

ACIDIC CLOUD WATER AND CATION LOSS FROM RED SPRUCE FOLIAGE

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(Received December 12, 1987; revised May 24, 1988)

Abstract. Declines of red and Norway spruce in North America and Europe are occurring at high elevations where cloud interception is a major source of water and chemical deposition and the mean pH of cloud water is markedly lower than that of rainfall. At the summit of Whitetop Mountain (1700 m) in the southern Appalachians the chemistry of ambient cloud water was compared on a cloud event basis to that of cloud water-generated throughfall from red spruce saplings. Large shifts occurred in the relative importance of all the cations measured as cloud water became throughfall, whereas the relative importance of the major anions (SO_4^{2-} , NO_3^- , Cl^-) remained relatively constant. Hydrogen ion and NH_4^+ percentage contributions were reduced to two-thirds and one-third of their original percentages respectively, whereas the other four major cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) all at least doubled in importance. Losses of Ca and Mg from native red spruce foliage were observed to intensify markedly with increases in the acidity of cloud water. On sites where the available pools of certain cations are already marginal, losses of cations caused by acidic cloud water may contribute to nutrient deficiencies.

1. Introduction

Cloud moisture deposited from the impaction of wind-driven droplets has been shown to be a significant source of water and chemicals to high elevation forests (Lovett *et al.*, 1982; Mohnen, 1987). In eastern North America and central Europe, the pH of cloud droplets is commonly below 4.0 and occasionally below 3.0, and the concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , and other ions are markedly higher in cloud water than in rainfall from the same location (Lovett *et al.*, 1982; Bosch *et al.*, 1986; Mohnen, 1987). The deposition of acidic cloud water is of considerable interest in light of observations that foliar loss of cations is markedly intensified as H^+ concentration increases (Fairfax and Lepp, 1975; Evans, 1982; Scherbatskoy and Klein, 1983; Bosch *et al.*, 1986; Kreutzer and Bittersohl, 1986; Rodenkirchen, 1986; Mengel *et al.*, 1987).

The recent decline of red spruce (*Picea rubens* Sarg.) in eastern North America and Norway spruce (*Picea abies* L. Karst) in Europe has been documented to be particularly acute at higher elevations (Siccama *et al.*, 1982; Johnson and Siccama, 1983; Scott *et al.*, 1984; Zoettl and Huettl, 1986), where forests are frequently immersed in clouds. Foliar Mg deficiencies and low foliar Ca concentrations have accompanied decline symptoms in Norway spruce in high elevation forests across central Europe (Rehfuess *et al.*, 1983; Zech and Popp, 1983; Zoettl and Huettl, 1986). German scientists have hypothesized that foliar leaching of Ca and Mg caused by acidic deposition is one of

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several primary factors in this 'high altitude Norway spruce disease' (Bosch *et al.*, 1986; Rehfuess and Bosch, 1986; Zoetl and Huettl, 1986).

While the above studies indicate that foliar leaching of cations by cloud water may be a process of concern, none have directly investigated the impact of naturally occurring cloud water on that foliar cation loss. The present investigation was undertaken to estimate the contribution of cloud water to the loss of cations from the foliage of red spruce growing on the summit of Whitetop Mountain in southwestern Virginia.

2. Methods

An atmospheric monitoring station has been established by the Tennessee Valley Authority in a clearing at the summit (1682 m) of Whitetop Mountain in southwestern Virginia. As part of the Mountain Cloud Chemistry Program, its primary purpose is to determine the magnitude and form of total pollutant exposure from precipitation, cloud water, and dry deposition at the site, with particular emphasis on characterizing cloud water chemistry and deposition. During 3 three-week periods in 1986 (April–May; July–August; September–October), the chemistry of ambient cloud water was compared to red spruce cloud water throughfall. Ambient cloud water was collected during individual cloud events by a CWP active cloud water collector, and cloud water throughfall, resulting from interception by the foliage of 4 red spruce saplings, was collected in plastic throughfall collars.

