Olson, R. K., W. A. Reiners, and G. M. Lovett. 1985. Trajectory analysis of forest canopy effects on chemical flux in throughfall. *Biogeochemistry* 1:361-373.
- Parker, G. G. 1983. Throughfall and stemflow in the forest nutrient cycle. *Adv. Ecol. Res.* 13:57-133.
- Pritchett, W. L. 1979. *Properties and Management of Forest Soils*. John Wiley and Sons, New York. 500 pp.
- Reiners, W. A. and R. K. Olson. 1984. Effects of canopy components on throughfall chemistry: An experimental approach. *Oecologia* 63:320-330.
- Tukey, H. B., Jr. 1971. Leaching of substances from plants. In Ecology of Leaf Surface Micro-organisms. Edited by T. F. Preece and C. H. Dickinson. Academic Press, N.Y.
- Ulrich, B., R. Mayer, and P. K. Khanna. 1979. Deposition von luftverunreinigungen und ihre auswirkungen in waldokosystemen des Sollings. *Schriften Forstl. Fak. Univ. Gottingen u. Nds. Forstl. Vers. Anst., Bd. 58.* 291 pp.
- United States Department of Agriculture. 1980. Classification of Soil Series of the United States, Puerto Rico, and the Virgin Islands. USDA, Soil Conservation Service.
- United States Department of Agriculture. 1986. Soil Survey of Greene County, Virginia. USDA, Soil Conservation Service, Richmond, Virginia. In press.
- Yawney, H. W. 1964. Oak site index on Belmont limestone soils in the Allegheny mountains of West Virginia. USDA For. Serv. Res. Pap. NE-30. 16 pp.
- Yawney, H. W., A. L. Leaf, and R. E. Leonard. 1978. Nutrient content of throughfall and stemflow in fertilized and irrigated Pinus resinosa Ait. stands. *Plant Soil* 50:433-445.

Estimates of tree crown areal histories by tree ring analysis: use in throughfall studies.

Abstract

Northern red oak crown areas were estimated for two forested sites by a two step procedure using annual growth ring chronologies and published regression equations. These equations related total crown area to total crown dry weight. The usefulness of crown area estimates in throughfall studies was demonstrated by applying nutrient ion exchange data, collected beneath northern red oak crowns in 1984 to 1982 and 1930 crown area estimates. Smaller nutrient ion exchange estimates in 1930 were due to smaller crown area estimates. Application of these techniques for estimating historical ion exchange chemistry in forest canopies would require modifications to increase accuracy. Other factors affecting the validity of this approach are discussed.

Introduction

Chemical enhancement of throughfall can involve a number of physical processes and chemical sources in addition to substances removed from the atmosphere by rain. These sources include organic and inorganic substances leached from within leaves (Mecklenburg et al. 1966, Tukey 1971, 1980), and dry deposited gases, aerosols and particulates washed from leaf surfaces (Fowler 1980, Miller and Miller 1980, Lindberg et al. 1986). Canopy nutrient status (Mahendrappa and Ogden 1973; Yawney et al. 1978; and Khanna and Ulrich 1981), stand structure (Olson et al. 1981) and canopy structure (Reiners and Olson 1984, Olson et al. 1985) also influence throughfall chemistry. Parker (1983) reviewed numerous studies indicating the influence of canopy area, leaf densities and canopy roughness in capturing dry deposition between rain events. The influence from overlapping canopies of neighboring trees may also be an important factor. These variables combine in the forest canopy to produce specific throughfall chemistries. However, there is no direct way of knowing how these processes may have changed as atmospheric chemistry changed in the past several decades.

This paper describes a method for estimating chemical exchanges between rainfall and tree crowns in the recent and distant past. The method uses dendroecology techniques, the

relationship between stem diameter and tree crown variables, and recent throughfall chemistry data. Dendroecology techniques have been used to correlate trends in tree growth ring widths to trends in climatic variables (Fritts 1966, 1976; Fritts et al. 1971, DuVick and Blasing 1981), and trends in regional-scale air quality variables (McLaughlin et al. 1983). Tree crown variables (e.g. total leaf dry weight and total leaf area) are directly related to annual increment cross sectional area, and therefore diameter at breast height, in any given year. Regression equations have been developed to express this relationship for coniferous and deciduous species (Whittaker and Woodwell 1967; Telfer 1969; Waring et al. 1977; Rogers and Hinckley 1979; Kaufmann and Troendle 1981; Jurik et al. 1985; Blanche and Hodges 1985). Measurements of annual growth rings can provide a means of estimating tree crown area chronologies.

Ion exchange data from tree crowns applied to chronological estimates of crown area provide estimates of ion exchange in crowns of individual trees for years when ion exchange was not measured. Specific objectives were to: 1) estimate total crown leaf areas of selected northern red oak (Quercus rubra L.) trees from 1930 to 1982 using growth ring widths, and 2) give an example of how crown area estimates could be used to estimate past ion exchange chemistry.

Materials and Methods

Site characteristics. Two forested sites containing northern red oaks in the main tree canopies were used in this study. One of the sites was located in the Shenandoah National Park (SNP), Greene Co., Va. ($38^{\circ} 21'$ North latitude, $78^{\circ} 32'$ West longitude). The SNP site has a mean elevation of 615 m and is on the WSW-facing side of a ridge with an average slope of 50%. It receives an average of 109 cm of precipitation annually. Northern red oak site index was calculated to be 16.4 m (base age 50 years) using a published equation (Hahn and Carmean 1982). Northern red oak occupies 12% of the total canopy area. The second site is located in the Fernow Experimental Forest (FEF), Tucker Co., W. Va. ($39^{\circ} 3'$ North latitude, $79^{\circ} 40'$ West longitude). This site has an average elevation of 725 m, faces NNE, and has an average 30% slope. It receives 147 cm of mean annual precipitation. Northern red oak site index (base age 50 years) is 25.6 m (Yawney 1964). Northern red oak accounts for 4% of the total canopy area.

The two sites were characterized further by measuring basal areas, and estimating total foliar dry weights and leaf areas of overstory and understory species. Basal areas were measured by point sampling techniques (Avery and Burkhardt 1983) at 90 points per site using a 2.5 m² b.a.f. optical prism. Point locations were chosen at random.

Forest canopy characterization. Leaves were collected in litterfall traps during the fall of 1983. Leaf traps were made of redwood, and were 75 cm square and 10 cm deep. Tops of the traps had beveled edges, and bottoms were fitted with fiber glass screening to allow moisture to pass through. Traps were spaced every 30 m at the SNP and every 40 m at the FEF on transects extending through the longest dimension of each site. Traps were placed at both sites on October 1 prior to leaf fall, and were emptied on October 8, 21, and November 5, and 18 at the SNP; and October 8, 14, 21, 28 and November 4 at the FEF. Leaf fall was complete by the last collection date at each site.

In the laboratory, leaves were placed in paper bags, air-dried, separated and weighed according to species. Leaves were remoistened in order to measure foliar areas of each species, on each collection date, at each site. Leaf areas were measured using a Li-Cor Model Li-3000 portable leaf area meter.

Increment core collection and measurement. An increment borer (25.4 cm bit) was used to extract growth ring increment cores from 15 healthy, codominant northern red oaks at the SNP and FEF. Two increment cores were removed from opposite sides of each tree at d.b.h. on an axis perpendicular to the slope of the terrain. Cores were placed in plastic soda straws for transport to the labora-

tory. Cores were collected at the SNP during September 1982, and from the FEF during May 1983.

In the laboratory, the two cores from each sample tree were glued into grooves cut in a block of wood. Cores were then sanded to a point where growth ring increments could be delineated clearly. Chronologies of the two cores were cross dated (Fritts 1976, Stokes and Smiley 1968). This insures that annual increments measured in each pair of cores correspond to each other and to the actual year in which they were produced. Growth ring increments for the period 1930 to 1982 were measured to the nearest 0.01 mm using an ADDO Tree-Ring Measuring Machine, Model 2. Annual increment measurement error for cores collected at both sites was found to be less than ± 0.05 mm.

Crown leaf area estimates. A two step procedure was used to estimate red oak crown annual leaf areas from 1930 to 1982. First, tree diameters were calculated for each year and used in a regression equation to estimate total crown foliar dry weights. Foliar dry weight estimates were then used to estimate total crown leaf areas. This was done using regression equations developed for each site from dry weight and area measurements of northern red oak leaves.

Diameter at breast height was measured to the nearest 1.0 mm for each sample red oak. A time series of outside bark diameters was calculated by subtracting the width of

successive annual increments from the previous diameter increment beginning with 1982 and ending in 1990. Annual changes in bark thickness were accounted for by assuming bark growth to be 10% of wood growth. No attempt was made to account for loss of bark thickness due to sloughing. A time series of total crown foliar dry weights for sample red oaks at each site was generated using a published regression equation (Loomis and Blank 1981). This equation correlated ($r^2 = 0.96$) crown foliage weights and d.b.h. measurements of northern red oaks in Michigan and Pennsylvania. Fifty-six vigorous, dominant or codominant trees representing a wide range of diameter classes and live crown ratios were used for the analysis.

