Copyright Warning

Effects of ozone and acid mist on foliar leaching from eastern white pine and sugar maple

GARY M. LOVETT AND JEAN G. HUBBELL

Institute of Ecosystem Studies, The New York Botanical Garden, Mary Flagler Cary Arboretum,
Box AB, Millbrook, NY 12545, U.S.A.

LOVETT, G. M., and HUBBELL, J. G. 1991. Effects of ozone and acid mist on foliar leaching from eastern white pine and sugar maple. Can. J. For. Res. 21: 794–802.

Upper canopy branches of mature eastern white pine (*Pinus strobus* L.) and sugar maple (*Acer saccharum* Marsh.) were exposed in the field to ozone (25, 70, or 140 ppb) for 5 h, followed by acid mist (pH 5.0 or 3.8) for 1 h, and the exchange of major ions between the mist and the foliage was measured. The two species responded similarly to the pollutants: ozone exposure did not affect canopy exchange of any ions, but the pH 3.8 mist approximately doubled the leaching of Ca^{2+} and Mg^{2+} relative to the pH 5.0 mist. Hydrogen ions were released from the branches of both species in the pH 5.0 treatment but taken up from solution in the pH 3.8 treatment. Consideration of ionic balance in the chemical exchange indicates that organic acids were released from the branches of both species. In the white pine, it appears that these acids were deprotonated in the pH 5.0 solution, but not in the pH 3.8 solution. In the sugar maple, some acid deprotonation appears to have occurred under both pH treatments. In a related experiment, sugar maple branches that were moderately damaged by pear thrips (*Taeniothrips inconsequens* Uzel) did not have canopy exchange rates different from undamaged branches. Canopy exchange in the damaged branches did not respond to ozone treatment. Hydrogen ions were retained at pH 3.8 and released at pH 5.0, as in the undamaged branches. In the damaged branches, leaching of Ca^{2+} and Mg^{2+} tended to be higher at pH 3.8, although the results were not statistically significant. Overall, we conclude that short-term ozone exposures that do not produce visible damage do not affect foliar leaching, but that the acidity of rain can have a significant effect on Ca^{2+}, Mg^{2+}, and H^+ exchange in white pine and sugar maple canopies. The net effect of those canopies on the acidity of the rain passing through them will depend on the initial acidity of the rain.

LOVETT, G. M., et HUBBELL, J. G. 1991. Effects of ozone and acid mist on foliar leaching from eastern white pine and sugar maple. Can. J. For. Res. 21 : 794–802.

Des branches de pin blanc (*Pinus strobus* L.) et d'érable à sucre (*Acer saccharum* Marsh.) matures, situées dans la partie supérieure du couvert, furent exposées sur place à 25, 70 ou 140 ppb d'ozone pendant 5 h, suivi d'un brouillard acide à pH 5,0 ou 3,8 pendant 1 h, et les échanges entre le brouillard et le feuillage furent mesurés pour les principaux ions. Les deux essences ont réagi de la même façon aux polluants. L'exposition à l'ozone n'a affecté l'échange d'aucun ion dans le couvert, mais le brouillard à pH 3,8 a approximativement doublé le lessivage du Ca^{2+} et du Mg^{2+} comparé au brouillard à pH 5,0. Des ions hydrogène étaient libérés par les branches des deux essences avec le traitement à pH 5,0 et prélevés de la solution avec le traitement à pH 3,8. La balance ionique dans les échanges chimiques indique que des acides organiques étaient libérés des branches des deux essences. Chez le pin blanc, il semble que ces acides avaient perdu des protons avec la solution à pH 5,0 alors que ce n'était pas le cas avec la solution à pH 3,8. Chez l'érable à sucre, une certaine perte de protons par acidification semble être survenue avec les traitements aux deux pH. Dans une expérience reliée à la première, les branches d'érable à sucre qui étaient moyennement endommagées par le thrips du poirier (*Taeniothrips inconsequens* Uzel) n'avaient pas de taux d'échange différents des branches non endommagées. Les échanges n'étaient pas affectés par le traitement à l'ozone chez les branches endommagées. Les ions hydrogène étaient retenus à pH 3,8 et relâchés à pH 5,0, comme chez les branches non endommagées. Dans les branches endommagées le lessivage de Ca^{2+} et de Mg^{2+} avait tendance à être plus élevé à pH 3,8 même si la différence n'était pas statistiquement significative. En résumé, nous concluons que des expositions à l'ozone de courte durée, qui ne produisent pas de dommages visibles, n'affectent pas le lessivage foliaire mais que l'acidité de la pluie peut avoir un effet significatif sur les échanges de Ca^{2+}, de Mg^{2+} et de H^+ dans les couverts de pin blanc et d'érable à sucre. Les effets nets de ces couverts sur l'acidité de la pluie qui les traverse dépendra de l'acidité initiale de la pluie.

[Traduit par la rédaction]

Introduction

Deficiencies of K, Ca, and Mg have been suggested as potential causal factors of recent forest decline in eastern North America and central Europe (Tomlinson 1983; Ulrich et al. 1980; Zoettl and Huettl 1986; Schulze 1989; Bernier and Brazeau 1988). Excessive leaching of nutrients from the foliage of trees as a result of pollutant exposure may initiate or accelerate nutrient deficiencies (Krause et al. 1982), although some foliar leaching occurs naturally in all plants (Tukey 1980). The pollutants most often mentioned as enhancing foliar leaching are acidic wet deposition (rain, mist, fog, and dew) and ozone. For acidic deposition, the

proposed mechanism is the exchange of deposited H^+ for Ca^{2+}, K^+, and Mg^{2+} on exchange sites in the cuticle, epidermal cell walls, or apoplastic spaces in the foliage (e.g., Tukey 1980; Lovett et al. 1985). Ozone, on the other hand, is suspected of damaging cell membranes, causing leakage of cellular contents, which may then be lost via leaching in subsequent rain events (Krause et al. 1982; Evans and Ting 1974).

