Rates of mineral element leaching from leaves of nine plant species from a southern Appalachian forest succession subjected to simulated acid rain

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HAINES, B., J. CHAPMAN AND C. MONK (Botany Department, University of Georgia, Athens, Georgia 30602). Rates of mineral element leaching from leaves on nine plant species from a forest succession subjected to simulated acid rain. Bull. Torrey Botanical Club 112:258-264. 1985.—Rates of mineral element leaching from plants subjected to simulated acid rain were determined for plants from a forest succession. Early successional plants were the herbs Erechtites hieracifolia and Erigeron canadensis and the early successional shrub-tree was Robinia pseudo-acacia. Later successional species were Pinus strobus, Carya illinoensis, Liriodendron tulipifera, Quercus prinus, Acer rubrum and Cornus florida. Simulated rain consisted of deionized water plus a salt and an acid component to produce pH values of 5.5, 4.5, 3.5 and 2.5. Solutions were applied through a raindrop simulator at 0.9 cm/hr for 10 periods of 1 hr each. Leachate from the leaves was collected and analyzed for NH₄—N, NO₃—N, K, Ca, Mg, and P. Rates of leaching ranged from 0.006 to 11.3 mg of element/10 dm²/hr. There were highly significant differences in leaching rates among species but no significant differences among pH treatments for the elements analyzed. Highest leaching rates occurred in Erechtites and Erigeron. The absence of a pH effect on leaching rates is consistent with the absence of evidence of acid rain damage to the leaves of the plants tested.

Key words: acid rain, leaching, element cycling, forest succession, Appalachian, leaves.

Acid rain occurs in Europe (Brosset 1973; Kallend et al. 1983), North America (Likens and Butler 1981), Central America (Johnson, Cole and Gessel 1979), and South America (Galloway et al. 1982; Haines et al. 1983). Acid rain can result from the release of oxides of S and N into the atmosphere from burning of fossil fuels and subsequent washout of these oxides in rainwater. Acid rain may also result from natural element cycling processes (Galloway et al. 1982; Haines 1983; Dosso, Guillaumet and Hadley 1981). Acid rain resulting from combustion of fossil fuels can be considered a disruption of background S and N cycling processes. This alteration of S and N cycling has the potential to disrupt element cycling processes between plants and soils upon which plant production is partly dependent. Understanding the magnitude and consequences of the disruptive effects of acid rain on nutrient cycling and plant production is critical to the development of alternative ecosystem management strategies which balance potential costs of controls of emissions of S and N oxides against potential environmental damage.

The leaf is the most physiologically active of plant organs exposed directly to acid rain. The present study was designed to determine the effects of simulated acid rain at pH values of 5.5, 4.5, 3.5, and 2.5 on rates mineral elements leach from leaves. The effects simulated acid rain droplets of pH 2.5, 2.0, 1.5, 1.0 and 0.5 had on the same leaves were reported earlier (Haines, Stefani and Hendrix 1980). The present study is part of a larger effort to characterize the effects of acid rain on the nutrient processing behaviors of leaves, leaf litter, roots, and soils from a southern Appalachian deciduous forest at the U.S. Forest Service Coweeta Hydrologic Laboratory, near Otto, North Carolina (Haines and Waide 1980).
Materials and Methods. The nine species selected for study represent dominants in various stages of southern Appalachian secondary succession. *Erigeron canadensis* L. and *Erechtites hieracifolia* (L.) Raf. are composites which together commonly comprise up to 50% of the biomass the first year of succession following forest clearcutting and herbicide treatment (Johnson and Swank, 1973). After 6 or more years *Robinia pseudacacia* L. dominates by forming dense thickets. It later thins out to be occasionally encountered within the deciduous forests. *Pinus strobus* L. was selected to represent the plantation pine stands in the area as well as the pines mixed with the hardwoods on the higher and drier ridge tops.