Nutrient ion exchange data. Bulk rainfall and bulk throughfall were collected weekly at the SNP and FEF for 16 weeks from June 5 through September 25, 1984. Bulk rainfall samplers were located in open areas, bulk throughfall samplers were randomly located beneath three northern red oaks. The volumes of the weekly rainfall and throughfall samples were measured in order to determine ion deposition (kg ha^{-1}). When rainfall or throughfall samples overflowed collector bottles, the maximum volume of 510 ml was used to calculate deposition. Concentrations of total P, K, Ca, Mg, and Na were determined by a Jarrell-Ash Model 955 Atom Comp argon plasma emission spectrograph. Concentrations of

ammonium and nitrate (following reduction to ammonium) were determined by distillation of basic ammonium and titration to an endpoint. Sulfate was determined by the turbidimetric method (Anonymous 1983) using a model 900-3 Klett-Summerson photoelectric colorimeter. Proton concentrations were measured as pH using a Beckman combination pH electrode with a Ag/AgCl reference element.

Ion exchanges were determined to be the difference in average chemical deposition of bulk throughfall and bulk rainfall. Ion exchanges by northern red oak crowns were estimated for 1982 and 1930 by equating 1982 total crown areas with ion exchange chemistry measured in 1984, and proportionally estimating 1930 ion exchange chemistry. This method makes some gross assumptions concerning the similarity of crown areas, and chemical and physical properties of the crowns between 1930 and 1984. But, it emphasizes the dynamic nature of crown area and ion exchange chemistry estimates between 1930 and 1982.

Results

Forest canopy characteristics. Leaf area totals determined from leaf fall for all species were $66.7 \times 10^3 \text{ m}^2 \text{ ha}^{-1}$ at the SNP, and $48.8 \times 10^3 \text{ m}^2 \text{ ha}^{-1}$ at the FEF (Table 9). Total basal area was $27.8 \text{ m}^2 \text{ ha}^{-1}$ at the SNP, and $38.8 \text{ m}^2 \text{ ha}^{-1}$ at the FEF. Chestnut oak (Quercus prinus L.), northern red oak, and yellow-poplar (Liriodendron tulipifera L.) com-

Table 9. Forest canopy size and species composition as percent of total canopy area, and percent of total canopy mass for species of leaves collected in litterfall traps, and percent of total basal area at the Shenandoah National Park (SNP), Greene Co., Va., and Fernow Experimental Forest (FEF), Tucker Co., W. Va. sites.

	Leaf areas		Dry weights		Basal areas	
	SNP	FEF	SNP	FEF	SNP	FEF
	m ² /ha		kg/ha		m ² /ha	
Totals	66,675	48,836	4,997	2,576	27.75	38.78
			% of total			
Q. r.	12.20	4.23	13.99	7.18	10.41	7.09
Q. c.	1.48	-	2.00	-	0.50	-
Q. a.	7.30	-	8.20	-	5.62	-
Q. p.	48.12	-	51.03	-	35.14	-
Q. v.	2.85	-	2.54	-	7.10	-
P. spp.	-	-	-	-	8.90	-
L. t.	12.12	31.60	10.36	31.21	8.00	28.86
P. s.	0.40	3.68	0.32	3.88	0.29	8.74
F. g.	-	13.81	-	10.79	-	15.68
A. s.	0.35	20.57	0.26	20.15	0.40	15.63
A. r.	1.59	4.33	1.02	4.50	2.49	3.95
F. a.	4.73	4.65	2.58	5.86	1.91	7.89
T. a.	-	1.45	-	1.63	0.40	3.14
P. o.	0.63	3.11	1.78	4.66	0.50	-
C. f.	3.40	1.94	2.04	0.36	3.50	-
A. p.	0.08	2.53	0.04	2.06	0.11	-
C. spp.	3.77	1.89	2.94	2.52	5.01	2.86
Misc.	0.98	6.21	0.90	5.20	-	-
S. a.	-	-	-	-	2.70	-
N. s.	-	-	-	-	4.60	-
B. l.	-	-	-	-	0.11	1.93
U. spp.	-	-	-	-	0.11	0.72
B. a.	-	-	-	-	-	3.35
R. p.	-	-	-	-	2.20	0.16
Totals	100.00	100.00	100.00	100.00	100.00	100.00

Q. r.=Quercus rubra L., Q. c.=Q. coccinea Muenchh., Q. a.=Q. alba L., Q. p.=Q. prinus L., Q. v.=Q. velutina Lam., P. spp.=Pinus strobus L., P. rigida Mill., and P. virginia Mill., L. t.=Liriodendron tulipifera L., P. s.=Prunus serotina Ehrh., F. g.=Fagus grandifolia Ehrh., A. s.=Acer saccharum Marsh., A. r.=A. rubrum L., F. a.=Fraxinus americana L., T. a.=Tilia americana L., P. o.=Platanus occidentalis L., C. f.=Cornus florida L., A. p.=A. pensylvanicum L., C. spp.=Carya spp., Miscellaneous spp. at the SNP include: S. a.=Sassafras albidum (Nutt.) Nees, and N. s.=Nyssa sylvatica Marsh., and at the FEF include: B. l.=Betula lenta L., B. a.=B. alleghaniensis Britt., and U. spp.=Ulmus spp., R. p.=Robinia pseudoacacia L.

prised 72% of the total overstory and understory leaf area at the SNP (Table 9). Those same three species plus pines occupied 62% of the total basal area at the SNP.

White oak (Quercus alba L.), white ash (Fraxinus americana L.), black (Quercus velutina Lam.), and scarlet (Quercus coccinea (Muenchh.)), oaks occupy an additional 16% of leaf area at the SNP. Understory species with greatest leaf areas were hickory (Carya spp.), dogwood (Cornus florida L.), and red maple (Acer rubrum L.) with about 9% of the total canopy area.

Dominant and codominant yellow-poplar, sugar maple (Acer saccharum Marsh), and American beech (Fagus grandifolia Ehrh.) comprise 64% of the canopy area and 60% of the basal area at the FEF (Table 9). White ash, northern red oak, black cherry (Prunus serotina Ehrh.), and American basswood (Tilia americana L.) comprise nearly 14% of total canopy leaf area. The understory includes red maple, hickory, and yellow (Betula alleghaniensis Britt.) and black (B. lenta L.) birch which account for more than 6% of the leaf area.

Equations of foliar area estimates. Northern red oak crown areas can be estimated by regression equations of the form:

$$Y = b_1x + b_0, \text{ where;}$$

Y is total foliar area (cm²), and

x is total foliar dry weight (g).

Equation coefficients (b_1 and b_0) for the SNP are 118.37 and

-147.75, and 109.46 and 31.22 for the FEF. Correlation coefficients for both equations were > 0.99 . The slopes of these lines were significant ($P < 0.001$, F-tests), and were different from each other ($P < 0.10$, t-test).

Total foliar areas ($\text{m}^2 \text{ ha}^{-1}$) and total foliar dry weights (kg ha^{-1}) of all species at both sites were related best as simple linear regression equations. Equation coefficients (b_1 and b_0) for the SNP are 12.48 and 275.83 ($n=16$, $r=0.99$), and 19.50 and -164.13 ($n=14$, $r=0.98$) for the FEF. The slopes of both lines are significant ($P < 0.01$, F-tests), and were different ($P < 0.01$, t-test) from each other. There is no statistical difference between the intercepts ($P > 0.10$, t-test).

Total foliar areas ($\text{m}^2 \text{ ha}^{-1}$) and total basal areas ($\text{m}^2 \text{ ha}^{-1}$) of all species at both sites were related best as simple linear regression equations. Equation coefficients (b_1 and b_0) for the SNP are 3257.16 and -511.39 ($n=14$, $r=0.98$), and 1503.27 and -1400.12 ($n=9$, $r=0.97$) for the FEF. The slopes of both lines are significant ($P < 0.01$, F-tests), and are different ($P < 0.01$, t-test) from each other. There is no statistical difference between the intercepts ($P > 0.10$, t-test).

Northern red oak crown area estimates. Estimated total foliar areas of 15 northern red oaks at each site increased from 1930 to 1982 as diameters and age increased (Fig 3

a,b). Age at d.b.h. averaged 73 years at the SNP and 68 years at the FEF (Table 10). Average d.b.h. of northern red oaks at the SNP is 50.8 cm compared to 46.6 cm at the FEF. Sums of crown leaf areas of the 15 trees at each site over the 53 years period ranged from more than 2100 m² to more than 3400 m² at SNP, and from 1500 m² to 2750 m² at FEF.

Ion exchange. Estimated amounts (g ha⁻¹) of ions exchanged by northern red oaks are indicated in Table 11. Ion exchange estimates increase 62% at the SNP and increase 55% at the FEF from 1930 to 1982. This increase reflects directly the increase in estimated crown areas due to increasing diameters with age during the 53 years period.

Once annual growing season exchanges have been calculated for specific ions, total ion exchange for the 53 years period can be approximated. For example, potassium losses from crowns were 108 kg ha⁻¹ at the SNP and 248 kg ha⁻¹ at the FEF over the period. Accurate estimates of dry deposition to tree crowns during the 53 years period would facilitate determining how much of these losses were due to ion leaching and how much was due to washing of dry deposition.