Several studies have attempted to determine these effects experimentally. As for acid rain, studies done on seedlings have shown statistically significant effects on leaching only

for solution pH values below 3.3 (Wood and Bormann 1975; Scherbatskoy and Klein 1983). Schier (1987) sprayed a 12-year-old red maple (*Acer rubrum* L.) plantation with acidified mist and found no significant increases in foliar leaching at pH 4.2 relative to pH 5.2, but statistically significant increases in leaching of Ca^{2+}, Mg^{2+}, and Fe^{3+} at pH 3.2. Values of pH below 3.3 occur very infrequently in rain in eastern North America and Europe, but are more common for fogs on mountaintops (Lovett et al. 1982; Weathers et al. 1988) and in southern California (Waldman et al. 1982). Horntvedt et al. (1980) reported increased leaching of cations from Norway spruce (*Picea abies* L.) trees sprayed with acidified rain, but the results were not analyzed statistically. Thus, the experimental evidence is somewhat ambiguous, but generally does not indicate strong effects of acid rain on foliar leaching at typical ambient acidities of rain in eastern North America (pH 3.8–4.5). Lovett et al. (1985), using an approach based on the charge balance in natural forest throughfall, inferred that acid rain in Tennessee doubled cation leaching from oak (*Quercus*) and yellow-poplar (*Liriodendron tulipifera* L.) forests. This inference involved assumptions about the preindustrial chemistry of throughfall, which could not be tested.

Only two studies have examined the effects of ozone exposure on foliar leaching: Krause et al. (1982) showed a small increase in Ca^{2+} and Mg^{2+} leaching from Norway spruce seedlings as a result of ozone exposure, but Skeffington and Roberts (1985), in an attempt to repeat the experiment on Scots pine (*Pinus sylvestris* L.), could find no significant effects.

Our goal was to test the hypothesis that ozone and acid mist influence foliar leaching from white pine (*Pinus strobus* L.) and sugar maple (*Acer saccharum* Marsh.), both of which are important species in forests of eastern North America and are thought to be sensitive to air pollution (e.g., Reich et al. 1987; Botkin et al. 1972; Reich and Amundson 1985). To our knowledge, this study represents the first evaluation of the effects of ozone and acid mist on foliar leaching from mature trees.

Methods

Upper canopy branches of mature, field-grown white pine on the grounds of the Mary Flagler Cary Arboretum in Millbrook, New York, were studied using a 20-m scaffold tower erected in a grove of trees during the summer of 1987. A similar study was performed in a nearby sugar maple stand during the summer of 1988. We used branch chambers (Fig. 1) to expose the branches to known concentrations of ozone and acid mist (Hubbell and Lovett 1988). A chamber consisted of a transparent Teflon bag (0.05 mm wall thickness) of about 0.8 m^3 volume, suspended from an external frame attached to the tower. Air was blown through the chamber at about 1.5 m^3/min, after having passed through a charcoal filter (to remove ambient ozone) and over an ultraviolet light to add ozone to the air in a controllable concentration. The air also passed through a coarse-particle filter to remove any charcoal dust. The air was diverted laterally upon entry into the chamber to prevent excessive ventilation of the branch, and the positive pressure from the blower inflated the chamber. The air exchange in the chamber was approximately 2 air changes per minute, permitting the temperature in the chamber to remain within 3°C of ambient.

Mist was applied to the branch through spray heads that used pressurized air to atomize a stream of artificial rain. The number and position of the spray heads were different in the 1987 and 1988

experiments, but the total amount of water delivered was 2000–2500 mL/h in both years. This amount of water is equivalent to about 2–2.5 mm of rain over the approximately 1-m^2 horizontal projected area of the chambers. Although the droplet size spectrum of the mist was not measured, the droplets were small enough to disperse within the chamber but large enough to deposit on the branches by gravitational sedimentation. During the misting periods, the branches were kept wet and dripping; we manually redirected the spray as necessary to produce a uniform spray over the entire branch.

Each experiment involved exposing branches to ozone for 5 h, and then misting for 1 h. This treatment mimicked a typical summertime situation in which high ozone concentrations in the late morning and afternoon are followed by a late-afternoon rain shower. Three ozone levels were chosen, based on our (unpublished) ozone monitoring data: 25 ppb, representing a "clean air" situation; 70 ppb, representing a typical summer day at our location; and 140 ppb, representing a high concentration for our location. These concentrations did not produce any visible ozone damage on these branches. Two acid levels were used in the mist: pH 5.0, representing a background condition, and pH 3.8, representing a typical pH for a summer rainstorm in this area (e.g., pH 3.8 was the mean pH of rainstorms occurring at our site during June–August 1988). The mist solution was an artificial rain that contained salts in concentrations characteristic of rainfall in this area and that was acidified to the proper pH with H_2SO_4. The concentrations of other ions used in the mist solution were (in mg/L): Ca^{2+}, 0.08; Mg^{2+}, 0.05; Na^+, 0.07; K^+, 0.03; NH_4^+, 1.2; NO_3^-, 1.8; and Cl^-, 0.15.

We conducted our experiments on three white pine and two sugar maple trees, using several branches from each tree, for a total of nine experimental branches per species. All nine branches received all six treatments (three ozone × two acid mist), in random order, between mid-July and early September. This period was chosen because it was after the end of leaf expansion and before the onset of senescence in these trees. Because the branches were treated multiple times, we waited at least 4 days between treatments of the same branch to permit recovery from any effects of the previous treatment. The 4-day respite period was chosen because Sutton and Ting (1977) reported that *Phaseolus vulgaris* L. plants recover from acute ozone injury (800 ppb for 1 h) in 3–5 days, depending on environmental conditions. Botkin et al. (1972) reported that some white pine recover from acute ozone injury (700–900 ppb for 7–10 h) in 3–7 days, while some others that develop visible symptoms never recover at all. We know of no studies on repair of injury from low-level ozone exposure (e.g., 25–140 ppb for 5 h used in this study), but we assume that it would be faster than recovery from acute exposure.

This experimental design allows maximum replication of the treatments for a given position of the tower, but does not allow direct examination of any cumulative effects, because the branches did not receive repeated exposures to the same treatment. The branches were exposed to ambient air and rainfall between experiments. However, we waited at least 24 h after the end of a natural rainfall before beginning an experimental leaching treatment. We analyzed the data for trends in the mean canopy exchange rates over the course of the experiment, which could give some indication of cumulative effects due to both experimental and ambient exposure.

