

Precipitation and throughfall chemistry for a montane hardwood forest ecosystem: potential contributions from cloud water

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This study analyzed the chemical composition of cloud water, bulk precipitation, and throughfall in a hardwood forest at the top of a watershed in the Virginia Blue Ridge Mountains to further investigate canopy–atmosphere interactions. The composition of both cloud water and bulk precipitation was dominated by H^+ , NH_4^+ , SO_4^{2-} , and NO_3^- . On average, cloud water was four times more acidic than bulk precipitation (251 vs. 63 $\mu\text{equiv./L}$ in 1986 and 158 vs. 40 $\mu\text{equiv./L}$ in 1987, respectively) and had higher NH_4^+/Ca^{2+} ratios (22.2 vs. 0.7 in 1986 and 9.4 vs. 1.2 in 1987, respectively), indicating possibly below-cloud scavenging of primary aerosols by rain, dry deposition of Ca^{2+} , and (or) differential dissolution of NH_3 gas in cloud water and rainwater. Acidity in throughfall was less than that in bulk precipitation (H^+ of 40 vs. 63 $\mu\text{equiv./L}$ in 1986 and 25 vs. 40 $\mu\text{equiv./L}$ in 1987, respectively). Potassium and Ca^{2+} were leached from the canopy, whereas NH_4^+ and NO_3^- were retained by the canopy. Cloud water was a major source for the retained NH_4^+ and NO_3^- . Deposition of cloud water during the warm season was estimated from precipitation–throughfall volume relationships to be approximately 5.21 cm in 1986, an increase of about 23% over precipitation inputs, and approximately 5.42 cm in 1987, an increase of about 8% over precipitation. The resulting inputs of major ions from cloud water may, however, equal or exceed that of precipitation at the ridgetop site and may contribute significantly to canopy fertilization and acidification. Further study is needed to determine the spatial extent down the watershed and the ultimate effects of this enhanced deposition to high elevation forests.

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Afin de mieux connaître les interactions entre l'atmosphère et le couvert forestier, cette étude a analysé la composition chimique de l'eau des nuages, de la pluie incidente et de la pluie sous couvert. Il s'agit d'une forêt d'arbres feuillus sise au sommet d'un bassin hydrologique situé dans les montagnes Blue Ridge de Virginie. La composition de l'eau des nuages et de la pluie incidente était dominée par H^+ , NH_4^+ , SO_4^{2-} et NO_3^- . En moyenne, l'eau des nuages était quatre fois plus acide que l'eau de la pluie incidente (251 par rapport à 63 $\mu\text{equiv./L}$ en 1986 et 158 par rapport à 40 $\mu\text{equiv./L}$ en 1987, respectivement) et avait des rapports NH_4^+/Ca^{2+} (22,2 par rapport à 0,7 en 1986 et 9,4 par rapport à 1,2 en 1987, respectivement) indiquant la possibilité d'un balayage des principaux aérosols par la pluie, de la déposition sèche de Ca^{2+} , ou bien la dissolution différentielle du gaz NH_3 dans l'eau des nuages et de la pluie. L'acidité de la pluie sous couverture végétale a été moindre à celle de la pluie incidente (H^+ de 40 par rapport à 63 $\mu\text{equiv./L}$ en 1986 et 25 par rapport à 40 $\mu\text{equiv./L}$ en 1987, respectivement). Le K^+ et le Ca^{2+} ont été lessivés du couvert, pendant que le NH_4^+ et le NO_3^- ont été retenus par le couvert; l'eau des nuages a été une source majeure de cette rétention du NH_4^+ et du NO_3^- . À partir des relations entre la pluie incidente et la pluie sous couverture végétale, le dépôt de l'eau des nuages durant la saison chaude a été estimé, approximativement à 5,21 cm en 1986, une augmentation d'à peu près 23% au-dessus des pluies sous couvert, et approximativement à 5,42 cm en 1987, une augmentation d'à peu près 8% au-dessus des pluies. L'addition des ions majeurs provenant de l'eau des nuages peut, cependant, égaler ou excéder celle des pluies au site au sommet de la chaîne et peut contribuer significativement à l'acidification et à la fertilisation du couvert. Une autre étude est nécessaire afin de déterminer l'extension spatiale vers le bas du bassin hydrologique et les effets ultimes de cette intensification des dépôts pour les forêts des hautes élévations.

[Traduit par la revue]

Introduction

In mature forest ecosystems, the predominant surface for deposition of water and chemical elements is the forest canopy. Atmospheric deposition to the canopy is influenced by several factors, such as forest type and the form, chemistry, and amount of deposition. Water collected beneath the canopy as throughfall is the net result of deposition and canopy–water interactions. The volume and composition of throughfall essentially integrates various processes of atmospheric deposition, along with the cycling of elements within the canopy. Thus, the examination of throughfall in forests can help to explain the nature of

atmosphere–canopy interactions (Lovett and Lindberg 1984).