Discussion

Validity of crown area estimates. The ability to estimate tree crown area from stem diameter rests in the physiological relationship between the demand of crown leaves for water and nutrients, and the corresponding cross-sectional area of

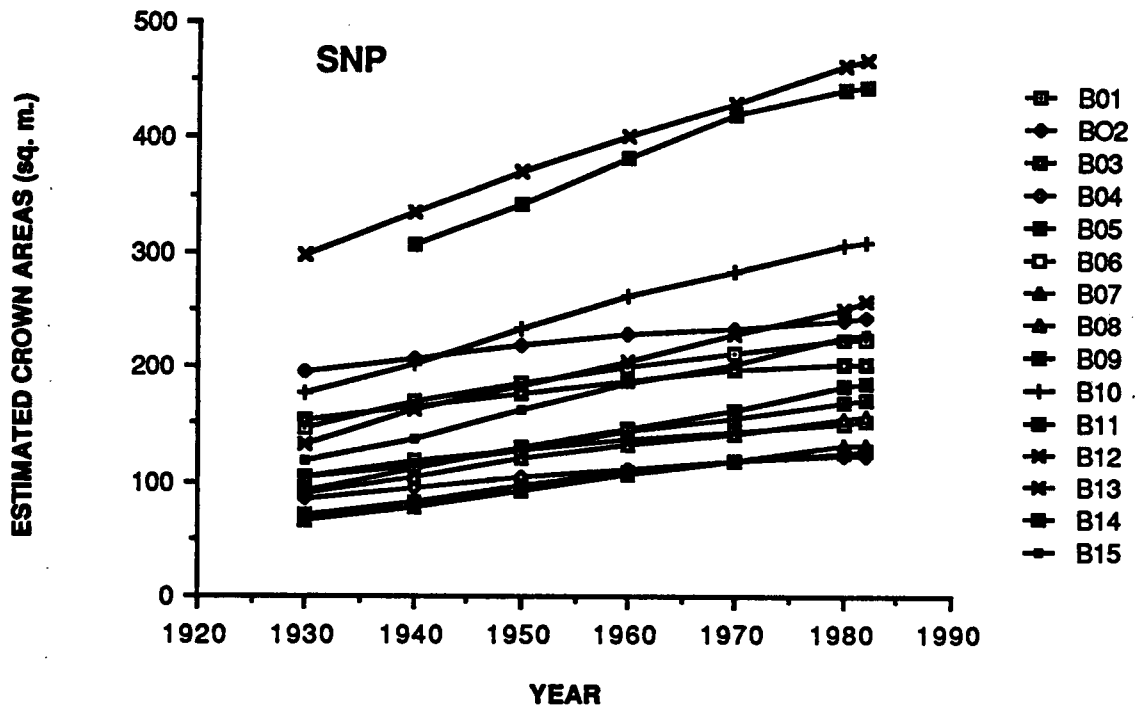


Figure 3a. Estimated crown leaf area chronologies of 15 northern red oak trees calculated from annual growth rings from 1930 to 1982 at the Shenandoah National Park (SNP), Greene Co., Va. Crown areas were estimated from foliar dry weight estimates by a regression equation. Foliar dry weights were previously estimated, by an equation, from individual annual diameter measurements.

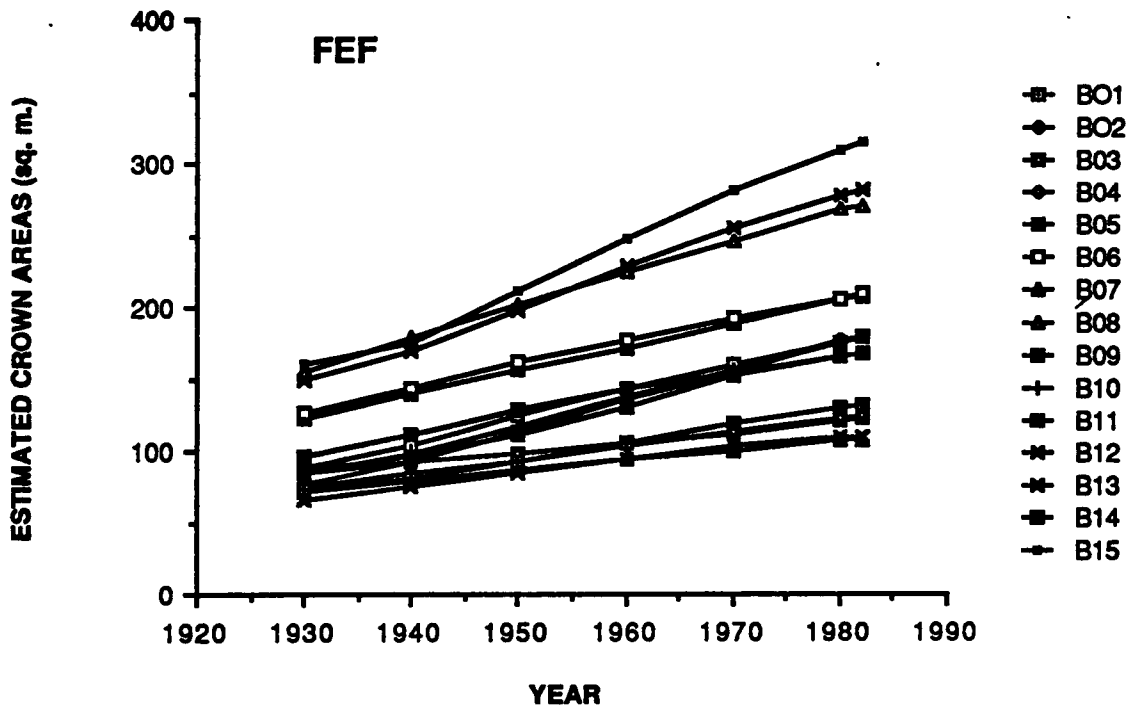


Figure 3b. Estimated crown leaf area chronologies of 15 northern red oak trees calculated from annual growth rings from 1930 to 1982 at the Fernow Experimental Forest (FEF), Tucker Co., W. Va. Crown areas were estimated from foliar dry weight estimates by a regression equation. Foliar dry weights were previously estimated, by an equation, from individual annual diameter measurements.

Table 10. Diameters at breast height (d.b.h.) and approximate age at d.b.h. of 15 northern red oak trees at the Shenandoah National Park (SNP), Greene Co., Va., and the Fernow Experimental Forest (FEF), Tucker, Co., W. Va.

Tree #	SNP		FEF	
	Age (y)	dbh (cm)	Age (y)	dbh (cm)
1	77	51.5	108	46.5
2	141	53.9	62	46.6
3	89	48.1	72	36.1
4	77	34.2	66	36.3
5	68	35.0	64	51.2
6	99	39.7	67	51.4
7	58	36.0	66	33.2
8	58	40.6	60	61.0
9	66	45.4	62	44.3
10	69	63.5	72	46.4
11	78	42.8	61	37.8
12	76	83.2	68	33.6
13	70	55.8	62	62.7
14	66	80.5	63	44.3
15	<u>55</u>	<u>51.8</u>	<u>66</u>	<u>46.6</u>
Ave.	73	50.8	68	46.6

Table 11. Total amounts of ions exchanged by northern red oak crowns at the Shenandoah National Park (SNP), Greene Co., Va., and the Fernow Experimental Forest (FEF), Tucker, Co., W. Va. determined from the difference in average ion concentrations between bulk rainfall and bulk throughfall collected weekly from June 5 to September 25, 1984, and estimated ion exchanges by northern red oak crowns in 1982 and 1930.

	SNP			FEF		
	1984	1982	1930	1984	1982	1930
	kg/ha	g/ha		kg/ha	g/ha	
H ⁺	-0.02	- 20	- 12	-0.10	- 100	- 54
Na ⁺	-0.37	- 370	- 228	1.23	1230	671
NH ₄ ⁺	-0.55	- 550	- 340	-0.04	- 40	- 25
K ⁺	2.52	2520	1556	6.06	6060	3305
Ca ²⁺	0.49	490	303	1.33	1330	821
Mg ²⁺	0.17	170	105	0.32	320	174
NO ₃ ⁻	0.02	20	12	0	0	0
SO ₄ ²⁻	-0.34	- 340	- 210	5.01	5010	2732
PO ₄ ³⁻	0.08	80	49	0.23	230	125

NOTE: Negative values indicate ion retention, and positive values indicate ion loss by crowns.

xylem tissue that meets this demand. Thus it was possible to estimate total crown weights of northern red oaks from diameter measurements using a regression equation constructed from data of northern red oaks in stands similar to those of this study.

A two step approach was used to estimate crown areal histories over a 53 years period from tree diameters for the purpose of estimating ion exchange from crowns. This approach would be useful for estimating ion exchange in stands where past chemical measurements were not taken. The validity of crown area estimates of the 15 northern red oaks on each site depends on: 1) the accuracy of regression equations used in making estimates, and 2) stand dynamics over the time period of interest.

The regression equation of Loomis and Blank (1981) is a good predictor of northern red oak total crown dry weight as indicated by the high coefficient of determination. Northern red oaks at the SNP and FEF fit the description of trees used to develop this equation. Equations developed at each site relating northern red oak leaf dry weights to leaf areas are good predictors of leaf area as indicated by their high correlation coefficients. Used in sequence these equations should provide reasonable chronological estimates of northern red oak total crown areas from diameter measurements.