The CWP Active Cloud Water collector draws cloud moisture through a bank of Teflon strings with a propeller-type fan while effectively excluding rain (Daube *et al.*, 1987). Data collected over a 7-mo period in 1986 had previously revealed that the chemistry of the water collected by the CWP active collector was indistinguishable from that collected by an ASRC passive cloud water collector, as described by Falconer and Falconer (1980).

Cloud water throughfall intercepted by the 4 red spruce saplings (3 to 4 m tall), growing in young stands adjacent to the monitoring site, was collected in polyethylene collars which encircled the base of the trees and extended about 30 cm beyond the dripline of each tree. Cloud water throughfall collected in the collars ran through funnels into bottles below. Two of the young trees were situated on the edge of a clearing and two were located in the interior of a rather dense stand of young spruce. At the beginning of each cloud event, the collars were cleaned of debris, washed with distilled water, and dried. After a cloud event had begun, collections were initiated on all trees when one collar had collected 100 to 125 mL of throughfall. Subsequently, collections were made hourly to coincide with cloud water collections by the ambient collectors. Water retained on the collar at the time of collection was pipetted into the sample bottle as well. Sampling was discontinued during rain events.

Field pH and conductivity measurements were made within 5 hours of event cessation on both types of throughfall samples using a 15 mL subsample. The remaining sample was preserved with 0.1 mL chloroform and stored at 5 °C until laboratory analyses could be performed. Anion (NO_3^- , SO_4^{2-} , Cl^-) and cation (K^+ , Na^+ , NH_4^+ , Ca^{2+} ,

Mg²⁺) concentrations were determined using a BIO-RAD 301 ion chromatograph. A BIO-RAD TSK K-ANION PW column was used with 1.5 mM potassium hydrogen phthalate (pH adjusted to 5.5) eluent to analyze for anions, and BIO-RAD monovalent and divalent columns were used with 2 mM HNO₃ eluent to analyze for cations. Measurements of pH on all samples were repeated in the laboratory; as laboratory pH measurements were virtually indistinguishable from field pH measurements, only the laboratory measurements are reported here. A minimum of three calibration standards were included with every 10 field samples, and duplicate analyses were conducted 2 to 5 days after initial analyses.

Hourly chemistry data from cloud and from throughfall samples were separately pooled on a volume-weighted basis across each cloud event. Throughfall data were also pooled on a volume-weighted basis across the 4 trees for each cloud event. Very small events (less than 700 mL collected from all four trees) and events in which rain contaminated cloud water samples were eliminated. The resulting data set was comprised of 14 events – 1 spring, 7 summer, and 6 autumn.

3. Results

Over the 14 cloud events studied, a wide range in cloud water pH was observed (2.91 to 4.64), with a mean volume-weighted pH of 3.63. The cloud water cation pool was dominated by H⁺ (63%) and NH₄⁺ (26%), while the remaining 11% was comprised largely of Na⁺ and Ca²⁺; the cloud water anion pool was dominated by SO₄²⁻ (64%) and NO₃⁻ (32%) (Table I).

The sums of anions and cations in throughfall collected below the red spruce trees

TABLE I

Volume-weighted mean concentrations and percentage contributions to the sum of cations or anions for ambient cloud water and cloud-generated throughfall across the 14 cloud events. Standard deviations of the 14 event means given in parentheses.

	Cations							Anions			
	H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Sum	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Sum
	Concentration (µeq L ⁻¹)										
Cloud water	237 (331)	98 (101)	10 (24)	5 (3)	17 (4)	8 (4)	374 (435)	246 (164)	121 (109)	17 (14)	383 (431)
Throughfall	219 (222)	47 (180)	39 (37)	37 (63)	140 (150)	34 (32)	517 (806)	360 (339)	150 (218)	39 (56)	549 (939)
	Percent of total cations/anions (%)										
Cloud water	63 (15)	26 (12)	3 (3)	1 (2)	5 (4)	2 (4)	100	64 (8)	32 (8)	4 (4)	100
Throughfall	42 (12)	9 (6)	8 (6)	7 (7)	27 (9)	7 (3)	100	66 (6)	27 (6)	7 (7)	100

were generally elevated over those in ambient cloud water. Evaporation of deposited cloud water from needle surfaces during cloud events is probably the major factor causing this increase in ionic strength of throughfall solutions, as proposed by Unsworth (1984) and demonstrated by Adams and Hutchinson (1987).