Within the mature hardwood forest at Coweeta, among the 42 species present, 6 were chosen which collectively comprise more than half of the stand basal area (Day and Monk 1974). This was as convenient number of species to investigate and as a group they probably account for about half of the nutrient processing by trees on the watershed. The more xeric sites favor *Carya glabra* (Miller) Sweet. The more mesic sites support *Liriodendron tulipifera* L., *Acer rubrum* L. and *Carya glabra* (Miller) Sweet. The more xeric sites support *Quercus coccinea* Muench. L., *Q. prinus* L. and *Q. velutina* L. and *Carya glabra* seeds and seedlings of *Q. coccinea* in soil from the deciduous forest and left in the winter, planted in 1 gallon plastic pots in soil from the hardwood forest and left in a forest clearing for 1 year. Insufficient seeds and seedlings of *Q. coccinea* were found so the species was not used. *Carya glabra* seedlings were also insufficient, thus commercially available *C. illinoensis* (Wangen.) K. Koch seeds were germinated and established in a hardwood forest soil. Stabilized potted plants were transported to a greenhouse facility in Athens, Georgia. The herbs *E. canadensis* and *E. hieracifolia* were germinated from seed and transplanted to Coweeta soil for the summer 1978 experiments and again for the summer 1979 study. From preliminary leaching experiments during summer 1978 it was determined that dust from within the greenhouse accumulated on plants at such high rates that leaching of elements from within the leaves was undetectable. During spring 1979, woody plants were re-potted in fresh soil from the deciduous forest at Coweeta and the plants were placed in chambers covered with 4 mil transparent polyethylene and ventilated with filtered air at 3.05 m/min. Air was filtered through Cambridge Filter Corporation (Syracuse, New York) CM 166 glass paper, certified to remove 90% of 0.3 micron diocylphthalate smoke.

The overall sampling design was 9 species × 2 replicates × 4 simulated acid rain pH levels for a total of 72 individual plants × ten trials, generating 720 samples, each of which was analyzed for six chemical elements. That is, for each species, two individual plants were randomly allocated to each of 4 treatment groups receiving artificial acid rain solutions having pH values of 5.5, 4.5, 3.5 or 2.5.

The artificial acid rain solution consisted of deionized water plus a salt and an acid component. The salt component simulated the average element content of rainfall at Coweeta (Swank and Henderson 1976) and contained the following amounts of elements in mg/liter: Ca 0.23; Na 0.17; K 0.08; Mg 0.05; NH$_4$-N 0.02; and PO$_4$-P 0.007. The acid component was made with reagent grade acids to produce the ratio of SO$_4$$_2$; NO$_3$; Cl of 10:7:1 reported by Cogbill and Likens (1974) for New York State acid rain. The pH values of simulated rain solutions were determined with a glass electrode. No attempt was made to duplicate the organic N or P compounds found in natural rainwater.

Rain was applied with a rain simulator consisting of 1) a reservoir with a 100 liter capacity containing the artificial acid rain; 2) a variable speed water pump (Flotec Inc. Norwalk, CA, Model R251-1100V with 316 stainless steel pumping head Model 834, viton seals with 3/8 IPS inlet and outlets); 3) a water filter to remove any particulates; 4) a rotating pressure joint (Schrader Rotating Joint No. 834, Scovill Mfg., Wake Forest, NC); 5) an electric motor and gear assembly to rotate the pressure joint at 4 revolutions per minute, (Motiondiser M236, Herbach and Rademan, Inc., Philadelphia, Pa); 6) a support arm with a radius of 99 cm suspended and balanced beneath the rotating pressure joint; and 7) a stainless steel nozzle with raindrop tip assembly type RD2 (Delavan Agspray Products, Lexington, TN). When operated at 2.75 × 10$^5$ Pa the system delivered between 0.9 and 1.0 cm (x = 0.98, S.D. = 0.06) cm of artificial...
rain per hour which approximates an average rainfall intensity of 0.89 cm/hour for Coweeta (W. Swank, personal communication). The raindrop size frequency distribution was determined by the flour method of Laws and Parsons (1943) during three rotations of the spray head. The percentages of the total number of droplets for each droplet diameter interval were 1% > 2mm; 6% 0.8 to 2mm; 7% 0.60 to 0.84 mm; 19% 0.50 to 0.59; and 67% 0.42 to 0.49 mm.

Leachates from plants were collected in 44 to 93 cm polyethylene garbage bags. Bags fitted to plants were opened at both ends and dropped over the plant canopy. One end of the bag was gathered up and tied to the plant stem beneath the plant canopy. The other end of the bag was tied to a plastic support ring. This arrangement created a plastic catchment trough with a defined sampling geometry situated beneath the plant canopy. Four different sizes of catchments were used so as to match canopy and catchment sizes.