Water and chemicals in the atmosphere enter forest ecosystems through a variety of deposition processes. Precipitation and dry deposition are important sources for a variety of chemical species (Schlesinger et al. 1982). In addition, occult precipitation (*sensu* Dollard et al. 1983) from fog and clouds can represent significant inputs to valley and mountain ecosystems, respectively (Fuzzi et al. 1985; Lovett et al. 1982).

The chemical composition of aqueous solutions is altered by several exchange processes as they pass through plant canopies. Some ions, particularly inorganic N, can be retained by the canopy from leaf uptake and from immobilization by epiphytic communities (Evans 1984; Gilliam 1987). One of the predominant processes affecting throughfall composition involves the exchange of H^+ in deposition

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with cations from the canopy. These cations originate from dry-deposited materials on leaf surfaces and from leaching of ions out of leaf tissues (Tukey 1980).

Lovett et al. (1985) demonstrated that increased H^+ deposition increases leaching of cations from the canopy. This response has important implications regarding the significance of cloud-water chemistry and deposition in mountainous forest ecosystems, since clouds are generally much more acidic than precipitation and frequently envelop mountain peaks (Schemenauer 1986).

The objectives of this paper are to compare the solution chemistry of precipitation, throughfall, and cloud water for a montane hardwood forest and to describe the potential contributions of clouds to the water and chemical budgets of the forest.

Methods

Study site

This study was carried out on the Shaver Hollow watershed in the northern end of the central section of Shenandoah National Park, Virginia (38°72'N, 78°20'W). Shaver Hollow is drained to the northwest by the North Fork of Dry Run and has a predominantly west to northwest aspect. The study area of this watershed is approximately 223 ha, ranging in elevation from 503 to 1034 m.

The Shaver Hollow catchment is primarily underlain by the Pedlar Formation, a Precambrian hypersthene granulite situated at the core of the Blue Ridge anticlinorium. Approximately one quarter of the catchment surface is occupied by loose rock and bedrock exposure of this material. Soils in the catchment are shallow Ultisols of low to moderate base availability. Analysis of the ridgetop soil near the study site indicated an organic carbon content of 2% in the subsurface soil and a 37 cm surface organic horizon. This ridgetop soil has relatively high cation exchange capacity in the subsoil (20 mequiv./100 g). Base saturation, however, is relatively low (4%). The soil pH for the site ranged from 5.3 to 5.5 (J.R. Webb, personal communication).

The watershed supports primarily second-growth forest; most of this area was logged heavily prior to the establishment of Shenandoah National Park in 1936. Shaver Hollow is dominated by chestnut oak (*Quercus prinus* L.) and northern red oak (*Q. rubra* L.), with several northern hardwood species and eastern hemlock (*Tsuga canadensis* (L.) Carr.) occupying wetter covers (Harrison et al. 1989).

The general climate of the region is described by a 50-year record of weather data collected by the National Park Service at Big Meadows Station, 15 km south of Shaver Hollow and at a similar elevation (1034 m). Temperatures range from a January mean of $-4^{\circ}C$ to a July mean of $19^{\circ}C$. Precipitation averages 135 cm annually, with a September maximum of 14.5 cm to a February minimum of 7.1 cm. Snowfall is common from November to March and represents approximately 8% of total annual precipitation (J. Watkins, personal communication).

Sampling

Precipitation and throughfall

Bulk-precipitation composition was sampled with a continuously open, 16 cm diameter polyethylene funnel connected to a polyethylene bottle. The top of the funnel was covered with a screen mesh to exclude large contaminants such as leaves, and the base of the funnel was plugged with glass wool to filter smaller contaminants. In 1986, the collector was placed at the top of a 16.5-m instrumented aluminum tower extending approximately 4 m above the forest canopy. The elevation of the site is 1014 m (this site will be referred to as site 1 to distinguish it from other study sites in the watershed). In 1987, the collector was mounted 1.5 m aboveground in a 6 m wide opening approximately 40 m from the tower in order to be colocated with a tipping bucket rain gauge

used to measure precipitation volume and an Aerochem Metrics collector used to sample wet-only precipitation for chemical analysis. Throughfall was sampled with continuously open collectors identical with those used for bulk precipitation composition. Ten collectors were located randomly in a circular, 0.08-ha plot located 20 m from the tower.

In 1986, samples were collected from 15 July to 18 November. In 1987, samples were collected from 14 April to 5 November. Samples were recovered from all collectors on a weekly basis. After sample recovery, the collectors were rinsed in the field with 175 mL of deionized water and then treated with 1–2 mL of chloroform to act as a biocide. Samples were carried to the field laboratory where sample volume and pH were measured. The samples were then refrigerated until transport to the analytical laboratory in the Department of Environmental Sciences at the University of Virginia (U.Va.).