The experiment was designed so that all nine replicate branches were used during one "rotation" before a new rotation was begun. Each rotation lasted approximately 1 week. The mist acidity was the same for all branches during any given rotation; the acidity for the first rotation was chosen randomly, then the acidity was alternated between the two treatment values (pH 5.0 and 3.8) for the subsequent rotations. Thus, over the course of the entire experiment there were nine replicates within each treatment cell. For each rotation, there were three replicates of each ozone level at a single mist acidity level. This design permitted us to examine the
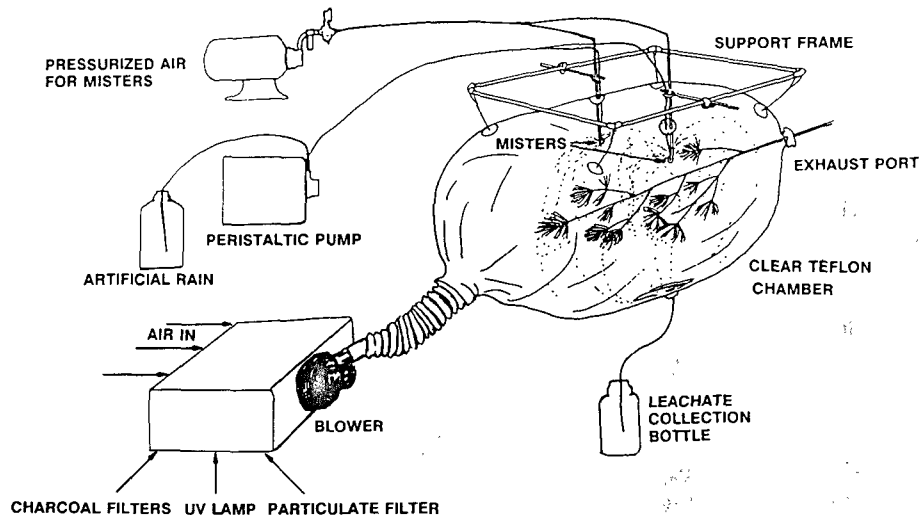
FIG. 1. Schematic diagram of branch chamber apparatus. Support frame is suspended from a canopy tower, while the branch remains attached to the tree.

trend of the mean exchange flux during the course of the experiment. At the end of the experiment, the branches were harvested and leaf area (one-sided area of leaves only, no twigs) was measured using a Li-Cor 3100 leaf area meter.

During 1988, when the sugar maple experiments were run, there was an outbreak of pear thrips (*Taeniothrips inconsequens* Uzel) on sugar maples throughout New York and New England. We were fortunate in that of the four sugar maples accessible from our tower, two were largely unaffected by the thrips, while two others were moderately damaged. The moderately damaged trees were not defoliated, but had undersized, withered-looking leaves that were a darker green than normal. (Pear thrips feeds on margins of leaves while they are still in the bud, and the leaves are generally not perforated when they emerge.) We took advantage of this situation by initiating a separate experiment to test ozone and acid rain effects on foliar leaching from the thrips-damaged leaves. Six branches were used on the two damaged trees in an experimental design incorporating two ozone levels (25 and 140 ppb) and two mist acidities (pH 5.0 and 3.8). Experimental procedures were exactly the same as for the experiment on undamaged branches.

Three or four chambers were run simultaneously on each day of experimental treatment. First, each branch to be treated was rinsed very briefly with a spray of deionized water such that all parts of the branch were wet and dripping for about 30 s. This rinse was intended to remove dry-deposited surficial material from the branch without leaching internally derived ions. The branches were shaken gently to remove excess water, then installed in chambers, and the ozone exposures were begun, usually at about 10:00. Because of the time required to install all branches in their chambers, the branches were generally dry by the time the ozone exposures began. Ozone concentration and temperature were measured in each chamber at approximately 20-min intervals. Ozone was measured with a Dasibi 1008-AH ozone analyzer calibrated before the field season from the National Bureau of Standards' traceable standards at the New York State Department of Environmental Conservation's Air Pollution Laboratory in Albany, New York. After 5 h, the ozone generation was stopped and the misting was begun. Leachate was collected through drains at the bottom of the chambers. After 1 h of misting, the leachate solutions were returned to the laboratory where they were filtered through Whatman 42 filters, and the pH and specific conductance were measured. Samples were then stored at 4°C for further chemical analysis. Analysis for SO_4^{2-}, NO_3^-, and Cl^- was performed (by ion chromatography) within 1 week, and analyses for Ca^{2+} and Mg^{2+} (by inductively coupled plasma emission spec-

troscopy), K^+ and Na^+ (by atomic absorption spectroscopy), and NH_4^+ (by Technicon autoanalyzer – indophenol method) were performed within 4 weeks.

Exchange fluxes (amounts of uptake or release) of ions from the branches were calculated as the difference between the amount of ion collected in the leachate and the amount in the mist applied to the branch. Both leaves and twigs were misted in the experiments, but we could not separate the contributions of each to the total exchange flux. Of the total volume of artificial mist delivered to the chambers, some unknown fraction was lost through the air outlet ports and the rest was deposited on branch and chamber surfaces. A small portion of this deposited water evaporated and the rest dripped into our collection bottle. To account for the evaporation, we added Br^- to the artificial mist as a tracer. Preliminary experiments showed no interaction (uptake or exchange) of Br^- with white pine or sugar maple foliage, indicating that the Br^- could be used as an inert tracer for evaporative loss. We added about 3 mg/L Br^- to the solution in the form of NH_4Br. Bromide concentrations were analyzed by ion chromatography.

The exchange fluxes of the ions were calculated as

$$[1] \qquad F = \frac{[C_L - (C_M BR)]V_L}{A}$$

where F is the exchange flux ($\mu g/m^2$), C_L is the concentration of the ion in the leachate, C_M is the concentration in the mist, V_L is the volume of the leachate, A is the one-sided area of the leaves, and BR is the bromide ratio (the concentration of Br^- in leachate divided by the concentration in the mist). The measured bromide ratios indicated that on average, 9% ($\pm 4\%$ sd) of the deposited water evaporated from the branch and chamber surfaces. "Blank" experiments were run without branches in the chamber to verify that no release or uptake of ions occurred from the experimental apparatus.