Plants were placed two abreast in a circle beneath the rotating nozzle. After 30 min of rain, plants on the inside of the circle were changed with those on the outside circle to cancel out any asymmetries in rain distribution. The rain solution was sampled for chemical composition 3 times during each 60 min rain episode. The concentrations were averaged for the 3 samples. After 60 min of simulated rain, 200 ml aliquots of leachate were collected from the polyethylene bags for chemical analysis.

One pH treatment was applied to one group of plants on a given day. One cycle of application of all 4 pH treatments required about 1/2 weeks. This was repeated for 10 cycles over a 114 day period from July to November 1979. Water samples were analyzed for NH$_4$-N colorimetrically according to Koroleff (1976), for NO$_3$-N colorimetrically according to Strickland and Parsons (1960) and for K, Mg, Ca, and P with a plasma emission spectrograph.

Element loss rates were calculated from the following relationship: mg element/10 dm$^2$/hr = (C$_1$ - C$_n$)V/LA \cdot T where C$_n$ is concentration of element at the nozzle, C$_1$ is concentration of element in leachate beneath experimental plant, LA is total leaf area of plant, V is volume of leachate collected, and T is time.

Resulting data were subjected to analysis of variance using programs of the statistical analysis system (Helwig and Council 1979).

Results. When leaching rates for the 9 plant species, 4 pH levels and the 10 rain trials were subjected to analysis of variance, highly significant differences occurred among plant species for most elements (Table 1). These elements were NH$_4$-N, NO$_3$-N, Ca, P, K and Mg. The leaching rate of Mg did not differ significantly among species. There were significant differences between rain trials (time) except for Mg. Plots of leaching rate by species (not shown) and rain pH vs. time show that leaching rates of some ions increase with time; others decrease with time and others are quite variable.

There were no significant pH effects on leaching rates between pH 2.5 and 5.5, thus the leaching rates are averaged together across pH levels and are shown by species and by element in Table 2. Rates of leaching were highest for K, Ca, Mg and NO$_3$-N in the herbaceous plants Erigeron and Erechites. Rates of leaching from woody plants

<table>
<thead>
<tr>
<th>Element leached</th>
<th>Plant Species</th>
<th>Rain pH</th>
<th>Trial</th>
<th>Species x Rain pH</th>
<th>Species x Trial</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$</td>
<td>0.0001</td>
<td>0.07</td>
<td>0.0001</td>
<td>0.55</td>
<td>0.0001</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>0.01</td>
<td>0.14</td>
<td>0.0006</td>
<td>0.51</td>
<td>0.0001</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0001</td>
<td>0.15</td>
<td>0.0011</td>
<td>0.26</td>
<td>0.0012</td>
</tr>
<tr>
<td>P</td>
<td>0.0001</td>
<td>0.6</td>
<td>0.0001</td>
<td>0.59</td>
<td>0.0001</td>
</tr>
<tr>
<td>K</td>
<td>0.0001</td>
<td>0.82</td>
<td>0.0001</td>
<td>0.99</td>
<td>0.0001</td>
</tr>
<tr>
<td>Mg</td>
<td>0.20</td>
<td>0.3</td>
<td>0.45</td>
<td>0.39</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 1. Probabilities that differences in leaching rates between plant species and between simulated acid rain treatments occurred by chance alone as determined by analysis of variance.
Table 2. Mean leaching rates in mg of element/10 dm²/hr (with standard error) from mature plant leaves. For a given element, leaching rates followed by the same letter are not significantly different according to Duncan's multiple range test.