The effects of competition between trees over a 50 years period are likely to affect the accuracy of the two step approach used in estimating crown areas. Numbers of leaves and stem diameters of trees and thus leaf area index and stand basal area of the main tree canopy of a forest normally increase each year (Spurr and Barnes 1980). Crown area estimates could be made more accurate by using equations specific to smaller time increments over the period of interest. Because individual tree crown estimates over time will be influenced by stand dynamics, factors such as mortality and relative crown class should be considered in making crown area estimates more accurate. Annual growth of the 15 red oaks at both sites over the 53 years period, however, did not show suppression or release. This suggests that the death of neighboring trees did not strongly affect growth of these sample trees.

Relative shade tolerance between species at each site also will influence stand dynamics. Shade tolerance plays a role in determining dominant and codominant positions within the canopy. Over the life of a stand, species composition will thus influence canopy architecture. Larger total canopy area corresponding to a smaller total basal area at the SNP compared to those of the FEF may be due in part to differences in species' shade tolerance between the sites. More than likely, this apparent anomaly occurred because of

different leaf trap positions and conditions of leaf trapping between the sites. In retrospect, it appears that at least 2 of the 8 traps at the SNP were in swales. In this position traps would tend to collect a disproportionately greater number of leaves than had they been in an area less influenced by topography.

Estimates of past crown areas and amounts of ion exchange were made for northern red oak since ion exchange data were available for this species. Estimates of this kind could be made for whole forest canopies. Equations to estimate historical canopy areas would be needed. Ion exchange data collected with no regard for a particular species could be applied to canopy estimates to estimate canopy exchange. Leaf areas of sampled main tree canopy species were estimated by using the leaf trapping method and point sampling techniques described for this study. Leaf dry weights or basal areas served as independent variables in separate equations for the SNP and FEF. Equations estimating canopy variables from stem diameters are available for multiple species in other parts of the Eastern hardwood forest (Monk et al. 1970; Jurik et al. 1985).

Regardless of whether equations are developed to estimate leaf areas of a single species or many species, they need to be validated. Validation involves comparing leaf area estimates made by trapping leaves to estimates made by using

developed equations. Data for this comparison should be collected independently of data used in developing the equations. The equation of Loomis and Blank (1981), and equations estimating northern red oak leaf area from dry weight have not been validated for the SNP and FEF. The approach is, nonetheless, conceptually sound. It represents a first attempt which when refined may be helpful in defining past trends in throughfall chemistry.

Chemical estimates. The validity of ion exchange estimates depends on 1) the accuracy of crown area estimates, and 2) accurate data describing the chemical and meteorological environment of tree crowns in any given year. The first component has already been discussed. Forest canopies combine many physical and chemical factors which influence throughfall chemistry. As forests age, canopy size increases. Along with increases in canopy areas of mature forests there have been increases in the atmospheric content of certain chemicals since the turn of the century. Changes in atmospheric chemistry probably would induce proportional changes in bulk rainfall and bulk throughfall chemistry. Changes in these variables would thus be evident in nutrient ion exchange in tree crowns.

Anthropogenic emissions of sulfur dioxide and oxides of nitrogen have increased since the late nineteenth century, and have increased rapidly from 1960 to the present (NRC

1986). Increased emissions of these precursors of acid precipitation are related to national trends in fossil fuel consumption. Therefore, estimating throughfall chemistry in 1930 from throughfall chemistry data could be considered a worst-case scenario. The chemical variables which man has increased in the atmosphere, and which combine in the canopy to enhance throughfall were probably less abundant in 1930. Thus, 1930 crown ion exchange estimates are probably high by an unknown amount. Unfortunately the issue of whether acid deposition is linearly related to pollutant emissions is unresolved (Oppenheimer et al. 1985; Hidy 1986; Newman and Benkovitz 1986; Oppenheimer et al. 1986). McLaughlin et al. (1985) indicate that there is a fairly linear relationship between emissions and deposition. Further research in this area would be useful in evaluating the effects of increased emissions to forest ecology.

Under the scenario of increasing SO_2 and NO_x in the atmosphere, it is possible to hypothesize an increase in base cation leaching from foliage, and increases in base cation, nitrogen, and sulfur content in throughfall. A number of studies suggest that increased acidity in rainfall increases nutrient leaching from forest canopies and therefore has the potential to alter nutrient cycling (McLaughlin 1985). Accurate estimates of historical rainfall and throughfall chemistry might indicate changes in

chemical processes (e.g. ion exchange) in forest canopies. However, we still do not know how rapidly trees will resupply crowns to replace leached nutrients, and what this resupply means to a tree in terms of energy costs, and nutrient resources. Comparisons of mineralization rates in soil to canopy leaching losses would be key in determining long-term ecosystem damage.

Estimates of tree crown (or forest canopy) area in conjunction with ion exchange data could be useful in modeling long-term trends in throughfall chemistry. Crown area estimates could be made more accurate by including elements of stand competition and growth dynamics. Estimates of past ion exchange chemistry must account for changes in atmospheric chemistry. A model of this sort may be valuable in determining changes in chemical processes in forest ecosystems by man-made emissions into the atmosphere.

References

- Anonymous. 1983. Methods of chemical analysis of water and wastes. Environmental monitoring and Support Laboratory Office of Research and Development. U. S. Environmental Protection Agency, Cincinnati, Ohio. 430 pp.
- Avery, T. E., and H. E. Burkhart. 1983. Forest measurements, Third Edition. McGraw-Hill, New York, 331 pp.
- Blanche, C. A., and J. D. Hodges. 1985. A leaf area-sapwood area ratio developed to rate loblolly pine tree vigor. Can. J. For. Res. 15:1181-1184.
- Duvick, D. N. and T. J. Blasing. 1981. A dendroclimatic reconstruction of annual precipitation amounts in Iowa since 1680. Water Resources Res. 17: 1183-1189.
- Fowler, D. 1980. Removal of sulfur and nitrogen compounds from the atmosphere in rain and dry deposition. In Proceedings of the International Conference of the Ecological Impact of Acid Precipitation. Edited by D. Drablos, and A. Tollan. SNSF project, Oslo, Norway.
- Foster, N. W. 1985. Acid precipitation and soil solution chemistry within a maple-birch forest in Canada. For. Ecol. Manage. 12:215-231.
- Fritts, H. C. 1976. Tree Rings and Climate. Academic Press, New York.
- Fritts, H. C. 1966. Growth-rings of trees: their correlation with climate. Science 154: 973-979.
- Fritts, H. C., T. J. Blasing, B. P. Hayden and J. E. Kutzbach. 1971. Multivariate techniques for specifying tree-growth and climate relationships and for reconstructing anomalies in paleoclimate. J. Appl. Meteorology 10:845-864.
- Hahn, J. T., and W. H. Carmean. 1982. Lake States site index curves formulated. USDA For. Serv. Gen. Tech. Rep. NC-88, 5 pp.
- Hidy, G. M. 1986. Letter to the Editor. Science 233:10.
- Jurik, T. W., G. M. Briggs, and D. M. Gates. 1985. A comparison of four methods for determining leaf area index in successional hardwood forests. Can. J. For. Res. 15:1154-1158.
- Kaufmann, M. R. and C. A. Troendle. 1981. The relationship of leaf area and foliage biomass to sapwood conducting area in four subalpine forest tree species. Forest Sci. 27:477-482.
- Khanna, P. K. and B. Ulrich. 1981. Changes in the chemistry of throughfall under stands of beech (*Fagus sylvatica*) and spruce (*Picea abies*) following the addition of fertilizers. Acta Oecol. Plant 2:155-164.
- Lindberg, S. E., G. M. Lovett, D. D. Richter, and D. W. Johnson. 1986. Atmospheric deposition and canopy interaction of major ions in a forest. Science 231:141-145.

- Loomis, R. M. and R. W. Blank. 1981. Estimating northern red oak crown component weights in the Northeastern United States. USDA, Forest Service, Research Paper NC-194. 9 pp.
- Mahendrappa, M. K., and E. O. Ogden. 1973. Effects of fertilization of a Black spruce stand on nitrogen contents of stemflow, throughfall, and litterfall. *Can. J. For. Res.* 3:54-60.
- McLaughlin, S. B., T. J. Blasing, L. K. Mann, and D. N. Duvick. 1983. Effects of acid rain and gaseous air pollutants on forest productivity: A regional approach. *J. Air Poll. Contr. Assoc.* 33:1042-1048.
- McLaughlin, S. B. 1985. Effects of air pollution on forests: A critical review. *J. Air Poll. Contr. Assoc.* 35:512-534.
- McLaughlin, S. B., T. J. Blasing, D. N. Duvick, T. N. Doyle, and L. K. Mann. 1985. Summary of a two year study of forest responses to anthropogenic stress. 291 pp. Draft copy prepared by Oak Ridge National Laboratory, Oak Ridge, TN.
- Mecklenburg, R. A., H. B. Tukey, Jr., and J. V. Morgan. 1966. A mechanism for the leaching of calcium from foliage. *Plant Physiol.* 41:610-613.
- Miller, H. G. and J. D. Miller. 1980. Collection and retention of atmospheric pollutants by vegetation. In *Proceedings of the International Conference of the Ecological Impact of Acid Precipitation*. Edited by D. Drablos, and A. Tollan. SNSF project, Oslo, Norway.
- Monk, C. D., G. I. Child, and S. A. Nicholson. 1970. Biomass, litter and leaf surface area estimates of an oak-hickory forest. *Oikos* 21:138-141.
- National Research Council. 1986. Acid Deposition Long Term Trends. National Academy Press, Washington, D.C. 506 pp.
- Newman, L., C. M. Benkovitz. 1986. Letter to the Editor. *Science* 233:11-12.
- Olson, R. K., W. A. Reiners, C. S. Cronan, and G. E. Lang. 1981. The chemistry and flux of throughfall and stemflow in subalpine balsam fir forests. *Holarctic Ecology* 4:291-300.
- Olson, R. K., W. A. Reiners, and G. M. Lovett. 1985. Trajectory analysis of forest canopy effects on chemical flux in throughfall. *Biogeochemistry* 1:361-373.
- Oppenheimer, M. C. B. Epstein, and R. E. Yuhnke. 1985. Acid deposition, smelter emissions, and the linearity issue in the Western states. *Science* 229:859-862.
- Oppenheimer, M. C. B. Epstein, and R. E. Yuhnke. 1986. Letter to the Editor. *Science* 233:12-14.
- Parker, G. G. 1983. Throughfall and Stemflow in the Forest Nutrient Cycle. *Adv. Ecol. Res.* 13:57-133.
- Reiners, W. A. and R. K. Olson. 1984. Effects of canopy components on throughfall chemistry: An experimental approach. *Oecologia* 63:320-330.