Cloud water

Cloud water was sampled on an event basis 2.5 m above the tower at site 1 with a passive collector developed at the Atmospheric Sciences Research Center, State University of New York, Albany (Castillo et al. 1983; Schemenauer 1986). The criterion used for determining the onset of a cloud event was visibility of less than 1 km for more than 15 min. When a cloud event began, a clean preweighed polyethylene bottle was connected to the collector using Tygon tubing. The collector was uncovered, and the first 10 mL or 15 min of sample was discarded. After this initial rinsing of the collector with cloud water, bottles were changed at 1-h intervals for the duration of the event. After retrieval of each bottle, the sample was weighed and the field pH measured as quickly as possible, usually within 1. When over 50 mL of sample was left after the pH measurement, the sample was split into two aliquots. One aliquot was shipped to the Illinois State Water Survey (ISWS) laboratory and one was transported to the U.Va. laboratory. If the remaining volume had less than 50 mL, the sample was shipped to the ISWS laboratory for analysis in 1986 and to the U.Va. laboratory in 1987. The U.Va. aliquots were treated with chloroform to retard microbial growth; all aliquots were refrigerated until analysis. Comparison of over 100 samples between the two laboratories showed that, on average, analyses agreed to 5% or better for all constituents.

A cloud event was considered finished if less than 10 mL of cloud water were collected in 20 min or if the visibility increased to more than 1 km for more than 15 min. The volume criterion was based on the amount of cloud water required for complete chemical analysis. After an event, the collector was rinsed thoroughly with 1–2 L of deionized water sprayed using a plastic garden sprayer. The collector was rinsed until the conductivity of the rinsate was within $5 \mu\text{mho/cm}$ ($1 \text{ mho} = 1 \text{ S}$) of the deionized water. Samples of the rinse water were routinely collected and analyzed to verify that the collector was clean. Cloud water was sampled from July to November in 1986 and from April to November in 1987. Cloud-water data in this paper correspond to 87 hourly samples from 22 events. Cloud-water samples that were collected during periods of precipitation were not included in this analysis.

Chemicals Analyses

Analysis of field pH incorporated a 2-point calibration with buffers and an Orion Research Ionalyzer 501 with a Corning glass semimicro combination pH electrode. At the U.Va. laboratory, pH was remeasured using a 2-point calibration with buffers and an Orion 501 Digital Ionalyzer with a Corning plastic-bordered combination electrode. There were no significant differences between the field and U.Va. laboratory measurements. Data presented here correspond to pH values measured at the U.Va. laboratory.

At the U.Va. laboratory, concentrations of SO_4^{2-} , NO_3^- , and Cl^- were measured using ion chromatography; base cations were measured by atomic absorption spectrophotometry; NH_4^+ concentration was measured by automated colorimetry. For the cloud-

TABLE 1. Composition for bulk precipitation, throughfall, and cloud water for site 1, July–November 1986 and April–October 1987 ($\mu\text{equiv./L}$)

	1986			1987		
	Bulk precipitation	Throughfall	Cloud water	Bulk precipitation	Throughfall	Cloud water
pH	4.2 (3.8–4.6)	4.4 (3.9–5.9)	3.6 (3.0–4.7)	4.4 (3.7–4.6)	4.6 (3.7–6.1)	3.8 (2.8–5.1)
H ⁺	63.1 (25.1–158.5)	39.8 (1.3–125.9)	251.2 (20.0–1000.0)	39.8 (25.1–199.5)	25.1 (0.8–199.5)	158.0 (7.9–1584.9)
Na ⁺	6.7 (0.0–30.9)	15.2 (3.1–164.2)	10.6 (0.7–42.1)	5.9 (0.5–21.7)	5.1 (0.7–33.9)	14.5 (0.3–109.9)
K ⁺	2.8 (0.8–15.1)	70.8 (40.1–301.8)	2.6 (0.3–6.1)	3.3 (0.4–31.0)	42.9 (8.6–135.8)	2.8 (0.1–14.3)
Ca ²⁺	20.0 (1.4–116.8)	67.2 (34.2–363.8)	7.4 (0.8–29.2)	9.2 (0.6–69.7)	39.8 (17.2–255.8)	10.8 (0.0–107.4)
Mg ²⁺	12.4 (1.6–58.4)	22.4 (9.2–77.8)	3.6 (0.1–14.2)	3.2 (0.1–17.4)	18.8 (7.6–84.0)	4.4 (0.0–46.6)
NH ₄ ⁺	14.0 (0.6–57.1)	8.5 (2.6–41.8)	64.6 (23.6–555.0)	10.6 (0.7–76.8)	15.0 (0.8–60.8)	101.9 (0.6–606.7)
NO ₃ ⁻	103.7 (30.2–415.3)	55.5 (30.6–179.5)	205.1 (19.3–372.3)	21.7 (6.6–71.7)	34.8 (0.7–365.0)	103.9 (6.1–455.4)
SO ₄ ²⁻	127.4 (59.0–320.2)	106.8 (10.8–359.2)	332.4 (18.4–1313.9)	67.9 (12.6–335.2)	92.8 (16.6–386.0)	220.6 (3.9–1006.6)
Cl ⁻	22.7 (7.3–173.2)	18.1 (7.5–91.8)	25.2 (1.6–110.8)	5.7 (1.0–13.8)	8.9 (2.8–40.8)	26.1 (2.1–144.6)

NOTE: Data are presented as the mean with the range in parentheses.

water samples sent to the ISWS laboratory, the anions listed above plus monovalent cations were measured using ion chromatography; bivalent cations were measured by atomic absorption spectrophotometry.

