

Effects of Collection Interval on Quality of Throughfall Samples in Two Northern Hardwood Stands

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ABSTRACT

The chemical stability of weekly and biweekly throughfall collection intervals were compared at two northern hardwood stands in the Great Lakes region. Throughfall concentrations of Cl^- , NO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and K^+ were not significantly ($p \leq 0.05$) affected by the increased collection time, whereas throughfall concentrations of NH_4^+ and H^+ collected biweekly were significantly different ($p \leq 0.05$) than concentrations of these ions in weekly samples. The 1-wk increase in collection interval at one stand decreased concentrations of NH_4^+ and increased concentrations of H^+ 88 and 131%, respectively. The chemical instability of these ions appeared to be related to biological assimilation and/or nitrification of NH_4^+ . Stability of these ions decreased with increasing concentrations of inorganic N in the throughfall. These changes in concentrations of NH_4^+ and H^+ may introduce sampling bias when estimating throughfall fluxes or concentrations of these ions from biweekly collections. The decreased stability of these ions with increased concentrations of inorganic N should be an important consideration when selecting sampling intervals for stands that receive differing deposition levels of atmospheric N or have different canopy retention rates of N.

THE DETERMINATION of the chemical inputs to soils from canopy throughfall is an integral facet of nutrient cycling and acid precipitation research (Parker, 1983). Although the chemical composition of throughfall is routinely determined in these types of studies, relatively little information has been reported concerning chemical stability of throughfall samples in the field. Furthermore, no standard sampling interval has been widely accepted and intervals from as long as 5 wk (Richter and Lindberg, 1988) to as short as 24 h (Cronan and Reiners, 1983) have been employed for throughfall collection. A number of studies have investigated the effects of collection interval on the sample quality of incident precipitation (Tang et al., 1987; Sisterson et al., 1985; dePena et al., 1985; Madsen, 1982; Galloway and Likens, 1978). However, extrapolating results from incident precipitation studies to throughfall may not be justified due to increased concentrations of solute, dissolved organic matter, and biological activity associated with throughfall compared with incident precipitation. Thus, the following experiment was initiated to determine the changes in the quality of throughfall given two different collection intervals.

METHODS

The study was performed at two northern hardwood stands (Oceana and Alberta) in the Lower and Upper Pen-

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insula of Michigan. The Oceana stand is located near Hesperia in the Lower Peninsula of Michigan, and the Alberta stand is located near Houghton in the Upper Peninsula of Michigan. Basal area of trees greater than 5 cm averages between 30.8 and 31.5 $\text{m}^2 \text{ha}^{-1}$ at the two sites. Sugar maple (*Acer saccharum* Marsh.) comprises 65.6 and 91.7% of the basal area of the Oceana and Alberta sites, respectively. Annual deposition of SO_4^{2-} and NO_3^- in precipitation between 1987 and 1989 at the Oceana site has been 50 to 85% greater than at the Alberta site.

Five throughfall collectors were located within a 30 by 30 m plot at each site. These collector locations were fixed over the duration of the study. The collectors consisted of a 4-L bottle fitted with a 16-cm diam. funnel. The bottles were painted black to minimize light transmission and the funnels were covered with a 3-mm mesh to eliminate large organic debris. Samples from bottles were collected weekly and composited by site.

To evaluate the effects of collection intervals on throughfall quality, a second set of throughfall collectors was installed within 1 m of each of the collectors at each site. These bottles were collected biweekly—six times during the summer and fall of 1988. The samples were composited in the same manner as the weekly samples to give a 2-wk field sample. Due to below normal rainfall, samples were collected only five times at the Oceana site. Only four collections at the Oceana site produced enough water to allow chemical analysis.