- Rogers, R. and T. M. Hinckley. 1979. Foliar weight and area related to current sapwood area in oak. *Forest Sci.* 25:298-303.
- Spurr, S. H. and B. V. Barnes. 1980. *Forest Ecology*, Third Edition. pp. 363-398. John Wiley and Sons, New York. 687 pp.
- Stokes, M. A., and T. L. Smiley. 1968. *An Introduction to Tree-Ring Dating*. The Univ. of Chicago Press, Chicago. 73 pp.
- Telfer, E. S. 1969. Weight-diameter relationships for 22 woody plant species. *Can. J. Bot.* 47:1851-1855.
- Tukey, H. B., Jr. 1980. Some effects of rain and mist on plants, with implications for acid precipitation. In *Effects of Acid Precipitation on Terrestrial Ecosystems*. Edited by T. C. Hutchinson and M. Havas. Plenum Press, New York.
- Waring, R. H., H. L. Gholz, C. C. Grier, and M. L. Plummer. 1977. Evaluating stem conducting tissue as an estimator of leaf area in four woody angiosperms. *Can. J. Bot.* 55:1474-1477.
- Whittaker, R. H. and G. M. Woodwell. 1967. Surface area relations of woody plants and forest communities. *Amer. J. Bot.* 54:931-939.
- Yawney, H. W., A. L. Leaf, and R. E. Leonard. 1978. Nutrient content of throughfall and stemflow in fertilized and irrigated Pinus resinosa Ait. stands. *Plant Soil* 50:433-445.
- Yawney, H. W. 1964. Oak site index on Belmont limestone soils in the Allegheny mountains of West Virginia. USDA For. Serv. Res. Rep. Pap. NE-30. 16 pp.

CONCLUSIONS

The research described in the previous four chapters was designed to further the knowledge of chemical processes that occur as rainfall percolates through a deciduous hardwood forest canopy. The main conclusions that resulted from investigating each research question are listed below.

1. Does leaf nutrient status affect nutrient ion exchange between northern red oak leaves and simulated acid rain solutions?

- * Nutrient ion and proton leaching and retention by northern red oak leaves exposed to simulated rain solutions of pH 5.6, 4.3, and 3.0 were typically not affected by leaf nutrient status.

- * Simulated rain solutions of pH 3.0 leached 1) more Mg from northern red oak leaves from the less fertile (versus fertile) site, and 2) the greatest amount of total cations from leaves of both sites.

- * Northern red oak leaves exposed to simulated rain solutions of pH 3.0 lost more Ca^{2+} , K^{+} , and Mn^{2+} during a 7 hour treatment period compared to a 2 hour treatment period. These ions leached from leaves at faster rates during the first 2 hours compared to the last 5 hours.

- * Hydrogen ions displaced 30% of all cations leached from northern red oak leaves in acid rain solutions of pH 4.3 regardless of nutrient status. In solutions of pH 3.0, hydrogen ion displacement of cations increased to 44%

of the total.

2. Does nutrient status of northern red oak crown leaves affect nutrient ion concentrations in bulk throughfall?

* Higher concentrations of Ca^{2+} , Mg^{2+} , NH_4^+ , Mn^{2+} , and SO_4^{2-} in bulk throughfall at the fertile site compared to that of the less fertile site are probably not due to differences in northern red oak crown leaf nutrient ion concentrations.

* These differences are likely due to higher large-particle dryfall ionic concentrations, higher rainfall volume, and greater leaf area at the fertile site compared to the less fertile site.

* Rainfall passing through northern red oak crowns at both sites was enriched with SO_4^{2-} , PO_4^{3-} , Ca^{2+} , Mg^{2+} , K^+ , Mn^{2+} , and Fe^{2+} , but lost NH_4^+ to the crowns.

3. Can past amounts of nutrient ion exchange be estimated for tree crowns and forest canopies?

* Estimates of tree crown or forest canopy area may be useful in estimating past trends in nutrient ion exchange within crowns and canopies. The validity of such estimates requires accurate historical meteorological data and estimates of historical atmospheric chemistry.

* This study suggests a technique, that when refined, could be used to estimate historical tree crown or forest canopy areas from growth ring chronologies by applying

regression equations which relate foliar variables to stem diameter.

APPENDIX

Nutrient element concentrations, pH, and electrical conductivity in bulk rainfall collected for 16 weeks at the Shenandoah National Park, Green Co., Virginia. Insufficient rain was collected for weeks 1 and 14 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Weeks							
	1	2	3	4	5	6	7	8
P	-	.117	.085	.044	.071	.005	0	.004
K	-	4.58	5.16	2.63	2.40	.173	0	0
Ca	-	2.34	1.81	1.04	.985	.151	1.06	2.62
Mg	-	.658	.654	.351	.317	.045	.321	.795
Mn	-	.078	.052	.026	.036	.000	.029	.086
Fe	-	.025	.031	.068	.037	.014	0	.014
B	-	.094	.197	.089	.110	0	.111	.254
Zn	-	.104	.074	.049	.035	0	.089	.051
Na	-	1.28	2.29	1.40	.986	.030	1.52	3.10
Mo	-	.004	.004	.004	.003	0	0	0
NH4	-	.20	.20	0	.20	.20	.53	1.1
NO3	-	.20	.53	.20	.35	.20	.35	.88
SO4	-	4.8	4.5	3.0	3.2	0	-	16.3
pH	-	5.35	5.79	4.66	5.19	5.62	5.93	4.94
Cond	-	27.3	72.5	18.1	23.0	5.70	37.0	66.0
	9	10	11	12	13	14	15	16
P	.031	.010	.043	.077	.101	-	.037	.043
K	2.35	1.35	1.05	.976	3.90	-	1.02	.669
Ca	.516	.509	.112	.244	2.27	-	.357	.157
Mg	.150	.169	.061	.068	.656	-	.275	.067
Mn	.023	.014	0	.012	.105	-	.004	.004
Fe	.019	.005	.011	.002	.016	-	0	.006
B	.058	.050	.032	.036	.137	-	.070	.027
Zn	.006	.026	.004	.001	.013	-	.003	.002
Na	.658	.641	.733	1.22	1.39	-	2.04	.617
Mo	.012	.001	.003	.016	.000	-	.015	.016
NH4	.35	.53	.35	.20	1.1	-	.88	.35
NO3	.35	.20	.20	.20	.53	-	.70	.20
SO4	3.3	3.2	1.6	1.7	7.4	-	1.6	1.7
pH	6.10	5.12	5.93	6.22	5.52	-	6.13	5.59
Cond	32.0	20.0	9.10	7.90	44.8	-	24.3	13.9

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Shenandoah National Park, Green Co., Virginia. Insufficient water was collected for weeks 1 and 14 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #1							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.031	.056	0	.017	.132	0	0
K	-	.137	0	.377	.076	.018	0	0
Ca	-	.587	1.17	.653	.673	.257	.865	2.04
Mg	-	.173	.344	.088	.216	.075	.238	.576
Mn	-	.000	.000	0	.012	.000	0	.014
Fe	-	.007	.015	.010	.004	0	0	0
B	-	.067	.138	.072	.095	0	.106	.333
Zn	-	.090	.089	.013	.040	.015	.056	.211
Na	-	1.04	1.94	.430	1.56	.166	2.02	3.52
Mo	-	.001	.012	.006	.010	0	0	0
NH ₄	-	.20	.88	0	.88	.20	.70	1.2
NO ₃	-	.20	.70	.35	.35	.20	.20	.70
SO ₄	-	5.7	3.7	3.8	4.6	3.31	2.3	14.5
pH	-	5.89	6.50	5.32	6.16	5.57	5.95	4.57
Cond	-	20.0	87.0	14.0	35.0	5.20	29.0	62.0
	9	10	11	12	13	14	15	16
P	.060	.042	.013	.031	.048	-	.005	.043
K	1.44	0	1.05	.126	.535	-	1.08	2.31
Ca	.206	.586	.643	.106	.662	-	.337	.340
Mg	.050	.088	.302	.040	.155	-	.136	.095
Mn	.005	.000	0	.012	.012	-	.004	.004
Fe	.010	.001	.006	.011	.006	-	.000	.010
B	.052	.038	.201	.109	.087	-	.116	.051
Zn	.011	.034	.006	.010	.010	-	.039	.055
Na	.421	.416	2.48	1.94	.966	-	1.99	1.65
Mo	.019	.003	.018	.150	.004	-	.042	.042
NH ₄	.20	.35	.18	.20	.20	-	.53	.53
NO ₃	.20	.20	.20	.20	.35	-	.35	.35
SO ₄	2.8	2.8	4.0	1.7	4.2	-	2.1	1.8
pH	5.03	4.59	6.15	6.22	5.63	-	6.05	6.08
Cond	12.8	41.0	20.0	10.9	26.1	-	22.3	23.0