After the analyses were completed, ion balances were calculated for each sample using the following formula:

$$\% \text{ imbalance} = \frac{\text{cation sum} - \text{anion sum}}{\text{cation sum} + \text{anion sum}} \times 100$$

Criteria for removing a cloud-water sample from the data base were an ion imbalance greater than 60% when the sum of the ions (cations and anions) was less than 50, greater than 30% when the sum of the ions was between 50 and 100, or greater than 15% when the sum of the ions was greater than 100. In addition, when any of the four dominant ions (H⁺, NH₄⁺, NO₃⁻, and SO₄²⁻) were not included in the analysis, the sample was removed from the data base. Ion balances were also calculated for bulk precipitation and throughfall, but samples were not removed from the data base if they did not meet the criteria listed above. This decision was made because it was felt that the throughfall and bulk precipitation samples contained ionic species that were not included in the standard analyses, in particular organic compounds for throughfall and metallic species for bulk precipitation. Less than 10% of the bulk precipitation and throughfall samples exceeded the ion imbalance ranges listed above.

It should be discussed that the 1986 ion imbalance for bulk precipitation was -36%, using the mean values shown in Table 1. Further analysis for total aluminum indicated values as high as 370 $\mu\text{equiv./L}$ during certain weeks in 1986 when there was very little precipitation. These high aluminum values in the bulk precipitation are attributed to the fact that the aluminum tower was newly erected in the spring of 1986 and was undergoing initial oxidation. Since there was very little or no rain during several of these weeks to "wash" the tower, these aluminum oxides were subsequently blown or splashed into the bulk collector that was attached directly to the tower.

Accuracy of the analyses was checked by analyzing at least one of two Environmental Protection Agency (EPA) standard solutions several times during each analytical run. Precision of the analytical measurements was calculated from duplicate analyses of the EPA solutions. Precision values were 7% or better for all analyses, except NH₄⁺, which was 12%. The data discussed here were analyzed primarily at the U.Va. laboratory. ISWS laboratory analyses were used for cloud samples in the few cases that U.Va. did not receive an aliquot.

Results and discussion

Solution chemistry

Volume-weighted mean concentrations for bulk precipita-

tion and throughfall and arithmetic means for cloud water collected at site 1 are presented in Table 1. Ranges of values are also included in Table 1. Figure 1 presents the same data as relative percent abundance of individual cations and anions. Based on the ranges, it is obvious that there is tremendous variability from week to week in the bulk precipitation and throughfall samples and from hour to hour or event to event in the cloud-water samples. The discussion that follows is based on comparisons of the mean values. Although cloud water was two to four times more concentrated for most ions, the order of dominance for ions in cloud water was similar to that of bulk precipitation. The dominant cation in both sample types was H⁺ (57 and 53% of total cations in cloud water and precipitation, respectively for 1986; 54 and 55% for 1987). The second most dominant cation in cloud water was NH₄⁺ (37% in 1986, 35% in 1987). For bulk precipitation, however, Ca²⁺ was the second most dominant cation in 1986 (17%) with NH₄⁺ the second most dominant cation in 1987 (15%). It should be noted that the volume weighted mean concentration of NH₄⁺ in bulk precipitation was similar in both 1986 and 1987 (14.0 vs. 10.6 $\mu\text{equiv./L}$, respectively) and that the change in order of cations was due to a higher Ca²⁺ mean concentration in 1986 (20.0 vs. 9.2, respectively). The dominant anion was SO₄²⁻ (59 and 50% of total anions in cloud water and precipitation, respectively, for 1986, and 63 and 71% for 1987), and the sum of SO₄²⁻ and NO₃⁻ in both sample types was greater than 90% of total anions for each year (Fig. 1).

There were, however, some notable differences in cloud-water and bulk-precipitation composition. Cloud water was four times more acidic than precipitation (251 vs. 63 $\mu\text{equiv. H}^+/\text{L}$ in 1986 and 158 vs. 40 $\mu\text{equiv. H}^+/\text{L}$ in 1987, respectively). As calculated from Table 1, the NH₄⁺/Ca²⁺ ratio for cloud water was far greater than that for bulk precipitation (22.2 vs. 0.7 in 1986, 9.4 vs. 1.2 in 1987, respectively), suggesting either (or a combination of) below-cloud scavenging of primary (Ca²⁺) aerosols by rain, considerable dry deposition of Ca²⁺, or differential dissolution of NH₃ gas in cloud water and rainwater. Altwicker and Meahar (1984) found that the NH₄⁺/Ca²⁺ ratio varied systematically between dry deposition and wet deposition, and their results indicate that the same ratio might be useful in distinguishing cloud-water deposition from rain deposition. It has been shown that untreated rain samples left for