Within 24 h after collection, pH was determined for all samples with a Fisher Accumet Model 810 pH meter. Samples were filtered with a 0.45 μm filter immediately after pH determination and then stored at 4 °C until anion and cation analysis was concluded. Major anion concentrations were determined by ion chromatography using a Dionex Model 2010 ion chromatograph. Ammonium concentrations were determined by an Orion/Scientific Products Model AC-200 Autoanalyzer. Samples were acidified using nitric acid after NH_4^+ analysis. Concentrations of Ca^{2+} , Mg^{2+} , and K^+ were determined using a Perkin-Elmer Model 5000 spectrophotometer.

Analysis

Differences between biweekly and weekly sampling methods were determined by subtracting the weekly fluxes or volume-weighted concentrations from the respective biweekly fluxes or concentrations for each 2-wk sampling period and specific ion. The proportional change in chemical composition was calculated (Eq. [1]) to evaluate relative chemical stability of the throughfall collected.

$$100\% \times (\text{Biweekly conc.} - \text{Weekly conc.}) / \text{Weekly conc.} \quad [1]$$

Paired *t*-tests were used to make statistical comparisons between the two collection intervals for each site. Pearson-product correlation coefficients were used to quantify the relationship of ions collected using the two collection intervals.

RESULTS AND DISCUSSION

Chemical Concentration

The effects of collection interval on chemical composition were evaluated by comparing the ion con-

Table 1. Mean concentrations for and differences between biweekly and weekly collection intervals and *p* value associated with *t*-test for each site and major ion.

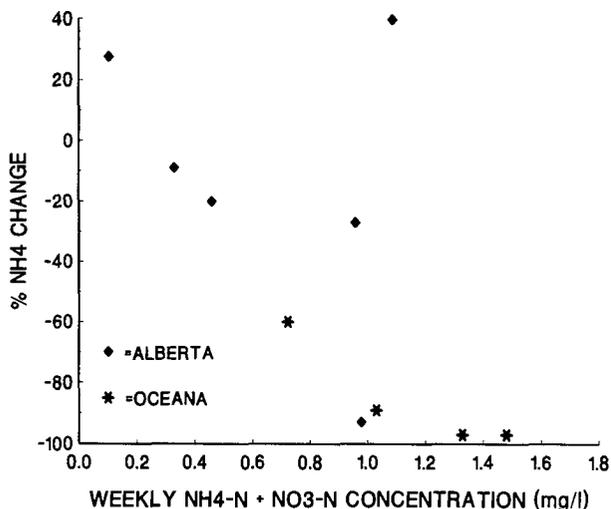
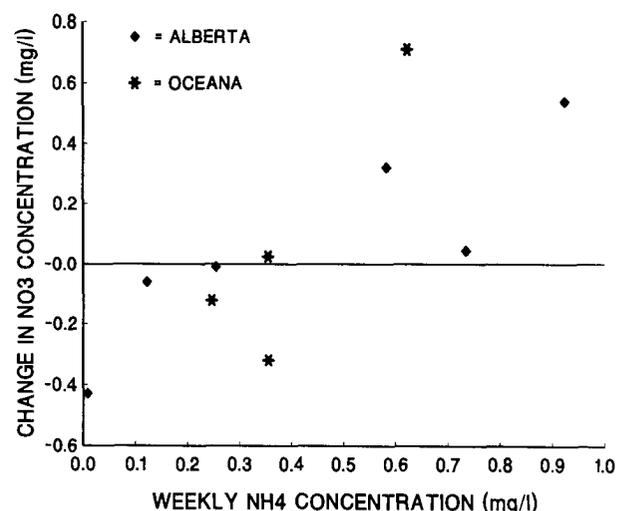
Major ion	Alberta				Oceana			
	Weekly interval	Biweekly interval	Difference (Biwk - Wk)	<i>p</i> value	Weekly interval	Biweekly interval	Difference (Biwk - Wk)	<i>p</i> value
	mg/L				mg/L			
H ⁺	0.0024	0.0018	-0.0006	0.234	0.0065	0.0150	0.0085	0.002
Cl ⁻	1.19	0.66	-0.53	0.083	0.65	0.72	0.07	0.168
NO ₃ ⁻	1.38	1.45	0.07	0.648	3.69	3.77	0.08	0.755
SO ₄ ²⁻	2.86	2.59	-0.27	0.272	4.05	4.09	0.04	0.744
NH ₄ ⁺	0.44	0.31	-0.13	0.496	0.40	0.05	-0.35	0.025
Ca ²⁺	2.24	1.81	-0.43	0.211	1.99	2.01	0.02	0.724
Mg ²⁺	0.45	0.35	-0.10	0.179	0.42	0.43	0.01	0.802
K ⁺	2.33	3.93	1.60	0.238	1.71	1.96	0.25	0.140
Inorganic N (NO ₃ - N + NH ₄ - N)	0.65	0.57	-0.06	0.531	1.14	0.89	-0.25	0.009