Results

In our initial analysis of the white pine data set, we noticed a relationship between the amounts of certain ions leached in any given experiment and the amount of natural precipitation the branch had experienced prior to the experiment. We therefore used the amount of precipitation that fell in the period since the previous experimental treatment of a branch as a covariate in the leaching analysis for both sugar maple and white pine. This precipitation covariate was not significant for any of the sugar maple data, but was signifi-

TABLE 1. Analysis of variance results (*p*-values) for foliar leaching experiments
(see text for explanation)

Ion	Tree		Precipitation		Ozone		Acid mist	
	WP	SM	WP	SM	WP	SM	WP	SM
Ca^{2+}	ns	ns	<0.001	ns	ns	ns	<0.001	<0.001
Mg^{2+}	ns	ns	<0.001	ns	ns	ns	<0.01	<0.01
K^+	ns	ns	<0.01	ns	ns	ns	ns	ns
Na^+	<0.05	ns	<0.01	ns	ns	ns	<0.05	ns
NH_4^+	ns	ns	ns	ns	ns	ns	ns	ns
H^+	ns	ns	<0.05	ns	ns	ns	<0.001	<0.001
NO_3^-	<0.05	ns	<0.001	ns	ns	ns	ns	ns
SO_4^{2-}	ns	ns	ns	ns	ns	ns	ns	ns
Cl^-	ns	ns	<0.05	ns	ns	ns	ns	ns

NOTE: WP, white pine; SM, sugar maple. The ozone × acid mist interaction was not significant for any ion in either species. ns, $p > 0.05$.

cant for Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, NO_3^-, and Cl^- in white pine, as shown in Table 1. The relationship between amount leached and antecedent precipitation was always negative, indicating that higher amounts of precipitation resulted in lower amounts of leaching in the subsequent experiment. This is consistent with the hypothesis that rain washes out an available pool of ions in or on the branch and that this pool may take several days to be replenished (Reiners and Olson 1984). We do not know why this relationship was apparent in white pine but not in sugar maple, but it may be related to natural rainfall patterns in the two different years that these species were used.

We tested whether the individual trees of each species were different in their leaching behavior by performing three-way analysis of covariance, using antecedent precipitation as the covariate and tree, ozone concentration, and mist acidity as the main effects. For all ions in sugar maple, and for all ions except Na^+ and NO_3^- in white pine, the tree effect was not significant (Table 1). Given the lack of significant differences between individual trees for most ions, and the marginal significance for Na^+ and NO_3^-, we pooled all trees in our further analysis of variance and analysis of covariance tests.

The main effects tested in this experiment were ozone concentration and mist acidity. As shown in Table 1, the ozone effect was not significant for any ions in either species. The acidity effect was highly significant ($p < 0.01$) for Ca^{2+}, Mg^{2+}, and H^+ in both species and marginally significant ($p < 0.05$) for Na^+ in white pine. The interaction between ozone and mist acidity was not significant for any ions in either species.

To illustrate the effects, the group means for Ca^{2+}, Mg^{2+}, K^+, and H^+ are shown in Figs. 2 (white pine) and 3 (sugar maple). Note that the *y*-axis scales are different in Figs. 2 and 3, illustrating that the sugar maple branches released much more Ca^{2+}, Mg^{2+}, and K^+ per unit leaf area than did those of the white pine. The complete lack of an ozone effect is striking in these graphs. For Ca^{2+} and Mg^{2+}, the pH 3.8 treatment approximately doubled foliar leaching relative to the pH 5.0 treatment. For H^+, the pH 5.0 treatment resulted in a net release of H^+ from the branches (acidification of the solution), while the pH 3.8 treatment resulted in a net uptake of H^+ by the branches

(neutralization of the solution). For K^+, the pH 3.8 treatment means are higher than those for pH 5.0, but not significantly different at $p = 0.05$.

To check for trends in canopy exchange during the course of the experiments, we computed the mean for each rotation, which was adjusted for the precipitation covariate in the case of white pine (least-square means, SAS general linear model procedure, SAS Institute, Cary, NC). These means are plotted versus rotation number for Ca^{2+}, Mg^{2+}, K^+, and H^+ in Figs. 4 and 5. These graphs show no general trends in canopy exchange from either species over the course of the experimental periods, except for the white pine pH 3.8 data, which showed less exchange of K^+, Ca^{2+}, Mg^{2+} in the later rotations.

The mean exchange fluxes of all the ions in the pH 3.8 and 5.0 treatments are expressed on a charge-equivalent basis in Table 2. For white pine, under the pH 5.0 treatment, the base cations lost from the branches are dominated by K^+, but under the pH 3.8 treatment, Ca^{2+} is the dominant base cation that is leached. For sugar maple, Ca^{2+} and K^+ contribute nearly equally to the total cation loss in the pH 5.0 treatment, but Ca^{2+} clearly dominates in the pH 3.8 treatment. While the pH 3.8 net exchange (anions–cations) for white pine is nearly in balance, the pH 5.0 exchange for white pine, and the sugar maple data for both pH levels, show significant anion deficits. Our interpretation of these deficits will be discussed later.

Direct comparison of the leaching rates from the two tree species is not statistically valid because the design was not randomized for this effect (all white pine experiments were done in 1987, and all sugar maple experiments were done in 1988). However, examination of Figs. 2 and 3 and Table 2 suggests major differences in the leaching rates of the two species under all conditions, with the sugar maple always showing higher rates of chemical exchange per unit leaf area.

In the experiment on the thrips-damaged branches of sugar maple, analysis of variance indicated no ozone effect on leaching of any ions. The only statistically significant effect of mist acidity was on H^+ exchange, which shifted from H^+ release in the pH 5.0 treatment to H^+ retention in the pH 3.8 treatment, similar to the effect on undamaged branches of sugar maple and white pine. Mean leaching rates of Ca^{2+}, Mg^{2+}, and K^+ in the pH 3.8 treatments were 46,