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Shenandoah National Park, Green Co., Virginia. Insufficient water was collected for weeks 1 and 14 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #2							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.129	.095	.024	.043	0	0	0
K	-	5.74	4.30	1.35	3.92	.830	1.14	.191
Ca	-	2.35	2.22	1.13	1.13	.122	1.41	2.57
Mg	-	.616	.705	.358	.355	.017	.378	.651
Mn	-	.157	.130	.066	.073	.000	.029	.230
Fe	-	.059	.066	.036	.021	.006	0	.008
B	-	.122	.196	.143	.135	0	.127	.190
Zn	-	.114	.085	.021	.040	.007	.075	.118
Na	-	1.74	2.97	1.24	1.37	.057	1.50	2.51
Mo	-	.004	.007	.006	.005	0	0	0
NH4	-	.20	.20	0	.35	.20	.53	1.1
NO3	-	.20	.70	.35	.20	.20	.20	1.4
SO4	-	10.0	3.7	4.1	3.4	0	2.4	16.3
pH	-	5.39	5.70	5.10	5.38	5.48	5.95	4.81
Cond	-	48.3	46.0	23.1	18.5	6.49	23.6	62.0
	9	10	11	12	13	14	15	16
P	.100	.011	34.9	.064	.224	-	0	.068
K	4.22	2.20	320.8	1.38	6.00	-	0	1.97
Ca	.716	.755	3.41	1.11	2.71	-	.263	.256
Mg	.187	.166	1.45	1.00	.660	-	.114	.081
Mn	.077	.071	.014	.012	.230	-	.004	.034
Fe	.015	.010	.038	.020	.030	-	0	.010
B	.094	.049	.076	.048	.126	-	.046	.037
Zn	.008	.045	.027	.097	.027	-	.005	.003
Na	.920	.475	198.4	3.22	1.32	-	1.29	.496
Mo	.019	.002	.051	.044	.003	-	.026	.030
NH4	.53	.20	223.7	.35	2.3	-	.70	.20
NO3	.20	.35	1.1	.20	.70	-	.20	.20
SO4	2.8	3.5	-	-	6.4	-	1.6	1.9
pH	5.36	4.85	-	6.37	5.15	-	5.59	6.09
Cond	18.5	25.5	-	21.4	29.2	-	14.4	14.5

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Shenandoah National Park, Green Co., Virginia. Insufficient water was collected for weeks 1 and 14 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #3							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.079	.085	.093	.062	0	.014	0
K	-	7.21	9.95	4.17	.244	.709	3.27	2.05
Ca	-	2.02	2.19	1.66	.759	.072	.895	1.95
Mg	-	.530	.716	.537	.243	.005	.253	.531
Mn	-	.078	.091	.066	.036	.000	.029	.108
Fe	-	.037	.025	.068	.022	.004	.012	.008
B	-	.161	.260	.182	.085	.017	.085	.148
Zn	-	.165	.156	.062	.023	.003	.069	.066
Na	-	2.25	3.72	1.70	1.10	.063	.882	1.58
Mo	-	.011	.006	.004	.004	0	0	0
NH ₄	-	.20	.20	0	.20	.20	.20	.53
NO ₃	-	.20	.70	.35	.35	.20	.20	.35
SO ₄	-	9.9	2.8	4.2	3.5	0	-	14.6
pH	-	6.03	5.05	5.34	5.06	5.54	5.73	4.40
Cond	-	91.5	49.5	27.0	20.2	5.92	19.1	62.0
	9	10	11	12	13	14	15	16
P	.047	.020	.028	.042	.148	-	0	.052
K	1.93	2.38	1.30	.886	5.99	-	0	1.43
Ca	.519	.414	.013	.155	1.76	-	.149	.160
Mg	.162	.102	.018	.050	.488	-	.112	.052
Mn	.023	.028	0	.004	.105	-	.004	.004
Fe	.005	.014	.003	.005	.020	-	0	.008
B	.065	.035	0	.031	.126	-	.070	.046
Zn	.006	.034	.003	.001	.014	-	.003	.003
Na	.645	.485	.212	.791	1.23	-	1.65	1.24
Mo	.013	.005	.007	.020	.006	-	.016	.020
NH ₄	.20	.20	.20	.20	.20	-	.35	.20
NO ₃	.20	.35	.20	.20	.53	-	.70	.20
SO ₄	5.1	3.8	1.6	1.8	7.7	-	1.6	1.8
pH	5.16	4.92	5.42	6.23	5.12	-	5.98	5.94
Cond	21.0	22.5	6.80	7.40	40.0	-	17.0	14.4

Nutrient element concentrations, pH, and electrical conductivity in bulk rainfall collected for 16 weeks at the Fernow Experimental Forest, Tucker Co., West Virginia. Insufficient rain was collected for week 1 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Weeks							
	1	2	3	4	5	6	7	8
P	-	.290	.006	.067	.072	.042	.021	.133
K	-	8.72	5.30	8.76	3.12	3.10	2.34	0
Ca	-	2.53	1.16	1.42	.641	1.05	1.04	1.13
Mg	-	.640	.256	.228	.107	.214	.242	.284
Mn	-	.157	.074	.101	.053	.073	.044	.072
Fe	-	.055	.024	.049	.028	.023	.012	0
B	-	1.00	.044	.047	.018	.069	.085	.090
Zn	-	.086	.016	.016	0	0	.025	.010
Na	-	.686	.191	.170	.104	.574	.784	.344
Mo	-	.004	0	.001	.005	0	.002	0
NH ₄	-	.20	.20	.20	.53	.35	.35	1.1
NO ₃	-	.35	.20	.20	.20	.88	.20	.70
SO ₄	-	12.2	6.5	5.4	4.8	6.8	4.0	6.9
pH	-	4.33	4.54	4.58	4.54	4.12	5.50	4.93
Cond	-	40.0	30.1	57.0	27.0	44.0	22.0	30.0
	9	10	11	12	13	14	15	16
P	.015	0	.047	.064	.060	.029	.036	.060
K	1.62	3.69	3.38	5.79	4.56	11.2	8.64	1.51
Ca	.911	1.14	2.20	.628	1.19	2.37	3.81	.719
Mg	.199	.203	.580	.126	.203	.219	.746	.214
Mn	.076	.070	.142	.043	.121	.215	3.67	.042
Fe	.018	.023	.026	.014	.016	.025	.033	.014
B	.069	.093	.226	.076	.048	.144	.182	.095
Zn	.023	.029	.127	.013	.005	.027	.019	.005
Na	.630	.551	2.26	.484	.388	.394	2.35	1.72
Mo	0	.001	.006	.009	.004	0	.009	.011
NH ₄	.35	.20	1.4	.20	.53	1.2	.70	.20
NO ₃	.20	.20	.35	.20	.20	1.2	1.4	.53
SO ₄	5.0	9.9	11.2	1.6	9.1	8.6	15.1	1.8
pH	4.76	4.59	6.06	5.75	5.01	5.18	6.04	5.95
Cond	26.0	41.5	54.9	27.0	34.0	34.0	76.1	22.0

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Fernow Experimental Forest, Tucker Co., West Virginia. Insufficient water was collected for week 1 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #1							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.027	0	.018	.0217	.001	0	0
K	-	.425	0	0	.130	0	0	0
Ca	-	.708	.134	1.51	.745	.354	.477	.466
Mg	-	.161	.059	.158	.145	.096	.099	.106
Mn	-	.014	0	.013	.003	0	.000	.014
Fe	-	.027	0	.020	.011	.020	.009	.001
B	-	.083	.032	.070	.023	.069	.028	.032
Zn	-	.050	.030	.045	.010	0	.153	.031
Na	-	.682	.256	.644	.186	.574	.276	.209
Mo	-	.002	0	.005	.005	0	0	.008
NH4	-	0.53	.53	.20	.53	.70	.20	.35
NO3	-	0.70	.35	.20	.70	.70	.20	.35
SO4	-	9.3	2.45	5.4	2.6	3.9	3.4	4.3
pH	-	3.82	4.33	3.97	4.47	3.93	4.52	4.13
Cond	-	58.5	30.5	46.2	20.5	39.0	20.3	37.0
	9	10	11	12	13	14	15	16
P	.029	0	.000	.022	.054	.016	.022	.042
K	0	.458	.079	0	.957	.654	0	.309
Ca	1.04	.224	1.72	.545	.582	1.50	.847	.242
Mg	.051	.030	.555	.025	.036	.088	.308	.099
Mn	0	0	.019	.012	.012	.018	.013	.004
Fe	.009	.002	.026	.007	.009	.027	.011	.002
B	.030	.021	.336	.042	.039	.108	.158	.058
Zn	.008	0	.066	.020	.007	.028	.009	.004
Na	.188	.067	2.95	0	0	.288	2.19	.776
Mo	.025	.007	.018	.008	.006	.002	.022	.016
NH4	.53	.20	.70	.20	.70	.53	1.1	.20
NO3	.20	.20	.53	.35	.53	.53	.88	.20
SO4	4.0	1.8	7.6	3.2	4.8	3.1	4.5	2.4
pH	4.11	4.79	6.05	4.59	4.21	4.65	5.00	6.16
Cond	40.0	8.50	37.8	29.9	38.1	26.0	29.3	17.7