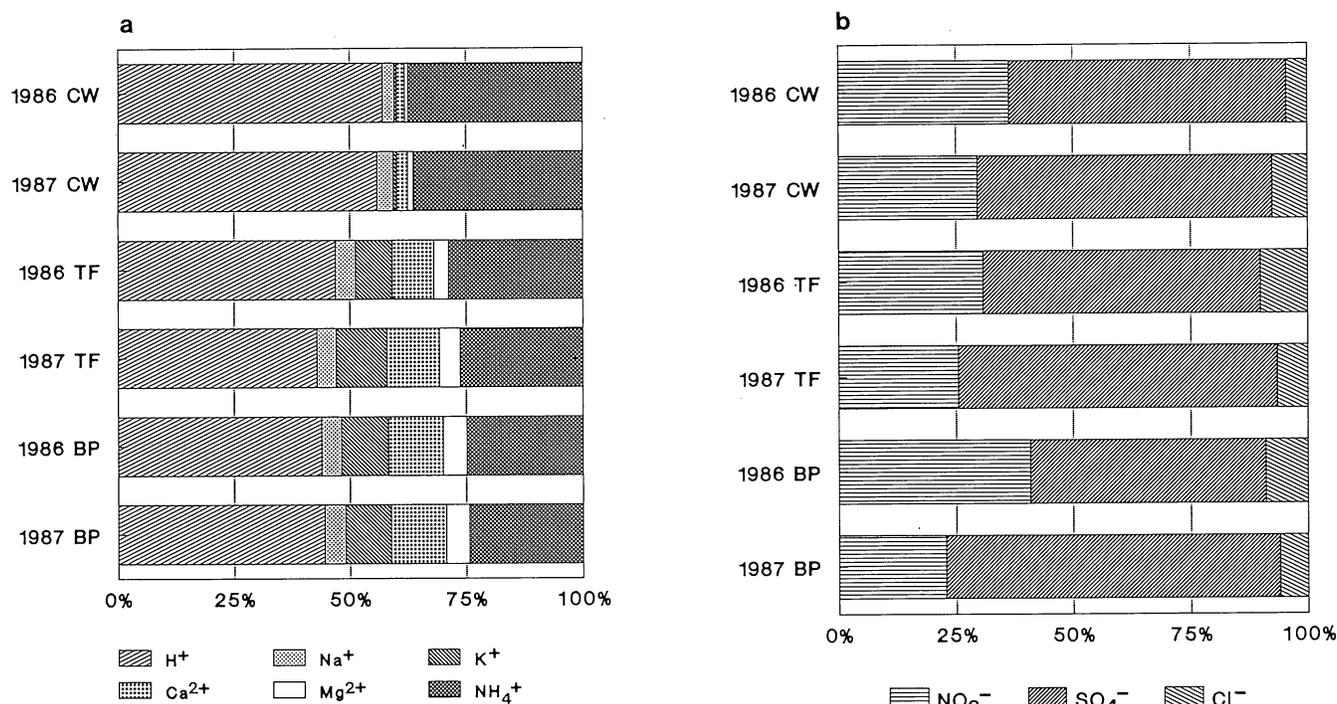


FIG. 1. Relative abundance of cations (a) and anions (b) in cloud water (CW), bulk precipitation (BP), and throughfall (TF) for Shaver Hollow, site 1.

a period of days show considerable loss of NH_4^+ due to microbial conversion in the collectors (Muller et al. 1982). However, since our collectors were treated with a biocide that could still be detected by smell when the samples were collected, we do not feel that the differences in the $\text{NH}_4^+/\text{Ca}^{2+}$ ratios were due to loss of NH_4^+ in the weekly samples.

Substantial chemical changes occurred as precipitation passed through the canopy (Table 1). Changes in solution composition as water moves through the forest canopy is consistent with results found in other hardwood forests (see Lindberg et al. 1986). Bulk-precipitation acidity was neutralized somewhat by the canopy (from 63 to 40 $\mu\text{equiv./L}$ in 1986 and from 40 to 25 in 1987). Base cations, particularly K^+ and Ca^{2+} , were removed from the canopy by either leaching out of leaf tissues or washing leaf surfaces. Potassium in throughfall was enriched 27 times relative to bulk precipitation in 1986 (70.8 vs. 2.8 $\mu\text{equiv./L}$, respectively) and 13 times relative to bulk precipitation in 1987 (42.9 vs. 3.3 $\mu\text{equiv./L}$, respectively). Calcium in throughfall was approximately three times that in bulk precipitation in 1986 (67.2 vs. 20 $\mu\text{equiv./L}$, respectively) and approximately four times that in bulk precipitation in 1987 (39.8 vs. 9.2 $\mu\text{equiv./L}$, respectively). Ammonium appeared to be retained by the canopy in 1986 (8.5 vs. 14.0 $\mu\text{equiv./L}$, throughfall vs. bulk precipitation, respectively), but removed from the canopy in 1987 (15 vs. 10.6 $\mu\text{equiv./L}$, throughfall vs. bulk precipitation, respectively).