A comparison of the composition of the total cation pools of cloud water and throughfall, on a percentage basis, revealed that large shifts in the relative importance of all the cations measured occurred as cloud water became throughfall (Table I). Hydrogen ion and NH_4^+ percentage contributions were reduced to two-thirds and one-third of their original percentages, respectively, whereas the other four major cations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) all at least doubled in importance. Calcium exhibited the largest increase in percentage, from 5% in cloud water to 27% in throughfall. The contribution of Ca^{2+} , K^+ , Na^+ , and Mg^{2+} combined increased from 11 to 49%. In contrast to the cations, the percentages of the total anion pool revealed no apparent change in the relative importance of SO_4^{2-} , NO_3^- , and Cl^- as cloud water became throughfall (Table I).

The large range in pH exhibited across these 14 cloud events allows an examination of the relationship between (a) the initial cloud water H^+ concentration for a given event, and (b) the magnitude of the percentage shifts which occurred in the cation pool as cloud water contacted spruce needles and became throughfall. In general, as the acidity of cloud water increased, the percentage contribution of H^+ to its total cation pool increased while the percentage contributions of both Ca^{2+} and Mg^{2+} decreased (Figure 1a–c). The inverse was true for throughfall solutions: As the acidity of cloud water increased, an increasing percentage of total cations in subsequent throughfall was attributable to Ca^{2+} and Mg^{2+} and a decreasing percentage to H^+ . The net change in Ca^{2+} and Mg^{2+} percentages between cloud water and throughfall across the range of cloud H^+ concentration is shown in Figure 2. Both plots indicate that these increases are a curvilinear function of H^+ concentration (linear function of pH). Both NH_4^+ and K^+ also exhibited shifts between cloud water and throughfall, with NH_4^+ declining in throughfall and K^+ increasing; however, neither of these shifts depended on cloud pH (Figure 1d–e).

4. Discussion

The increase in rates of Ca^{2+} and Mg^{2+} losses with increasing acidity observed in this study are consistent with results recently reported in two separate irrigation experiments using artificially acidified mist (Kreutzer and Bittersohl, 1986; Mengel *et al.*, 1987). In these young Norway spruce stands, the loss of Ca through foliar leaching was observed to increase 4 to 6.5 fold; Mg, 4.5 to 6 fold; and K, 2 to 3 fold, when the acidity of irrigation water was increased from pH 5.2 to pH 2.7. Zinc and Mn losses also increased dramatically (15- and 20-fold, respectively) in the Mengel *et al.* (1987) study. Our results indicate that a change in cloud acidity from pH 4.6 to pH 2.9 resulted in an 18-fold increase in Ca and a 25-fold increase in Mg concentration in the resulting throughfall. Additional evidence for intensifying foliar losses of Ca as pH declines exists for white