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Fernow Experimental Forest, Tucker Co., West Virginia. Insufficient water was collected for week 1 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #2							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.194	0	.005	.172	.051	.056	0
K	-	4.24	0	1.32	4.52	1.07	1.81	0
Ca	-	2.25	.964	1.61	.671	.938	.971	1.11
Mg	-	.533	.226	.278	.176	.236	.269	.285
Mn	-	.114	.048	.067	.040	.061	.058	.057
Fe	-	.031	.018	.035	.012	.017	.014	0
B	-	.128	.049	.098	.020	.101	.082	.116
Zn	-	.070	.050	.033	.003	0	.039	.016
Na	-	.810	.396	.621	.175	.711	.631	.714
Mo	-	.003	0	0	.005	0	0	.004
NH ₄	-	.35	.35	.53	.35	.35	.35	.88
NO ₃	-	.70	.35	.20	.20	.88	.20	1.2
SO ₄	-	14.8	5.5	6.8	3.8	5.8	4.2	6.0
pH	-	6.37	4.30	4.18	5.16	4.17	5.56	4.63
Cond	-	50.5	30.0	48.0	21.5	38.0	22.0	28.0
	9	10	11	12	13	14	15	16
P	0	.024	.039	.018	.073	.001	.046	.099
K	.092	1.95	2.07	2.85	2.93	4.10	4.06	2.18
Ca	.768	1.09	2.14	.628	.846	2.47	3.57	.476
Mg	.170	.153	.596	.122	.126	.329	.965	.136
Mn	.061	.056	.157	.058	.090	.520	.291	.034
Fe	.016	.016	.014	.011	.012	.021	.024	.009
B	.078	.043	.226	.053	.020	.144	.392	.046
Zn	.011	.019	.103	.009	.007	.039	.030	.006
Na	.428	.317	2.13	.272	.156	.315	4.83	.647
Mo	.008	.005	.007	.014	.005	0	.028	.014
NH ₄	.20	.70	1.1	.20	.53	.20	1.1	.20
NO ₃	.35	.35	.35	.20	.20	.53	1.1	.20
SO ₄	4.4	6.3	10.6	4.2	5.4	-	7.4	2.1
pH	4.47	4.41	5.73	4.71	4.60	-	5.98	6.13
Cond	28.0	40.0	52.1	20.1	31.7	-	72.5	33.0

Nutrient element concentrations, pH, and electrical conductivity in bulk throughfall collected for 16 weeks at the Fernow Experimental Forest, Tucker Co., West Virginia. Insufficient water was collected for week 1 to allow chemical analysis. Nutrient elements are in ppm, conductivity is in $\mu\text{mhos}/\text{cm}^2$

	Collector #3							
	Weeks							
	1	2	3	4	5	6	7	8
P	-	.087	.067	.116	.102	.005	.017	.098
K	-	4.02	0	3.44	2.33	2.15	1.83	2.40
Ca	-	2.54	.928	1.21	.947	1.22	1.04	1.20
Mg	-	.542	.223	.240	.132	.258	.224	.250
Mn	-	.199	.074	.094	.065	.085	.058	.086
Fe	-	.023	.029	.028	.015	.018	.016	0
B	-	.106	.032	.064	.023	.096	.076	.085
Zn	-	.053	.036	.018	.015	0	.025	.008
Na	-	.705	.226	.438	.095	.706	.606	.344
Mo	-	.004	0	.002	.007	0	.002	0
NH4	-	.20	.53	.20	.35	.53	.20	.35
NO3	-	.70	.20	.20	.53	.35	.20	.35
SO4	-	16.0	5.8	6.6	4.3	6.5	4.1	7.6
pH	-	4.48	4.30	4.47	4.44	4.31	5.66	4.81
Cond	-	46.5	30.0	39.9	30.0	35.5	22.1	31.5
	9	10	11	12	13	14	15	16
P	.067	.030	.030	.100	.059	.051	.023	.076
K	3.03	2.31	2.37	1.32	2.37	7.34	7.54	1.75
Ca	1.01	1.06	2.20	.671	1.12	2.63	3.71	.596
Mg	.237	.247	.550	.133	.205	.241	.961	.179
Mn	.061	.056	.142	.051	.121	.224	.215	.034
Fe	.022	.013	.026	.007	.011	.010	.035	.009
B	.107	.121	.261	.059	.025	.152	.480	.066
Zn	.063	.018	.163	.011	.003	.042	.029	.003
Na	1.08	1.22	2.12	.244	.173	.288	5.33	1.49
Mo	.005	.004	.005	.007	.003	.003	.023	.012
NH4	.53	.20	.88	.20	.53	.53	.35	.20
NO3	.20	.20	.53	.20	.70	.53	.88	.20
SO4	5.3	5.6	10.1	4.0	5.6	4.5	8.4	2.1
pH	4.75	5.41	5.88	4.81	4.77	5.18	6.37	6.13
Cond	26.0	32.0	49.4	17.0	28.5	28.9	74.2	33.0

Nutrient element concentrations (in ppm) in simulated acid rain solutions of three acidities following 7 hour and 2 hour exposures to northern red oak leaves from the Shenandoah National Park, Green Co., Virginia

Exposure #1									
7 Hour Exposure									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.054	.170	.088	0	0	0	0	0	.009
K	9.62	8.81	8.68	5.93	4.23	3.60	7.11	5.52	4.74
Ca	5.03	7.62	7.70	3.24	2.50	2.25	2.71	2.79	2.31
Mg	.772	1.02	1.16	.105	.172	.096	.084	.109	.162
Mn	.262	.493	.186	.000	.019	0	0	0	0
Na	5.77	6.17	6.64	7.82	6.88	7.84	12.0	9.72	9.79
NH4	1.2	2.5	2.5	.35	.20	.20	.20	.88	.20
NO3	2.6	2.8	1.9	.20	.20	.20	.20	.20	.20
pH	3.20	3.21	3.31	4.96	5.01	4.69	5.30	5.30	5.50
SO4	46.8	46.7	47.5	8.2	7.5	8.8	10.3	10.8	11.4

2 Hour Exposure									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.142	.216	.025	0	0	.028	0	0	.066
K	10.0	8.25	5.29	4.24	2.89	4.33	4.70	5.34	4.94
Ca	5.33	7.07	6.14	2.30	1.94	2.80	2.98	3.54	2.27
Mg	.634	.737	.544	.093	.064	.106	.082	.161	.098
Mn	.198	.295	.070	0	0	0	0	.006	0
Na	5.48	7.12	4.72	7.11	7.39	7.33	10.3	11.4	9.47
NH4	1.8	1.6	1.6	.20	.20	.20	.20	.20	.35
NO3	3.0	3.0	3.3	.20	.35	.20	.20	.20	.20
pH	3.15	3.18	3.17	4.57	4.66	4.51	5.25	5.20	5.20
SO4	46.9	47.8	46.7	8.00	7.70	7.30	11.8	10.6	11.7

Nutrient element concentrations (in ppm) in simulated acid rain solutions of three acidities following 7 hour and 2 hour exposures to northern red oak leaves from the Fernow Experimental Forest, Tucker Co., West Virginia

Exposure #1									
7 Hour Exposure									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.053	.230	.071	0	.111	0	0	.204	0
K	9.25	13.1	9.66	5.78	8.40	5.30	4.23	9.64	7.02
Ca	7.18	8.68	6.54	2.35	2.64	2.70	2.67	2.27	2.11
Mg	.537	.792	.489	.059	.114	.088	.072	.104	.064
Mn	.301	.800	.365	.000	.006	.019	0	.000	.000
Na	5.01	5.90	4.62	6.56	6.39	6.92	10.1	9.26	9.39
NH4	1.8	1.9	1.6	.20	.20	.20	.35	.53	.20
NO3	3.0	3.9	3.0	.20	.20	.20	.70	.20	.20
pH	3.22	3.34	3.20	4.90	5.71	4.97	5.29	5.58	5.27
SO4	47.8	48.7	47.1	9.40	12.7	8.30	12.0	12.0	11.3

2 Hour Exposure									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.028	.228	.058	0	.229	0	0	.108	.021
K	5.42	10.7	6.78	5.41	9.68	5.51	4.69	6.75	6.30
Ca	5.85	5.63	5.55	2.51	2.79	2.05	3.04	3.24	2.67
Mg	.359	.405	.310	.065	.101	.033	.072	.096	.062
Mn	.173	.237	.173	0	.019	0	0	0	0
Na	4.76	6.07	5.60	6.76	6.92	7.43	9.31	10.0	10.0
NH4	1.1	1.8	1.6	.20	.20	.53	.35	.35	.53
NO3	3.5	2.8	3.3	.20	.20	.20	.53	.35	.35
pH	3.16	3.16	3.15	4.70	4.96	4.76	5.16	5.40	5.16
SO4	50.1	47.2	45.3	6.90	7.60	8.00	11.2	11.4	14.8