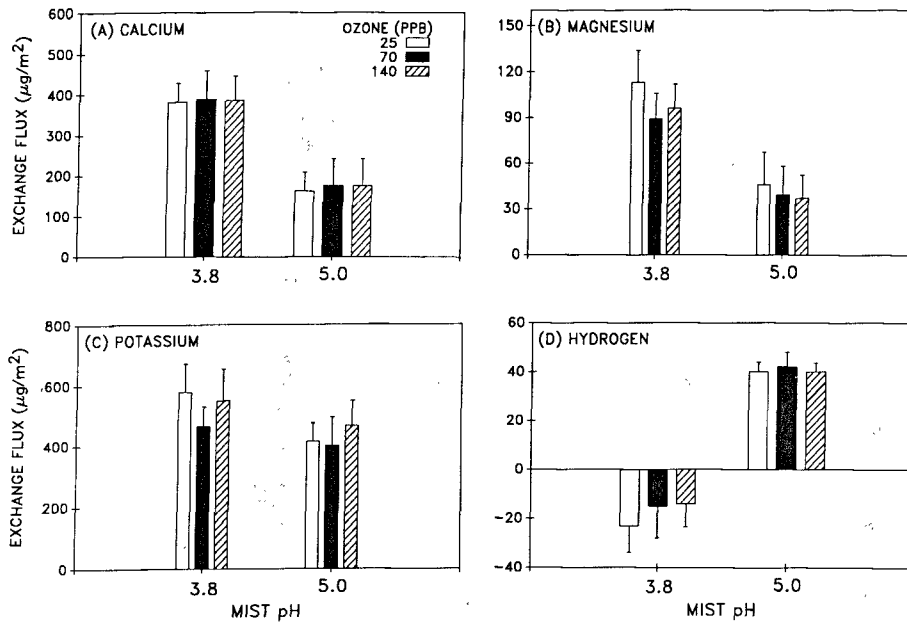FIG. 2. Canopy exchange of four ions in white pine (in μg/m^2 leaf area per 1 h of mist exposure) for two mist acidities and three ozone levels.

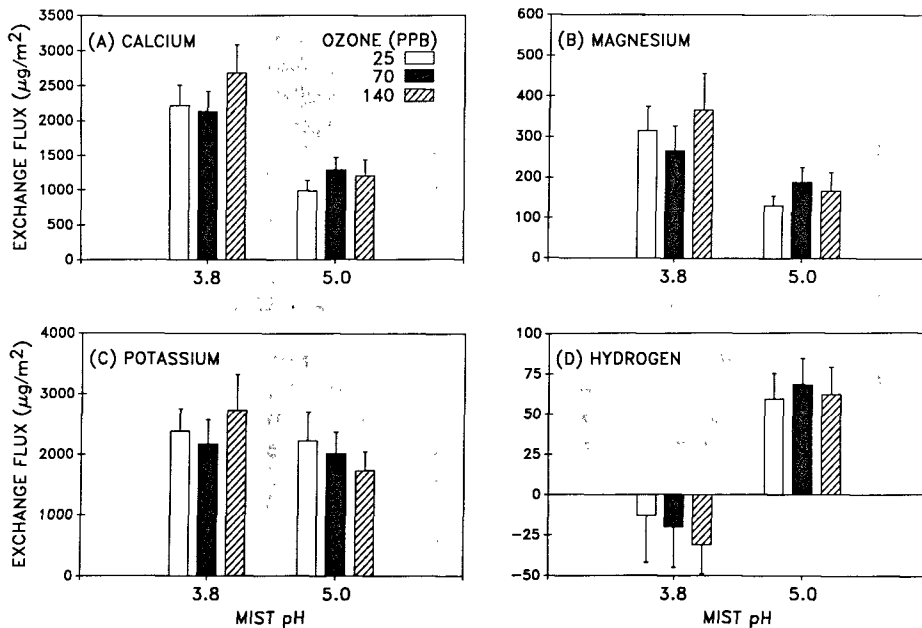FIG. 3. Canopy exchange of four ions in sugar maple (in μg/m^2 leaf area per 1 h of mist exposure) for two mist acidities and three ozone levels.

49, and 9% greater, respectively, than those in the pH 5.0 treatment, but none of those differences were statistically significant. Note that there were only six replicate branches in this experiment, compared with nine in the experiments on undamaged branches. Mean canopy exchange rates were, in general, not significantly different between damaged and undamaged sugar maple (using t-tests for each pH treatment and each ion). The single exception was for K^+ leaching, which was significantly ($p < 0.05$) higher in the undamaged branches in the pH 3.8 treatment.

Discussion

Perhaps the most striking feature of these results is the similarity of response in the two species, despite very dif-

ferent base-line rates of canopy exchange. In both species chemical exchange showed no response to ozone exposure, and in both species there was a strong response of Ca^{2+}, Mg^{2+}, and H^+ exchange to mist acidity, i.e., leaching of Ca^{2+} and Mg^{2+} approximately doubled, and H^+ exchange switched from retention at pH 3.8 to release at pH 5.0. The similarity of the responses between a broad-leaved deciduous tree and a needle-leaved evergreen conifer impart some confidence that these results may be applicable to trees in general.