centrations of the samples collected weekly and biweekly for each collection period and each site (Table 1). No significant differences ($p \leq 0.05$) in concentrations were found between the two collection intervals for SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺, Mg²⁺, or K⁺. Only NH₄⁺ and H⁺ at the Oceana site showed significant differences between collection intervals ($p \leq 0.05$). Concentrations of NH₄⁺ were consistently lower and H⁺ concentrations higher in the samples collected biweekly compared with samples collected weekly during each sampling period at the Oceana site. Although chemical composition of throughfall and incident precipitation differ, studies developed to determine the effect of collection interval on the chemistry of incident precipitation have also observed decreases in concentration of NH₄⁺ with increasing collection intervals (Tang et al., 1987; Sisterson et al., 1985; dePena et al., 1985; Galloway and Likens, 1978).

Biological assimilation or transformation of N has been suggested as a mechanism contributing to decreased concentrations of inorganic N species with increased sampling intervals (Sisterson et al., 1985; Richter and Lindberg, 1988). Comparisons from this study show that the decrease in concentrations of NH₄⁺ with increased collection time were strongly related to initial concentrations of inorganic N in the

throughfall samples (Fig. 1). The percent change in NH₄⁺ concentrations (Eq. [1]) were found to be weakly correlated with NO₃⁻ concentrations ($r = -0.543$, $p = 0.10$) and strongly correlated ($r = -0.631$, $p = 0.05$) with concentrations of inorganic N (NO₃-N + NH₄-N) measured in the samples collected weekly. These results suggest that biological activity is responsible for the decreased content of NH₄⁺ with increased collection time, and that the microbial activity responsible for the losses is limited by the availability of N in throughfall.

During several sampling periods, increased concentrations of NO₃⁻ were found in the biweekly samples compared to the weekly samples. This would imply that nitrification may be responsible for the lowered concentrations of NH₄⁺ in the biweekly samples. Differences in NO₃⁻ concentration between biweekly and weekly samples were significantly and positively correlated ($r = 0.775$, $p = 0.01$) with concentrations of NH₄⁺ in the weekly samples. Biweekly sample concentration of NO₃⁻ showed a net gain when concentration of NH₄⁺ in the weekly samples was greater than 0.35 to 0.40 mg/L (Fig. 2). At NH₄⁺ concentrations less than 0.35 mg/L, concentrations of NO₃⁻ in the biweekly samples were less than or equal to concentrations of NO₃⁻ in the samples collected weekly. Assimilation of

**Fig. 1.** Percent change in NH₄⁺ concentrations of the biweekly samples compared with the concentration of inorganic N in the weekly samples.**Fig. 2.** Change in NO₃⁻ concentration between biweekly and weekly sampling intervals compared with weekly NH₄⁺ concentration of weekly samples.

NO_3^- is evidently greater than nitrification additions when concentrations of NH_4^+ are low. However, when NH_4^+ concentrations are higher, NO_3^- concentrations increase as a result of decrease NO_3^- assimilation or increased nitrification. Decreased assimilation rates of NO_3^- under these conditions is likely related to the preferential assimilation of NH_4^+ compared with NO_3^- (Alexander, 1986).