Like NH_4^+ , anions exhibited a very interesting pattern when 1986 data were compared with 1987 data. In 1986, NO_3^- decreased by almost half from bulk precipitation to throughfall (103.7 vs. 55.5 $\mu\text{equiv./L}$, respectively), SO_4^{2-} decreased by 15% (127.4 vs. 106.8 $\mu\text{equiv./L}$, respectively), and Cl^- decreased by 19% (22.7 vs. 18.1 $\mu\text{equiv./L}$,

respectively). In 1987, however, the three anions listed above increased by 60, 37, and 54%, respectively, in throughfall compared with bulk precipitation. This difference in ion ratios between 1986 and 1987 is attributed to the location of the bulk precipitation collector. As stated above, in 1986, the bulk precipitation collector was mounted to the guard rail at the top of the tower. Any occurrence of clouds impinging on the site would result in cloud-water deposition directly onto the bulk collector or cloud water being blown into the collector from the tower guard rail. The high concentrations of the ions listed in Table 1 for bulk precipitation in 1986 compared with bulk precipitation in 1987 and compared with throughfall in 1986 suggest that significant amounts of cloud water may have been deposited into the bulk precipitation collector in 1986. This increased deposition of high-concentration cloud water provided an additional source of ions to the forest canopy that appear to have been retained. This possible retention of ions was not evident in the data for 1987 when the bulk precipitation collector was not located on the tower and, therefore, was not significantly affected by deposited cloud water.

As with NH_4^+ , the apparent leaching of NO_3^- in 1987 would at first lead to the conclusion that the ridgetop canopy was not nitrogen limited. However, by including a significant contribution from cloud water that does not appear in the 1987 bulk-precipitation measurements made near ground level, these results suggest a substantial uptake of nitrogen by the canopy. Whereas a determination of the aqueous aluminum chemistry in the bulk collector is beyond the scope of this work, it is possible that the presence of aluminum hydroxide in the 1986 bulk samples could have contributed to the lower H^+ and NH_4^+ values relative to NO_3^- and SO_4^{2-} than would be expected from the added deposition of cloud water.

TABLE 2. Weekly throughfall and precipitation amounts (cm) for cloud and no cloud weeks

Commencement date (m/d)	Throughfall	Precipitation	Ratio	Cloud or no cloud
1986				
7/22	0.96	0.8	1.2	Cloud
7/29	1.14	1.5	0.76	Cloud
8/05	3.01	5.5	0.55	Cloud
8/12	1.09	2.1	0.52	Cloud
8/19	5.76	4.9	1.18	Cloud
8/26	3.80	3.7	1.03	Cloud
9/02	0	0.5		Cloud
9/09	0	0		
9/16	0	0		
9/23	0.44	0.25	1.76	Cloud
9/30	0	0.2		No cloud
10/07	1.20	1.3	0.92	Cloud
10/14	0	0		
10/21	1.94	1.6	1.21	Cloud
1987				
4/21	1.77	2.0	0.89	Cloud
4/28	3.55	4.75	0.75	Cloud
5/05	0	0.11		No cloud
5/12	4.09	5.38	0.76	Cloud
5/19	5.53	5.48	1.01	Cloud
5/26	2.35	3.16	0.74	No cloud
6/02	3.11	3.31	0.94	Cloud
6/09	0.70	0.99	0.71	No cloud
6/16	1.26	1.62	0.78	No cloud
6/23	0.59	0.86	0.69	Cloud
6/30	0.59	0.69	0.86	Cloud
7/07	2.46	—	—	No cloud
7/14	0	0.03		No cloud
7/21	0	0		No cloud
7/28	1.06	1.35	0.79	Cloud
8/04*	0.56	0.84	0.67	Cloud
8/13	0.28	0.37	0.76	Cloud
8/20	2.12	3.1	0.68	No cloud
8/27	0	0		No cloud
9/03	Overflow	18.8		Cloud
9/10	3.47	4.1	0.85	Cloud
9/17	1.91	2.60	0.73	Cloud
9/24	0.72	1.24	0.58	Cloud
10/01	0.62	0.7	0.89	Cloud
10/08	0	0.03		No cloud
10/15	0.28	0.38	0.74	Cloud
10/22	1.70	1.96	0.87	Cloud

*Sampling interval 9 days.

Potential contributions from cloud water

The deposition of cloud water to vegetation surfaces has been estimated in several ways, and deposition at a variety of sites is reviewed by Schemenauer (1986). As discussed in that review, cloud-water deposition estimates have large uncertainties resulting from difficulties in determining and accurately quantifying the factors that control deposition. Among the factors expected to affect cloud-water deposition are wind speed, cloud liquid water content, the surface area and geometry of the vegetation, and cloud duration.

Lovett et al. (1982) used a modeling approach for estimating hydrological and chemical inputs to a subalpine balsam fir forest, based on the micrometeorology of turbulent transfer and detailed destructive sampling of vegetation. Since our national park site prevents this type of vegetation sampling, and given a lack of models for cloud-water deposi-

tion to deciduous forests, we have attempted to quantify the cloud-water deposition using precipitation-throughfall relationships.