Our data do not support the hypothesis that ozone exposure increases foliar leaching. Two caveats to this conclusion are worth noting. First, our ozone exposures did not produce visible damage to the leaves. In situations where
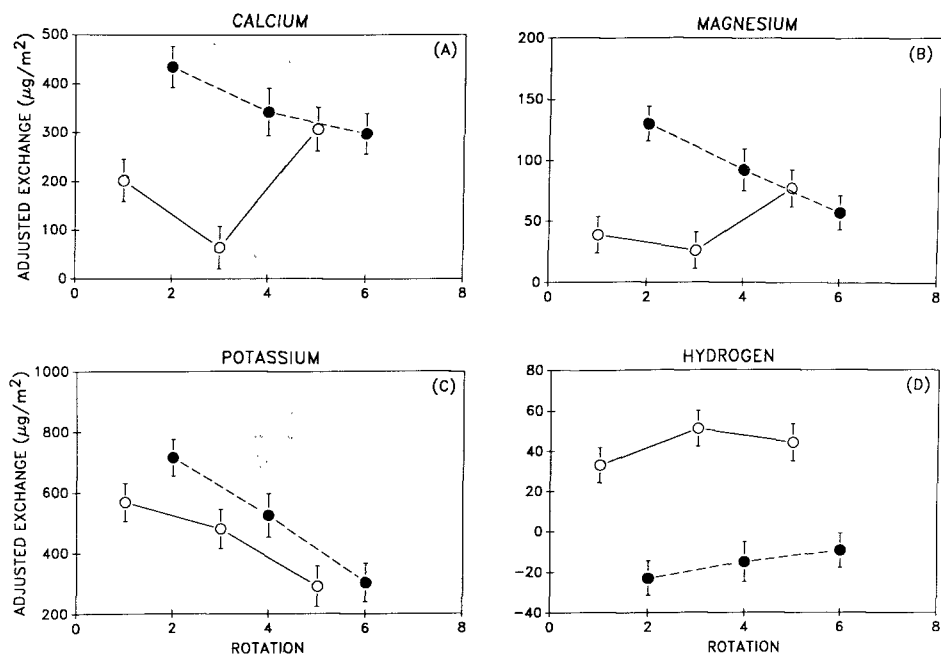
FIG. 4. Canopy exchange in white pine as a function of rotation number. Canopy exchange values are adjusted to account for the covariate "precipitation amount" (see text). Rotations lasted approximately 1 week, and the sequence represents a time course through the experimental period. ○, pH 5.0; ●, pH 3.8.
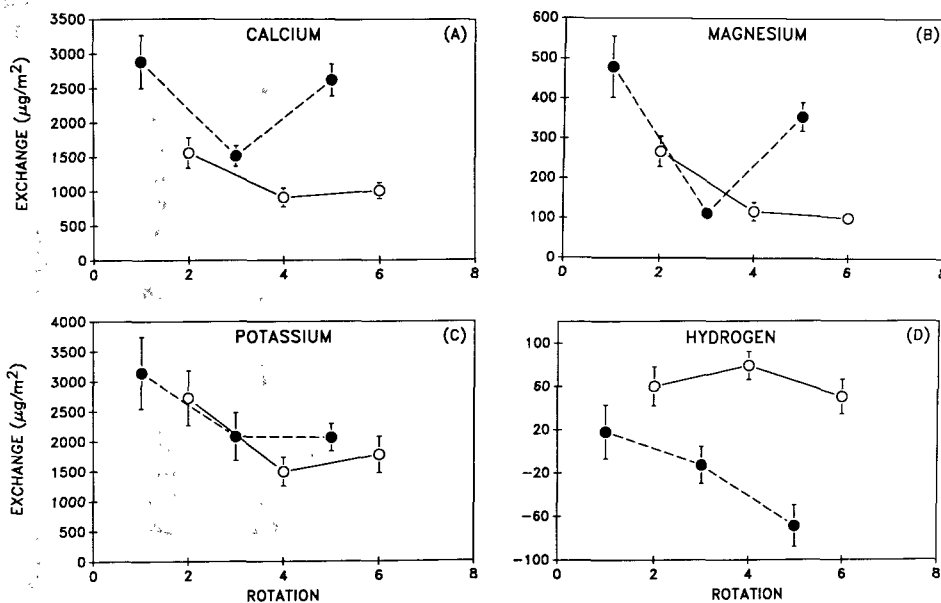

FIG. 5. Canopy exchange in sugar maple as a function of rotation number. The covariate precipitation amount was not significant for sugar maple, so these data were not adjusted. Rotations lasted approximately 1 week, and the sequence represents a time course through the experimental period. ○, pH 5.0; ●, pH 3.8.

ozone levels are high enough, and plants are sensitive enough, to result in visible necrosis, we would expect that foliar leaching of nearly all ions would increase, as it does in response to other injuries (Tukey and Morgan 1963). However, we suspect that foliar leaching would be a comparatively minor problem for a plant that had experienced substantial necrosis as a result of ozone injury.

Second, our ozone exposures were for 5-h periods, and we did not evaluate effects of chronic ozone exposure on foliar leaching. Photosynthetic and growth responses to ozone have been demonstrated in white pine, sugar maple,

and other species to result from the cumulative effects of long-term exposure (e.g., Reich and Amundson 1985). While chronic effects on foliar leaching remain a possibility, the proposed mechanisms of the response, membrane damage followed by solute leakage into intercellular spaces, suggest a short-term phenomenon. If a cumulative effect of chronic exposure were to occur, one would expect these branches to have exhibited increased exchange as our experiment progressed, as a result of both experimental and ambient ozone exposure. Figures 4 and 5 show that this did not occur consistently, and that the trends for the pH 3.8 treatments in

TABLE 2. Mean canopy exchange (μequiv./m^2) of the ions measured in this study, calculated from eq. 1

	White pine		Sugar maple	
	pH 3.8	pH 5.0	pH 3.8	pH 3.0
Cations				
Ca^{2+}	19 (1.6)	8.2 (1.4)	117 (9.4)	58 (5.2)
Mg^{2+}	8.2 (0.83)	3.3 (0.83)	26 (3.3)	13 (1.7)
K^+	14 (1.3)	11 (1.1)	62 (6.6)	51 (5.5)
Na^+	8.4 (1.2)	4.6 (0.59)	6.0 (1.3)	7.3 (1.3)
NH_4^+	8.1 (2.5)	3.0 (2.8)	−2.6 (8.3)	−7.7 (4.0)
H^+	−17 (6.2)	41 (2.5)	−21 (13)	63 (8.9)
Total	40 (8.3)	71 (5.6)	187 (25)	186 (17)
Anions				
SO_4^{2-}	21 (6.4)	21 (2.4)	57 (5.2)	74 (7.5)
NO_3^-	15 (1.7)	11 (1.2)	52 (8.1)	53 (6.2)
Cl^-	7.2 (0.85)	4.4 (0.73)	1.3 (1.8)	3.0 (2.0)
Total	43 (7.8)	36 (3.6)	111 (12)	131 (14)
Anion deficit	−2.8 (7.5)	35 (3.8)	76 (18)	55 (8.5)

NOTE: Numbers in parentheses are standard errors. Positive numbers represent efflux from the branches, and negative numbers represent influx. Data are for undamaged branches only.

white pine were generally toward less exchange in the later rotations of the experiment. We are not certain why this decrease occurred; it may indicate that the foliar pool of ions in white pines declined during the course of the season, but it is not clear why this should be reflected primarily in the pH 3.8 data. Explanations of Figs. 4 and 5 must await a more detailed knowledge of the physiology of this exchange process; at present, all that can be said is that the data are not consistent with a hypothesis of increased foliar leaching caused by cumulative ozone exposure.

The strong effect of mist acidity on Ca^{2+} and Mg^{2+} leaching, and the lack of any effect on the anions in either species, suggest a cation exchange mechanism. However, the exact location of the exchange sites, either on, within, or beneath the cuticle, remains unknown. The relative contributions of branches and foliage to the cation loss is also not known. The fact that a 15-fold increase in H^+ concentration (pH 5.0 to 3.8) resulted in only a twofold increase in base cation release indicates a rather low exchange efficiency for this reaction.

The lack of a significant acid effect on K^+ leaching may result from the fact that K^+ is present in plants mostly as an electrolyte. Being unbound to the plant tissue, K^+ could be subject to extensive leaching with whatever solution is applied. Calcium and Mg^{2+}, being more strongly bound in cell walls and other tissue, may require cation exchange eactions in order to be mobilized, and thus may respond more strongly to acid treatment.