The increased amounts of H^+ in the biweekly samples evident at the Oceana site also appear to be related to the biological assimilation or transformations of NH_4^+ . The Oceana site that had the greatest decreases in NH_4^+ content also had the greatest increases in H^+ . Changes in the H^+ concentrations were negatively correlated ($r = -0.689$, $p = 0.03$) with the percent change (Eq. [1]) of NH_4^+ in the samples. Assimilation of 1 mol of NH_4^+ by microorganisms involves a 1 mol gain of H^+ , whereas nitrification of 1 mol of NH_4^+ results in a 2 mol gain of H^+ to the solution (Binkley and Richter, 1987; Stevenson, 1986). Average losses of NH_4^+ and gains of H^+ for the Oceana site expressed as molar ratios were 2.4:1 rather than 1:1. Differences between the observed and expected ratios may be caused by lower dissociation of weak acids with decreased pH as a result of the release of H^+ ions. This would also explain why increases of H^+ were not observed with the minimal losses of NH_4^+ at the Alberta site.

The strong correlations between the initial amounts of inorganic N and the changes in throughfall concentrations of NH_4^+ , NO_3^- , and H^+ demonstrate that the degradation of throughfall samples are related to initial concentration of inorganic N in the throughfall. The Oceana stand, which had on the average 75% more inorganic N in the weekly samples than the Alberta site, also lost 139% more NH_4^+ from the biweekly samples than the Alberta site. Differences in concentrations of inorganic N in throughfall at the two stands were in part influenced by the initial concentrations of NH_4^+ and NO_3^- in precipitation received at the two stands. Volume weighted concentrations of inorganic N in incident precipitation at the Oceana site was 28% greater than at the Alberta site during the sampling period. Thus, stability of throughfall samples in these ecosystems decreased with increasing atmospheric deposition of inorganic N at the Oceana stand.

Chemical Fluxes

Differences between collection intervals for NH_4^+ and H^+ fluxes were significant ($p \leq 0.05$) at the Oceana stand, whereas differences at the Alberta stand were only significant for Ca^{2+} . Hydrogen and NH_4^+ fluxes estimated from biweekly sampling at the Oceana stand were respectively 226 and 21% of the estimates determined by weekly sampling. Although differences in Ca^{2+} concentrations for the two sampling intervals at the Alberta site were not significant ($p \leq 0.05$), differences in Ca^{2+} fluxes were significant. This appears to be related to an average 5.5% evaporation loss from samples collected biweekly compared to samples collected weekly.

CONCLUSIONS

Throughfall quality was found to decrease when an additional week was added to the collection interval. At the Oceana site sample concentrations of NH_4^+ decreased and H^+ increased 88 and 131%, respectively, when collectors were left in the field for an additional week. Changes in throughfall concentrations of NH_4^+ and H^+ are generally greater than have been found in studies of collection interval on incident precipitation (Sisterson et al., 1985; dePena et al., 1985; Madsen, 1982). This is probably due to the increased microbial activity, dissolved organics, and/or solutes in throughfall as a result of canopy processing.

Changes in throughfall NH_4^+ and H^+ collected biweekly appear to be related to the assimilation or nitrification of NH_4^+ by microorganisms. The magnitude of NH_4^+ losses were positively correlated to initial levels of inorganic N in the throughfall. The relationship between organic N concentrations and the chemical instability of throughfall has important implications for research projects employing throughfall collection and analysis to determine canopy exchange, chemical inputs to soils, or fluxes of nutrients in the ecosystem. In stands with high N fluxes, throughfall concentration and flux estimates of H^+ may be positively biased and NH_4^+ may be negatively biased when using collection intervals of 2 wk or more without preservatives to limit biological activity. Given this scenario comparisons of stands with differing levels of atmospheric deposition of inorganic N or stands with different rates of canopy retention of inorganic N would also suffer from these same biases.

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