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>NH₄-N</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>NO₃-N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erigeron canadensis n=79</td>
<td>.29a</td>
<td>11.3a</td>
<td>3.33a</td>
<td>9.06a</td>
<td>5.52a</td>
<td>−5.3c</td>
</tr>
<tr>
<td>Erechtites hieracifolia n=79</td>
<td>.03b</td>
<td>2.4b</td>
<td>1.69b</td>
<td>.31b</td>
<td>.26b</td>
<td>−0.93b</td>
</tr>
<tr>
<td>Robinia pseudo-acacia n=80</td>
<td>.05b</td>
<td>2.17b</td>
<td>0.54bcd</td>
<td>.09b</td>
<td>−.37b</td>
<td>−.73b</td>
</tr>
<tr>
<td>Carya illinoensis n=80</td>
<td>−.009b</td>
<td>−79bc</td>
<td>1.57bcd</td>
<td>−4.4b</td>
<td>−2.7b</td>
<td>−2.6b</td>
</tr>
<tr>
<td>Cornus florida n=80</td>
<td>−0.02b</td>
<td>.34c</td>
<td>0.98bcd</td>
<td>.05b</td>
<td>.21b</td>
<td>.35ab</td>
</tr>
<tr>
<td>Liriodendron tulipifera n=80</td>
<td>−.004b</td>
<td>.12c</td>
<td>.31bcd</td>
<td>−.03b</td>
<td>−.03b</td>
<td>−.34ab</td>
</tr>
<tr>
<td>Quercus prinus n=80</td>
<td>−.02b</td>
<td>.09c</td>
<td>.011d</td>
<td>.01b</td>
<td>.04b</td>
<td>−.34ab</td>
</tr>
<tr>
<td>Pinus strobus n=80</td>
<td>.006b</td>
<td>.07c</td>
<td>.006d</td>
<td>−.004b</td>
<td>.03b</td>
<td>.05a</td>
</tr>
<tr>
<td>Acer rubrum n=80</td>
<td>−.02b</td>
<td>.04c</td>
<td>.06d</td>
<td>−.001b</td>
<td>.06b</td>
<td>−.30ab</td>
</tr>
</tbody>
</table>

The table shows the mean leaching rates in mg of various elements per 10 dm²/hr from mature plant leaves, along with standard errors. The elements include NH₄-N, K, Ca, Mg, NO₃-N, and P. The leaching rates are compared across different plant species, and for each element, rates followed by the same letter are not significantly different according to Duncan's multiple range test.
were generally much lower, ranging from 0.006 to 2.2 mg/10 dm²/hr. Element absorption (negative leaching) by leaves of some species is suggested for NH₄—N, Mg, NO₃—N and P.

Discussion. Losses of all essential plant mineral elements and of dozens of organic metabolites from leaves by leaching have been demonstrated (Tukey 1966). Leaching of cations involves both their exchange off of leaf surfaces by hydrogen in the leaching solution and movement from translocation streams to and through leaf surfaces devoid of cuticle (Tukey 1970). Rainwater acidified by volcanic gases to pH 4.0 was found to accelerate the leaching of Ca, Mg, and K from tomato leaf discs compared with losses from discs in less acid rainwater (Kratky et al. 1974). Sulfuric acid at pH 3.0, sprayed onto Nicotiana tabacum (tobacco) leaves, significantly increased Ca loss, significantly decreased K loss and did not affect Mg loss compared to controls receiving water of pH 6.7 (Fairfax and Lepp 1975). This loss pattern was not readily explained. The increasing acidity of sulfuric acid mists, from pH 5.0 to pH 3.0, significantly increased K, Ca and Mg losses from Phaseolus (bean) and Acer (maple) leaves but did not affect Na loss (Wood and Bormann 1975).

Eaton, Likens and Bormann (1973) calculated that at least 27% of the cations leached from a deciduous forest canopy at Hubbard Brook, New Hampshire could be accounted for by exchange with hydrogen in the rain. In a study of throughfall chemistry in Quercus prinus L. (chestnut oak) canopies at Walker Branch, Tennessee, Hoffman, Lindberg and Turner (1980) found that the strong acid component of the rain was partly removed from rain by the leaf, the weak acid was displaced from the leaf, the total acidity was maintained during the leaf—rain interaction and both inorganic acids and organic acids were found in the weak acid component. Although not measured in the Walker Branch study, the conservation of the total acidity during the leaf—rain interactions suggests little effect of rain acidity on leaching of cations such as K, Mg, Ca and NH₄ from leaves. The effect of acid rain on the leaching of organic metabolites other than organic acids has apparently yet to be reported.

Studying the processing of acid rain by forest canopies in New England, Cronan and Reiners (1983) found that rain of pH 4.1 decreased in hydrogen ion but increased in base cation concentration as it passed through the hardwood canopy. Acid neutralization appeared to result from ion exchange of H⁺ to the leaves and the leaching of bases from the leaves. Rates of K leaching increased during the period of leaf senescence. Conifer throughfall showed both cation and anion enrichment relative to rainfall but little change in pH.