The anion deficits in Table 2 suggest that the branches release either (*i*) organic acids that deprotonate in solution to yield organic anions (which we did not measure) or (*ii*) salts of organic acids (e.g., potassium acetate). We note the rough equivalence of the H^+ released and the anion deficit in the pH 5.0 treatments of both species, which is consistent with the deprotonation of organic acids. It is likely that these organic acids are released into the pH 3.8 solutions as well, but in the case of white pine, their pK_a values are high enough so that they do not dissociate strongly at pH 3.8. Undissociated acidity has been measured by titration in natural throughfall samples by Cronan and Reiners

(1983), Hoffman et al. (1980), and Lovett et al. (1985). The fact that some dissociation appears to have occurred in the pH 3.8 treatment for sugar maple suggests that a different suite of organic acids may be released from that species.

The total efflux of non-H^+ cations (sum of Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+) increased in the pH 3.8 treatments, relative to pH 5.0, by 28 μequiv./m^2 in the white pine branches and 87 μequiv./m^2 in the sugar maple branches. To maintain a charge balance, a change in retention of H^+ or release of anions must occur in equivalent amounts. In the white pine, retention of H^+ accounted for 17 μequiv./m^2 (63%) of the change in non-H^+ cation release, while increased release of inorganic anions accounted for 7 μequiv./m^2 (26%). The missing 11% probably represents measurement errors or masking of H^+ retention by organic acid deprotonation in the pH 3.8 treatment. By masking we mean that additional H^+ could have been retained by the branches but that we would not be able to measure it because of simultaneous H^+ release by deprotonating organic acids in solution. For the sugar maple, H^+ retention appears to account for only 21 μequiv./m^2 (25%) of the change in non-H^+ cation release. It is not obvious how to account for the other 75%, since the release of inorganic anions actually decreases (though not significantly) in the pH 3.8 treatment. However, if our notions of organic acid deprotonation are correct, then the anion deficit of 76 μequiv./m^2 represents organic acids that deprotonated in solution to produce H^+ ions and organic anions. This could have masked 76 μequiv./m^2 of H^+ retention, suggesting that the actual amount of H^+ retention may have been as much as 97 μequiv./m^2. This approximates the sum of the changes in non-H^+ cation release (87 μequiv./m^2) and inorganic anion release (20 μequiv./m^2). The implication is that exchange for H^+ could account for all of the increase in leaching of non-H^+ cations in the sugar maple. The sulfuric acid in the pH 3.8 mist appears to inhibit slightly the release of inorganic anions, primarily SO_4^{2-}, from sugar maple.

The ion balance data for the pH 5.0 treatments imply that in the absence of acid rain, organic anions are major counter ions to cation leaching from both white pine and sugar maple, and that H^+ is the major cation leached. The H^+ uptake from the pH 3.8 solution is inferred to be a result of the cation exchange reaction, which is accelerated by the high H^+ concentration. The true extent of this reaction may be partially masked by organic acid deprotonation. Nonetheless, it is clear that the net effect of white pine or sugar maple canopies on the acidity of rain passing through them will depend on the initial acidity of that rain. The often-heard generalization that coniferous canopies acidify and deciduous canopies neutralize rain that falls on them appears to be only partially true.

While pH 5.0 may represent a typical value for unpolluted rain, our pH 5.0 treatment may not represent pristine conditions of canopy exchange. The SO_4^{2-} and NO_3^- pollutant deposition to these forests probably influences the leaching of these ions from our experimental branches, either through increased root uptake from the soil solution, or by washout of sulfur and nitrogen oxide gases deposited on the interiors of the leaves. Increased leaching of these anions from either source is likely to entrain some base cations, so that the level of foliar leaching of most ions in this study,

even in our "clean air, clean rain" treatments, is likely to be elevated over truly pristine conditions.

Extrapolation of these canopy exchange values to an entire canopy is not straightforward. Because the pH 3.8 treatment roughly doubled the release of Ca^{2+} and Mg^{2+} from the branches, one could say that an equivalent rain pH would be likely to double their release from whole canopies. This agrees with the result reported by Lovett et al. (1985) based on analysis of throughfall in deciduous canopies. However, this may overestimate the effect because much of the foliage in a forest canopy never experiences incident rainfall, but rather rainfall modified by foliage above. If the upper foliage reduces the acidity of the solution (acid precipitation case), then the leaching effect would be reduced at lower levels of the canopy. If the foliage naturally acidifies the solution (clean precipitation case), then the lower branches would see "acid rain" even under pristine conditions. Thus the net effect involves a rather complex interaction between the layers of foliage and the solution percolating through them. These interactions can be examined using multilayer throughfall models such as that developed by Lovett et al. (1989).

The physiological significance of foliar leaching depends on the ability of the trees to replace the lost nutrients by root uptake. Common sense indicates that if basic cations are in short supply, any increase in losses will be physiologically significant. Bernier and Brazeau (1988) suggest that deficiencies in K^+, and sometimes P, may be involved in the decline of sugar maple in Canada. The results of our study suggest that while acid rain may increase the leaching of K^+ from sugar maple foliage, the amount of increase is minor and cannot be discerned statistically given the high variance in leaching behavior. Schulze (1989) reports that cation (especially Mg^{2+}) deficiencies caused by inhibited root uptake and increased foliar leaching are the mechanisms by which acid deposition is damaging Norway spruce forests in Germany. Reich et al. (1988) examined short-term responses of potted white pine seedlings to ozone and acid rain, and found that acid rain increased the concentration of many nutrients (including K^+ and Ca^{2+}) in the foliage, probably as a result of increased mobilization of these elements in the litter and soil. Johnson et al. (1985) predicted such an effect on the basis of nutrient cycling models. Wood and Bormann (1975) found a similar result with white pine seedlings, although they found that foliar concentrations decreased again as pH was dropped below 3.0. In general, while there is some evidence that cation deficiencies exacerbated by acid-induced foliar leaching can lead to forest decline (e.g., Norway spruce, Schulze 1989), there is also contradictory evidence from greenhouse experiments, and the question remains undecided. It is clear from this study that realistic acid concentrations in rain can cause substantial changes in the canopy exchange of Ca^{2+}, Mg^{2+}, and H^+ in mature trees, and that the potential physiological and ecosystem-level effects of these changes deserve further careful research.