Meteorological data gathered at site 1 were analyzed for precipitation amount and cloud occurrence. Rain-gauge data were available from 22 July to 28 October 1986 and from 21 April to 29 October 1987. Weeks were divided into two groups: (i) weeks when there was precipitation but no cloud impinging on the mountain and (ii) weeks with precipitation and clouds impinging on the mountain. Time series of relative humidity measured with a Rotronics MP-100 sensor (a thin film capacitance-type sensor) were plotted for the periods of study. Cloud onset was delineated by a rapid increase in relative humidity to some stable value greater than 95%. Cloud dissipation was delineated by a rapid decrease in relative humidity below the 95% threshold. In

TABLE 3. 1986 and 1987 rain- and cloud-water composition and deposition for the same period as Table 1

	H ⁺	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1986				
Composition (μeq/L)				
Wet only (22.35 cm)	25.1	18.7	22.8	59.6
Cloud water	251.2	164.6	205.1	332.4
Deposition (kg/ha)				
Wet only	0.056	0.76	3.20	6.40
Cloud water	0.13	1.50	6.60	8.30
1987				
Composition (μeq/L)				
Wet only (66.65 cm)	34.7	18.0	19.0	54.8
Cloud water	158.0	103.0	102.7	219.4
Deposition (kg/ha)				
Wet only	0.23	2.20	7.90	17.6
Cloud water	0.086	1.00	3.50	5.70

comparison with a cloud detector developed by Krovetz et al. (1988) installed at site 1 in 1987, this method was found to be a good indicator of cloud occurrence. No attempt was made to sort weeks of cloud occurrence by duration of cloud event.

Precipitation amount measured with the tipping-bucket rain gauge and throughfall volume converted to depth were compared for weeks with cloud events and weeks without any cloud occurrence impinging the site. For the 14 weeks of the 1986 study period, 3 weeks had no precipitation. Only 1 week had precipitation with no cloud event, and for this week the precipitation was only 0.2 cm and the throughfall collectors were all empty. Thirteen weeks had precipitation and at least one cloud event. For 1 of these weeks, no throughfall was collected. The total amount of throughfall for the cloud-event weeks in 1986 was 19.34 cm and the total amount of precipitation for these same weeks was 21.65 cm. The resulting ratio of throughfall to precipitation for the cloud-event weeks was 0.89.

For the 27 weeks of the 1987 study period, 2 weeks had no precipitation. Eight weeks had precipitation with no cloud events. Of these, 3 had 0.1 cm or less and no throughfall, and 1 had equipment failure, which resulted in loss of rain gauge data. There were 17 weeks with precipitation and cloud events; one in which the throughfall collectors overflowed, resulting in loss of data. The total amount of throughfall for the no-cloud weeks in 1987 was 6.43 cm and the total amount of precipitation for these weeks was 8.87 cm. The resulting ratio of total throughfall to total precipitation for these no-cloud weeks was 0.72. For cloud-event weeks in 1987, the total throughfall was 29.83 cm and the total precipitation was 36.01 cm. The ratio of throughfall to precipitation for these weeks was 0.83.

As would be expected, the ratios of throughfall to precipitation vary from week to week. Table 2 presents the weekly throughfall and precipitation amounts for the weeks used to determine the totals listed above. The mean values of the throughfall and precipitation ratios were 1.01 for 1986 cloud weeks, 0.80 for the 1987 cloud weeks, and 0.73 for the 1987 no-cloud weeks. Standard deviations were 0.39, 0.11, and 0.04, respectively. Mann-Whitney *U* tests of the means showed that the 1986 cloud weeks vs. the 1987 no-cloud weeks (again, there were no 1986 no-cloud weeks that had precipitation and throughfall) were significantly different at the 0.16 level. The 1987 cloud weeks vs. the 1987

no-cloud weeks were significantly different at the 0.17 level.

Given the number of observations and the associated high variability in week to week ratios, statistical tests provide limited resolution in assessing these differences. Therefore, we also subjectively interpreted the distributions of the ratios to assess the differences. For the 1986 cloud weeks, 7 of the 9 weeks had throughfall to precipitation ratios above the mean value of the ratio for 1987 no-cloud weeks. Ratios for 6 of these weeks were above the no-cloud maximum ratio, and only 2 weeks had ratios below the no-cloud minimum ratio. For the 1987 cloud weeks, 12 of the 16 weeks had ratios above the mean ratio for no-cloud weeks, 8 of the 16 had ratios above the maximum no-cloud ratio, and only 2 were below the minimum ratio for no-cloud weeks. These comparisons, together with the results of the statistical evaluations, indicate that the ratios of the total throughfall to total precipitation for weeks with cloud events are generally higher than those for weeks without cloud events.