Rainfall percolating through the canopies of hardwood stands and Pinus rigida Miller stands during the growing season became depleted of H⁺ and enriched in NH₄—N, K, Na, Ca, Mg, and SO₄ (Swank and Swank 1983).

In a study of the effects of rain Ca and pH at 3.3 and 4.2 upon the Ca and K content of Malus domestica Borkh. (apple) leaves, Blanpied (1979) found that summer (June—July) rains decreased the Ca content of the leaves but that there was no rain pH or rain Ca content effect. In autumn (September—October) there was some reduction in Ca content of leaves exposed to low Ca, low pH rains but K content was not affected by pH or by Ca in rain during either summer or autumn. Blanpied concluded that the apparent decline of leaf Ca in apple leaves was probably not caused by acid rain. Throughfall chemistry remained almost identical to rainfall chemistry, indicating little leaching, when simulated sulfuric acid rains at pH 5.7, 4.0, 3.5 and 3.0 were applied to model forest plots planted with Acer saccharum Marsh. (sugar maple) and Alnus rubra Bong. (red alder) (Lee and Weber 1982).

In this study, rates of element leaching from mature plant leaves did not change with pH of simulated acid rain over a range of pH 2.5 to pH 5.5. Comparison of the findings of this study with other studies leads to the conclusion that acid rain increased element leaching from leaves in some studies, and in others, including ours, it did not. The comparison also leads to the question as to why there was no acid rain-induced leaching in our study. This may result from use of entire but heterogeneous canopies of only two plants for each species at each pH treatment, thereby creating a
relatively large error mean square term in the analysis of variance. Day and Monk (1977) reported a seasonal variation in leaf nutrient concentration which could contribute to the lack of significant differences. Studies of leaching rates from individual leaves, although more difficult to perform, could allow increased replication and sensitivity to small changes in pH-induced element leaching. In field studies where element enrichment of throughfall has been related to rainfall acidity, it is difficult to determine what fraction of the element enrichment was derived from within the leaf in relation to elements which arrived on the leaf as dry deposition and were then washed off of the leaf by rain. In our study, where plants were grown in filtered air, the contribution of dry deposition to elements in throughfall or leachate should have been relatively small. This absence of pH-dependent mineral element leaching is consistent with the absence of visible signs of damage to the plant leaves associated with pH treatments above 2.0 in two other studies. In one study, droplets of pH 2.0 produced brown necrotic spots on all of these species except Pinus, which developed necroses only at pH 1.0 and lower (Haines, Stefani and Hendrix 1980). In another study, foliar effects of simulated acid rains of pH 5.6, 4.0, 3.0 and 2.0 were evaluated for seedlings of L. tulipifera, Platanus occidentalis L, Liquidambar styraciflua L and Robinia pseudo-acacia. In general foliar damage, biomass reduction and photosynthetic rates were not affected until pH was decreased to 2.0 (Neufeld, Jernstedt and Haines 1985). Differences among species in susceptibility to damage were related to leaf surface characteristics (Haines, Jernstedt and Neufeld 1985).

The absence of pH-dependent mineral element leaching over the pH range 5.5 to pH 2.5 is consistent with the inference of little leaching of metallic ions from the Quercus prinus canopy at Walker Branch Tennessee (Hoffman, Lindberg and Turner 1980). These results suggest that acid rain at Coweeta, which averages 4.6 and ranges between 3.2 and 5.9 (Swank and Douglass 1975) has little effect on nutrient mobilization out of the forest canopy at Coweeta. If the pH were to decrease an order of magnitude from 3.2 to 2.2, the threshold for leaf damage would be approached (Haines, Stefani and Hendrix 1980) and increasing rates of acid rain-induced leaching of mineral elements could occur.

That leaching rates are higher from earlier successional species may be of ecological significance. The early successional plants used in this study have higher foliar element concentrations that the later successional species (Boring, Monk and Swank 1981). Higher foliar element content and higher element leaching rates in the early successional species suggests that the return of nutrients from foliage to the forest floor in solution may be greater in earlier stages of forest succession. Thus, element cycling processes appear to change as community structure changes during forest regeneration.

Literature Cited


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