Acknowledgments

BERNIER, B., and BRAZEAU, M. 1988. Foliar nutrient status in relation to sugar maple dieback and decline in the Quebec Appalachians. Can. J. For. Res. 18: 754–761.

BOTKIN, D.B., SMITH, W.H., CARLSON, R.W., and SMITH, T.L. 1972. Effects of ozone on white pine saplings: variation in inhibition and recovery of net photosynthesis. Environ. Pollut. 3: 273–289.

CRONAN, C.S., and REINERS, W.A. 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. Oecologia (Berl.), 59: 216–223.

EVANS, L., and TING, I.P. 1974. Effect of ozone on ^{86}Rb-labeled potassium transport in leaves of Phaseolus vulgaris L. Atmos. Environ. 8: 855–861.

HOFFMAN, W.A., LINDBERG, S.E., and TURNER, R.R. 1980. Precipitation acidity: the role of the forest canopy in acid exchange. J. Environ. Qual. 9: 95–100.

HORNTVEDT, R., DOLLARD, G.J., and JORANGER, E. 1980. Effects of acid precipitation on soil and forest 2. Atmosphere-vegetation interactions. In Ecological Impact of Acid Precipitation, Proceedings of an International Conference, 11 Mar. 1980, Sandefjord, Norway. Edited by D. Drablos and A. Tollan. SNSF project, Oslo, Norway, pp. 192–193.

HUBBELL, J.G., and LOVETT, G.M. 1988. A chamber for ozone exposure and misting of branches on mature trees. In Response of Trees to Air Pollution: The Role of Branch Studies. Workshop Proceedings, 5–6 Nov. 1987, Boulder, CO. Edited by W.E. Winner and L.B. Phelps. U.S. Environmental Protection Agency, Corvallis, OR. pp. 120–129.

JOHNSON, D.W., RICHTER, D.D., LOVETT, G.M., and LINDBERG, S.E. 1985. The effects of atmospheric deposition on K, Ca, and Mg cycling in two deciduous forests. Can. J. For. Res. 15: 773–782.

KRAUSE, G.H.M., PRINZ, B., and JUNG, K.D. 1982. Forest effects in West Germany. In Air pollution and the productivity of the forest. Izaak Walton League of America, Washington, DC, pp. 297–332.

LOVETT, G.M., REINERS, W.A., and OLSON, R.K. 1982. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical impacts. Science (Washington, D.C.), 218: 1303–1304.

――――― 1989. Factors controlling throughfall chemistry in a balsam fir canopy: a modeling approach. Biogeochemistry, 8: 239–264.

LOVETT, G.M., LINDBERG, S.E., RICHTER, D.D., and JOHNSON, D.W. 1985. Effects of acidic deposition on cation leaching from three deciduous forest canopies. Can. J. For. Res. 15: 1055–1060.

REICH, P.B., and AMUNDSEN, R.G. 1985. Ambient levels of ozone reduce net photosynthesis in tree and crop species. Science (Washington, D.C.), 230: 566–570.

REICH, P.B., SCHOETTLE, A.W., STROO, H.F., TROIANO, J., and AMUNDSEN, R.G. 1987. Effects of ozone and rain on white pine (Pinus strobus) seedlings grown in five soils. I. Net photosynthesis and growth. Can. J. Bot. 65: 977–987.

REICH, P.B., SCHOETTLE, A.W., STROO, H.F., and AMUNDSEN, R.G. 1988. Effects of ozone and acid rain on white pine (Pinus strobus) seedlings grown in five soils. III. Nutrient relations. Can. J. Bot. 66: 1517–1531.

REINERS, W.A., and OLSON, R.K. 1984. Effects of canopy components on throughfall chemistry: an experimental analysis. Oecologia (Berl.), 63: 320–330.

SCHERBATSKOY, T., and KLEIN, R.M. 1983. Response of spruce and birch foliage to leaching by acidic mists. J. Environ. Qual. 12: 189–195.

SCHIER, G.A. 1987. Throughfall chemistry in a red maple provenance plantation sprayed with "acid rain." Can. J. For. Res. **17**: 660–665.

SCHULZE, E.D. 1989. Air pollution and forest decline in a spruce (*Picea abies*) forest. Science (Washington, D.C.), **244**: 776–783.

SKEFFINGTON, R.A., and ROBERTS, T.M. 1985. The effects of ozone and acid mist on Scots pine saplings. Oecologia (Berl.), **65**: 201–206.

SUTTON, R., and TING, I.P. 1977. Evidence for the repair of ozone-induced membrane injury. Am. J. Bot. **64**: 404–411.

TOMLINSON, G.H., II. 1983. Air pollutants and forest decline. Environ. Sci. & Technol. **17**: 246A–256A.

TUKEY, H.B., JR. 1980. Some effects of rain and mist on plants with implications for acidic precipitation. *In* Effects of acid precipitation on terrestrial ecosystems. *Edited by* T.C. Hutchinson and M. Havas. Plenum Press, New York. pp. 141–150.

TUKEY, H.B., JR., and MORGAN, J.V. 1963. Injury to foliage and its effect upon the leaching of nutrients from above-ground plant parts. Physiol. Plant. **16**: 557–564.

ULRICH, B., MAYER, R., and KHANNA, P.K. 1980. Chemical changes due to acid precipitation in a loess-derived soil in central Europe. Soil Sci. **130**: 193–199.

WALDMAN, J.D., MUNGER, J.W., JACOBS, D.J., FLAGAN, R.C., MORGAN, J.J., and HOFFMAN, M.R. 1982. Chemical composition of acid fog. Science (Washington, D.C.), **218**: 677–679.

WEATHERS, K.C., LIKENS, G.E., BORMANN, F.H., BICKNELL, S.H., BORMANN, B.T., DAUBE, B.C., JR., EATON, J.S., GALLOWAY, J.N., KEENE, W.C., KIMBALL, K.D., McDOWELL, W.H., SICCAMA, T.G., SMILEY, D., and TARRANT, R.A. 1988. Cloudwater chemistry from ten sites in North America. Environ. Sci. & Technol. **22**: 1018–1026.

WOOD, T., and BORMANN, F.H. 1975. Increases in foliar leaching caused by acidification of an artificial mist. Ambio, **4**: 169–171.

ZOETTL, H.W., and HUETTL, R.F. 1986. Nutrient supply and forest decline in southwest Germany. Water Air Soil Pollut. **31**: 449–462.