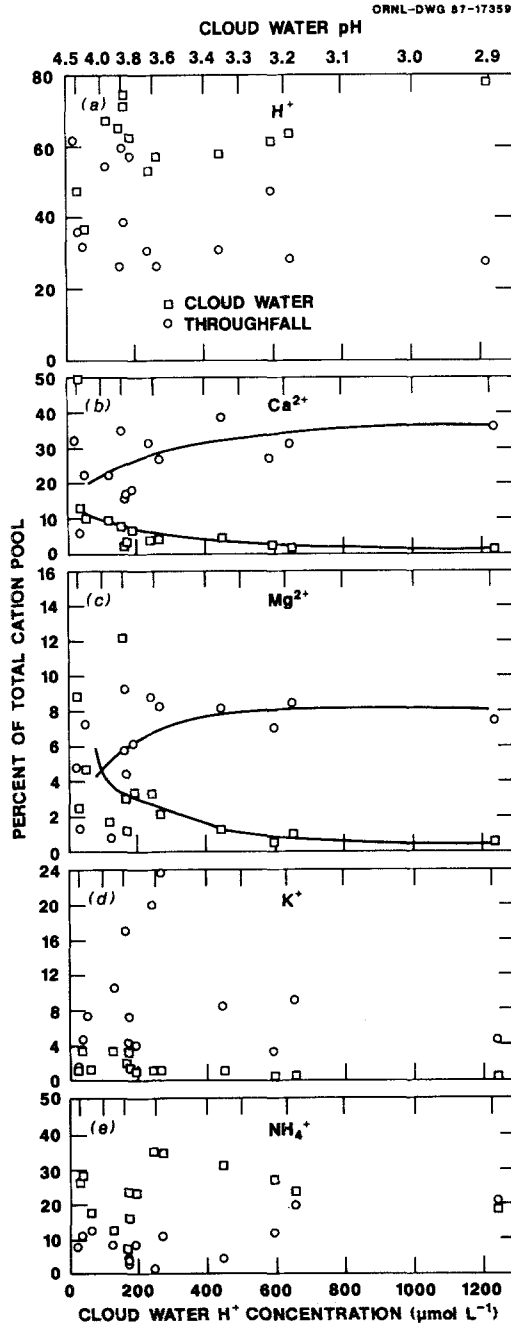


Fig. 1. Relationship between H^+ concentration of ambient cloud water and the percentage composition of the total cation pool for both cloud water and throughfall. Major cations (H^+ , Ca^{2+} , Mg^{2+} , K^+ , and NH_4^+) depicted for 14 cloud events.