Nutrient element concentrations (in ppm) in simulated acid rain solutions of three acidities following a 2 hour exposure to northern red oak leaves at two sites

Exposure #2									
Shenandoah National Park									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.066	.004	.031	.104	.058	.018	.029	.020	0
K	3.02	2.07	2.32	1.33	1.48	.939	1.32	.302	1.10
Ca	2.85	3.32	2.90	.957	1.17	1.07	.898	1.11	.954
Mg	.541	.364	.519	.168	.139	.172	.152	.131	.156
Mn	.346	.464	.170	.052	.066	.022	.059	.081	.022
Na	.536	.499	.454	2.21	2.09	2.19	3.90	4.02	3.88
NH4	.88	1.4	1.2	.20	.20	.20	.20	.35	.20
NO3	3.3	2.8	3.5	.20	.20	.20	.20	.20	.35
pH	3.11	3.07	3.08	4.56	4.59	4.64	5.25	5.17	5.14
SO4	45.8	47.5	47.0	7.30	7.20	7.90	8.40	8.30	8.10

Fernow Experimental Forest									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.053	.100	.015	.015	.046	.071	.033	.051	.040
K	2.66	1.32	4.67	1.23	1.74	2.75	1.07	1.56	2.55
Ca	3.13	2.78	2.54	1.06	1.18	.970	.952	1.10	.849
Mg	.316	.259	.346	.124	.129	.126	.111	.112	.110
Mn	.332	.377	.376	.037	.081	.081	.037	.081	.066
Na	.489	.499	.577	2.18	2.24	2.11	3.98	.3.80	3.76
NH4	1.2	1.4	2.3	.53	.20	.35	.88	.35	.53
NO3	3.2	4.0	1.9	.53	.20	.53	.20	.20	.20
pH	3.10	3.08	3.10	4.71	4.86	4.90	5.23	5.20	5.23
SO4	47.2	48.2	46.5	8.50	7.30	7.50	8.80	8.40	8.30

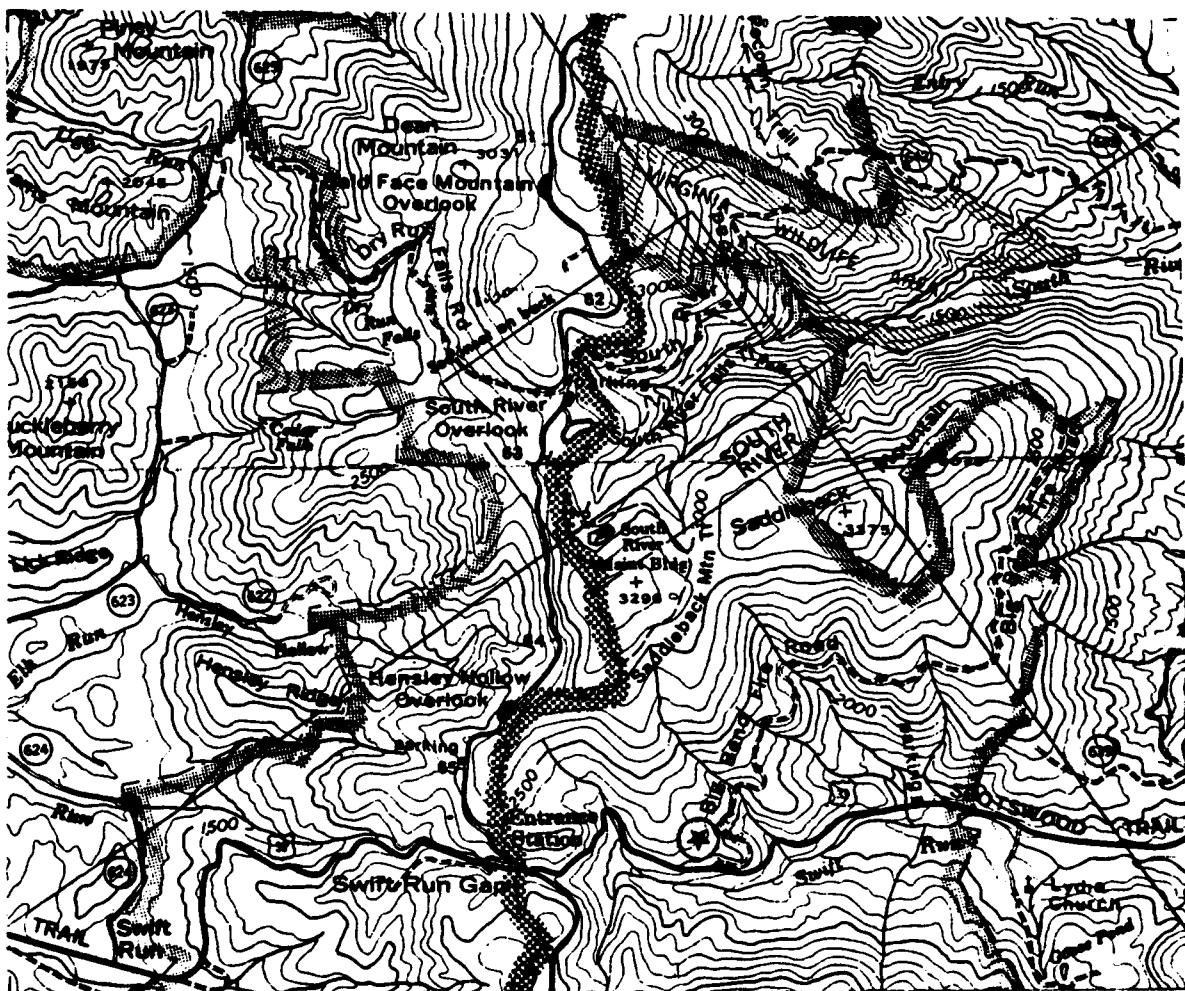
Nutrient element concentrations (in ppm) in simulated acid rain solutions of three acidities following a 2 hour exposure to northern red oak leaves at two sites

Exposure #3 Shenandoah National Park									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.029	.020	.037	.009	.047	.037	.025	.054	.006
K	5.87	2.44	4.32	4.25	1.97	3.16	3.21	2.41	2.18
Ca	3.64	3.67	4.04	1.42	1.64	1.60	1.10	1.22	1.24
Mg	.755	.491	.695	.242	.250	.303	.201	.184	.269
Mn	.532	.658	.252	.087	.126	.048	.029	.048	.000
Na	1.07	.714	.666	2.87	2.98	2.97	3.69	3.80	3.71
NH4	.20	.70	.70	.53	.70	.88	.35	.88	.53
NO3	4.4	4.7	5.1	.88	.88	.88	.53	.70	.88
pH	3.07	3.01	3.08	5.03	4.99	5.38	5.71	5.58	5.38
SO4	55.4	53.8	54.7	9.70	9.40	9.10	7.30	7.20	7.80

Fernow Experimental Forest									
Rep.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	.002	.010	.041	.019	.039	.044	.008	.021	.020
K	3.65	3.19	4.83	3.41	2.45	4.17	2.69	2.53	2.18
Ca	3.57	4.19	3.41	1.34	1.37	1.18	.912	.990	.862
Mg	.335	.358	.376	.160	.153	.152	.109	.107	.107
Mn	.407	.580	.629	.058	.078	.078	.010	.019	.029
Na	.624	.610	.595	2.86	2.86	2.82	3.60	3.57	3.58
NH4	1.4	.53	1.1	.88	.70	.70	.70	.35	.53
NO3	4.7	4.7	4.7	.88	.88	.88	.70	.70	.70
pH	3.12	3.12	3.07	4.88	4.72	5.02	5.71	5.77	5.70
SO4	54.0	53.7	54.4	9.40	9.20	9.00	7.20	7.40	7.60

Nutrient element concentrations (in ppm) of simulated acid rain solutions of three acidities in plastic bags without leaves. These solutions served as controls to solutions in which northern red oak leaves were placed following three harvests (Har.)

Har.	pH 3.0			pH 4.3			pH 5.6		
	1	2	3	1	2	3	1	2	3
P	0	.062	.012	0	.026	0	0	.018	.010
K	1.55	.478	.527	0	0	.148	.849	0	.170
Ca	5.14	1.14	1.08	2.66	.887	1.04	2.24	.872	.778
Mg	.118	.116	.103	.045	.092	.112	.034	.083	.083
Mn	0	.007	.000	0	.030	.000	.000	0	0
Na	5.53	.967	.591	6.32	2.15	2.90	8.98	3.96	3.77
NH ₄	.70	1.2	1.2	.20	.53	.88	.20	1.2	1.1
NO ₃	3.9	4.4	4.9	.70	.20	.88	.70	.53	.70
pH	3.08	3.06	2.97	4.37	4.34	4.41	5.41	5.43	5.73
SO ₄	46.8	48.1	55.4	6.50	7.30	9.60	10.5	8.40	6.80



Location of the research site in the Shenandoah National Park, Greene Co., Va. The site, designated by a star, can be located on the Swift Run U. S. G. S., 1:62,500 quadrangle at coordinates $38^{\circ} 2'$ North latitude, and $78^{\circ} 32'$ West longitude.

Location of the research site in the Fernow Experimental Forest, Tucker Co., W. Va. The site, designated by a star, can be located on the Parsons U. S. G. S., 1:62,500 quadrangle at coordinates 39° 3' North latitude, and 79° 40' West longitude.

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