Cloud-water deposition to the site can be estimated in two ways using these total value ratios. If direct deposition to the forest floor is of primary interest, then the ratio of throughfall to precipitation during weeks with no-cloud events can be used to estimate the amount of water intercepted by the canopy and subsequently lost to evaporation or utilized within the canopy. The ratio of 0.72 in 1987 is within the range of values reported for deciduous canopies (see Geiger 1965 for a discussion). By applying this ratio to weeks with cloud events, the expected throughfall for 1986 would have been 15.59 cm and for 1987, 25.93 cm. The cloud-water component of the total deposition to the forest floor would then have been 3.75 cm (24% increase to the forest floor) in 1986 and 3.90 cm (15% increase to the forest floor) in 1987.

To estimate cloud-water deposition to the canopy, canopy interception and subsequent evaporation of cloud water must be considered. Assuming the cloud-water loss to be similar to the precipitation loss, the resulting estimates of cloud-water deposition to the canopy are 5.21 cm for 1986 and 5.42 cm for 1987. For the 14 weeks of the 1986 study period, a total of 22.35 cm of precipitation was measured at site 1. For the 27 weeks of the 1987 study period, a total of 66.65 cm was measured. The cloud-water deposition estimates represent an increase in the water input to the canopy over precipitation of 23% for 1986 and 8% for 1987.

To estimate the contribution of cloud water to the ionic deposition of site 1, the estimated amount of deposited cloud water was combined with the mean cloud-water composition for each year of the study period. The values for the major ionic constituents are shown in Table 3. Also shown in Table 3 is the estimated deposition from precipitation for the same period. Since there was no wet only collector at site 1 during the 1986 study period, the 1986 wet-only estimates were obtained by using the precipitation composition from a National Acid Deposition Program site located at Big Meadows station. Big Meadows is only 15 km south of site 1 and 20 m higher in elevation, so the precipitation composition is likely to be representative of site 1. Comparison of 1987 wet-deposition data between the two sites showed a maximum difference of 30%, with wet deposition of H⁺ and SO₄²⁻ differing by 10% or less. The precipitation amount measured at site 1 was used for the volume. For 1987, wet-deposition data were collected at site 1 using an AeroChem Metrics collector.

As can be seen from Table 3, for the 1986 study period, whereas cloud water was estimated to have contributed only 23% of the total water to site 1, it was estimated to have contributed, relative to precipitation, approximately two times as much H^+ (0.13 vs. 0.06 kg/ha, respectively), NH_4^+ (1.50 vs. 0.76 kg/ha, respectively), and NO_3^- (6.60 vs. 3.20 kg/ha, respectively), and 30% more SO_4^{2-} (8.30 vs. 6.40 kg/ha, respectively). For 1987, cloud water contributed only 8% of the total water to site 1, but approximately 30% of the major ionic deposition.

It must be emphasized that the 1986 and 1987 deposition cannot be compared directly, because the study periods for the 2 years did not cover the same time intervals. In addition, sampling of cloud events was not distributed uniformly over the 2 years.

There are uncertainties in these estimates of cloud-water deposition to the forest canopy at site 1. Interception of both precipitation and cloud water depends on the canopy structure and wind speed. The early portion of the study period for 1987 was during the time that the canopy was increasing in leaf-area index and, therefore, the interception of water by the canopy was probably changing. There was only 1 week of rain with no cloud events during this canopy emergence period, and the amount of precipitation was only 0.12 cm. No throughfall was collected during that week, which indicated an amount of interception similar to the one rain event with no clouds in 1986 when the canopy was fully leafed. It is likely that wind speed was different for different rain and cloud events, which would result in different throughfall to precipitation ratios over the season. However, by considering the total values for throughfall and precipitation over the entire warm season, it is expected that the various combinations of high and low wind speed rain and cloud events would offset one another. A bias would occur if, for example, all the weeks with rain and no cloud had very high wind speeds and all the weeks with rain and cloud events had very low wind speeds. However, a review of the meteorological data collected at site 1 indicated a wide range of wind speeds for cloud events and for precipitation events. Variation in evaporation rates could also have an effect, both evaporation from the canopy and evaporation from throughfall collectors. Evaporation from the collectors should be similar for rain and cloud water, so any errors caused by evaporation from the collectors should not affect the ratios used to compute cloud-water deposition. Evaporation of intercepted water from the canopy might be expected to affect cloud water more than rainwater, since the input rates of cloud water would be much less than those for rain. Just as there were a few weeks with very small amounts of precipitation but no throughfall, there were probably times when cloud water was deposited but evaporated before the canopy became sufficiently wet to drip down to the throughfall collectors.

Whereas this initial attempt to estimate cloud-water deposition to a high elevation deciduous forest has uncertainties that cannot be quantified at this time, it does indicate that cloud water can contribute a significant amount of water to the canopy. Perhaps more importantly, it suggests that cloud water can contribute as much or more deposition than rain of ionic species that might affect the forest. Additional work is necessary to quantify the uncertainties in the deposition estimates and to determine what, if any, effects the enhanced deposition of ions from cloud

water has on the growth and development of high-elevation forests.

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