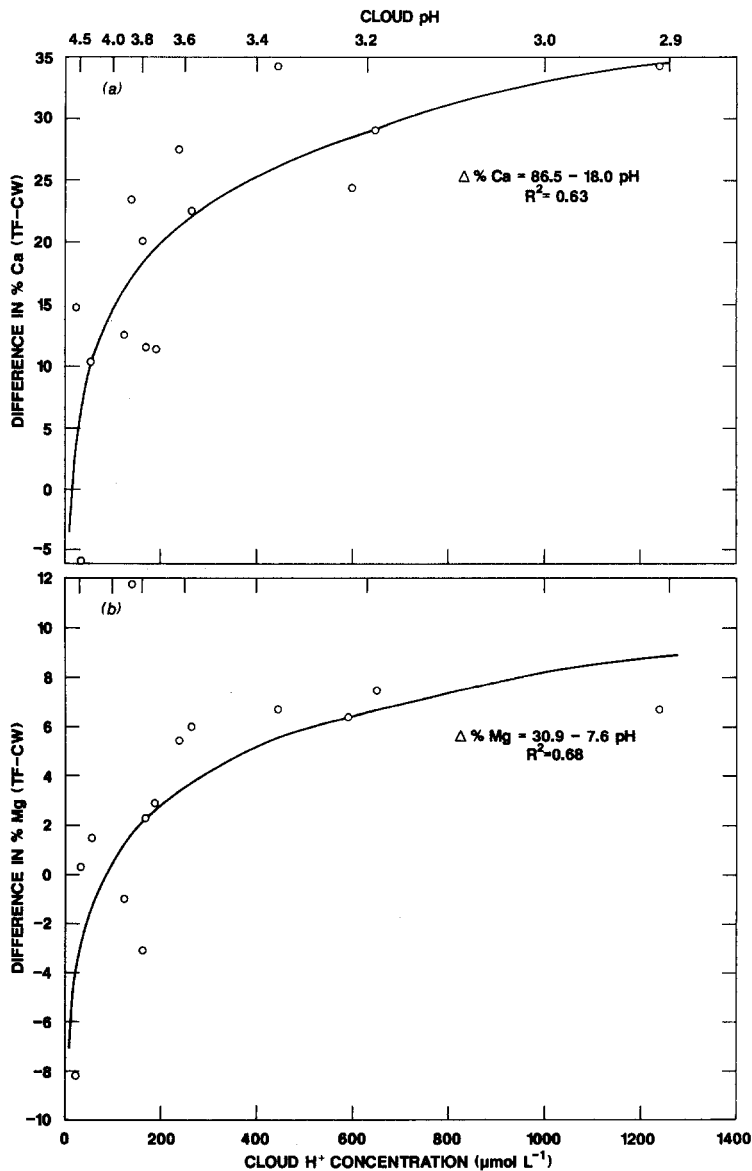


Fig. 2. Changes in the percentage of the sum of cations attributable to Ca^{2+} and Mg^{2+} between cloud water and cloud-generated throughfall plotted as a function of cloud H^+ concentration over the 14 cloud events. A positive change indicates a higher percentage in throughfall. Change in $\% \text{Ca} = (\text{Ca}_{\text{tf}} / \Sigma \text{Cations}_{\text{tf}} - \text{Ca}_{\text{cw}} / \Sigma \text{Cations}_{\text{cw}}) \times 100$, where tf = throughfall, cw = cloud water.

spruce (*Picea glauca* (Moench) Voss): Scherbatskoy and Klein (1983) found that the Ca leached from seedlings increased almost 6-fold when the pH of artificial mist was reduced from 4.3 to 2.8, whereas K leaching increased only 40%. Similar results have also been reported for various crop plants (Evans, 1982) and mosses (Rodenkirchen, 1986).

In addition to the neutralization of H^+ by what appears to be cation exchange with ions on sites interior to the foliar surface, the solubilization of alkaline coarse particles on the foliar surface may also be an important neutralization process (Hutchinson and Adams, 1987). Although alkaline dust no doubt was a source of Ca and Mg in leachates in our study, its contribution was most likely very small at this site because of the frequency of rain and/or cloud events which continually remove such dry deposition from foliar surfaces and which limit the time periods favorable to deposition of dust particles.

Leonardi and Flueckiger (1987) report that 4 mm of precipitation was sufficient to remove the bulk of dry deposition in a mature European beech (*Fagus sylvatica* L.) stand. According to our meteorological records, no cloud event was preceded by a period longer than: (1) 53 hr without a rainfall event of at least 5 mm, (2) 24 hr without a rainfall or major cloud event, and (3) 14 hr in which the ground surface was not wet. The autumn collection period was one of near continuous rain and/or clouds, in contrast to drier spring and summer collection periods; the data from the 43% of the events which were from this autumn period follow the identical pattern as those from the summer and spring. Subsequent to the throughfall experiment reported herein, we measured dry deposition rates of Ca and Mg by sedimentation of coarse particulates during two spring dry periods (35 and 72 hr duration). A polycarbonate Petri dish method of collection was used, a method which, if anything, overestimates alkaline earth deposition to leaf surfaces (Lindberg and Lovett, 1985). During these periods of no precipitation, dry deposition rates of Ca and Mg averaged 1.24 and $0.22 \mu\text{eq m}^{-2} \text{hr}^{-1}$, respectively. The average cloud throughfall event removed $108 \mu\text{eq m}^{-2}$ Ca and $23 \mu\text{eq m}^{-2}$ Mg. Thus, in a typical cloud event preceded by 14 hr of dry deposition, alkaline particles could contribute approximately 15% of the total Ca or Mg in throughfall. No tendency could be detected for cation concentrations or exchange rates to diminish over the course of a cloud event as would be expected if alkaline particles on the foliar surface were the predominant source of cations.

Establishing a relationship between the losses of Ca and Mg from spruce foliage by cloud water at high elevations and the decline in spruce forests on those sites requires documentation that such leaching can result in foliage deficient in at least one of these nutrients. Bosch *et al.* (1986) have experimentally demonstrated that accelerated foliar leaching of Norway spruce only results in foliar deficiencies of Ca and Mg when trees are growing on soils especially poor in these nutrients. Trees growing on soils fertilized with Ca and Mg compensated for increased foliar losses by increased uptake. The combination of high elevation and low levels of Mg in soil and foliage has been documented to be associated with forest decline symptoms in Norway spruce at numerous locations in the Black Forest (Zoetl and Huettl, 1986), the Bavarian Forest (Rehfuess *et al.*, 1983), and in the Fichtel Mountains (Zech and Popp, 1983).

The total mass of a given cation lost from foliage during a cloud event is dependent upon the volume of throughfall as well as the concentration of that cation in the throughfall solution. In this study, throughfall volumes per event (summed for the 4 trees) ranged widely, from 0.7 to 18.0 L, with a mean volume of 6.2 L. Two events alone, which combined low pH (3.23 and 3.35) and high volumes (16.3 and 5.2 L), accounted for 65 and 71% of the Ca and Mg loss in the 14 events combined. To relate this loss to the total amount of each cation in the standing foliar pool of each tree, we estimated that about 5% of the K, 16% of the Mg, and 36% of the Ca would be lost annually from the two most exposed trees. This calculation assumes 1950 g needle dry weight per tree (based on red spruce DBH-needle dry weight tables of Young [1981]), foliar tissue concentrations of 440 mg kg⁻¹ Mg, 1500 mg kg⁻² Ca (Friedland *et al.*, 1988, high elevation red spruce), and 5000 mg kg⁻¹ K (Likens and Borman, 1970), and an annual leaching rate equal to that observed in our 9 week observation period for the two most exposed trees. These assumptions probably overestimate losses during the winter months but, on the other hand, do not include leaching losses during precipitation events. Such losses could be biologically significant over the life of the needle (approximately 5 yr) in a system where the cation(s) was already in short supply and where soil leaching processes continually transport cations below the rooting zone.

No causes for the decline of red spruce at high elevations in the eastern United States have been pinpointed (Johnson and Siccama, 1983). Recently, a study on apparently healthy red spruce in the eastern U.S. has reported significantly ($p < 0.01$) lower foliar concentrations of Ca, Mg, and Zn in high elevation stands as compared to matching low elevation stands (Friedland *et al.*, 1988). The mean foliar Mg concentration (442 mg kg⁻¹) at 7 high elevation sites in New York and Vermont was much lower than the critical level for Norway spruce [700 to 800 mg kg⁻¹ (Bosch *et al.*, 1986)] and much lower than concentrations at 6 matching low elevation sites (700 mg kg⁻¹) or at other low elevation sites in Maine and Nova Scotia (700 to 1200 mg kg⁻¹). On these same 7 high elevation sites in Vermont and New York, as well as on high elevation sites in the White Mountains of New Hampshire and on Mt. Mitchell in North Carolina, foliar Ca concentrations were nearly half (1000 to 1460 mg kg⁻¹) those at the low elevation sites (2100 to 3250 mg kg⁻¹), foliar Zn levels (13 to 18 mg kg⁻¹) were not only lower ($p < 0.01$), but also at the low end of the range for *Picea* species (Stone, 1968). Adequate soil chemistry information was not available for these North American sites.

It would appear that, on certain high elevation sites, low or deficient foliar concentrations of certain cations (especially Ca, Mg, Zn) may be occurring. We hypothesize that these low concentrations are the result of the combination of (a) soils low in those cations and (b) sufficient acidic deposition (especially highly acidic cloud deposition) to amplify foliar cation losses. Other sources of stress – e.g., winter damages, drought, oxidants (O₃, H₂O₂) – no doubt are involved in spruce declines at high elevations. The importance of cloud water acidity relative to these other stresses remains to be determined.

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