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CONTROLS ON LEACHING FROM CONIFEROUS FOREST FLOOR MICROCOSMS

by CHRISTOPHER S. CRONAN

Department of Biological Sciences, Dartmouth College
Hanover, New Hampshire 03755 U.S.A.

KEY WORDS

Acid rain Biogeochemistry Coniferous ecosystem Forest floor Forest soils Microcosm Plant uptake Soil leaching

SUMMARY

Studies were conducted with coniferous forest floor microcosms to examine the potential influence of acid precipitation, temperature changes, and plant uptake upon the chemistry of soil leachate solutions. The experimental design included two temperatures and three different simulated throughfall chemistry treatments. When the acidity of throughfall inputs to the microcosms increased, the forest floors exhibited increased leaching losses of calcium, magnesium, potassium, and ammonium. The fact that aluminum losses did not increase correspondingly suggested that there may be a kinetic lag in the mobilization and leaching of aluminum. When microcosms were exposed to warmer temperatures, percolates showed increased leaching losses of calcium, potassium, ammonium, sulfate, nitrate, and organic anions. Forest floor microcosms exposed to simulated average field conditions behaved very much like field plots under the same environmental conditions; however, there were predictable differences in leaching losses between laboratory and field systems for those ions which are strongly controlled by plant uptake. In general, the exclusion of plant uptake from microcosms resulted in increased leaching of potassium, nitrate, ammonium, and sulfate relative to field plots.

INTRODUCTION

Solutions percolating through the soil horizons of forest ecosystems may be chemically modified by a variety of dynamic environmental variables or processes. The influence of each environmental factor upon the chemistry of soil leachates may vary for a given site or between different sites, depending upon the character of the vegetation, geological substrate conditions, geographic and topographic position, climate and site microclimate, soil physical-chemical properties, rainfall history, season, and site disturbance history. In recent years, numerous attempts have been made in biogeochemical research to develop predictions concerning the importance of different environmental variables in

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determining the nature of ion leaching losses from particular forest soils. Investigators have used a variety of field and laboratory experimental approaches, including: (i) experiments with field trenched plots and laboratory lysimeters designed to examine the influence of plants upon ion leaching[14,19]; (ii) studies with laboratory and field lysimeters to assess the consequences of atmospheric inputs of strong acid to plant-soil systems[1,3,12,21]; (iii) experiments concerned with the effects of partial soil sterilization on leaching[2]; (iv) studies examining the effects of critical nutrient limitation upon ion release and leaching[13]; and (v) correlation analysis between field environmental conditions and ion transport patterns through soils[11].

In this investigation, laboratory lysimeter studies were conducted under simulated natural conditions to examine the environmental variables which control ion leaching losses from coniferous forest floors. These experiments were intended to complement field studies of element transport being carried out in the New Hampshire subalpine zone[7], and were designed to test the effects of precipitation acidity, temperature, and plant nutrient uptake upon leaching losses from undisturbed forest floor microcosms. Precipitation pH was selected as a treatment factor, because of interest in the potential effects of regional acid precipitation on soil fertility. Temperature was chosen as a second factor to examine the influence of changing biological mineralization rates on leaching losses of ions. Finally, plant uptake of nutrients became an indirect third factor, because plants were intentionally excluded from the microcosms during selection of the forest floor cores and by clipping during the experiments. These microcosms could thus be compared with similar forest floors in the field where plants were present. The experimental design for this investigation focussed upon the following primary hypotheses. (i) Cation leaching from the forest floor increases as the acidity of precipitation and canopy throughfall inputs increases. This occurs as a result of mass action ion exchange between the precipitation-borne H-ions and exchangeable cations in the forest floor. (ii) Nutrient leaching losses from the forest floor are controlled by the availability of these nutrients in exchangeable and readily soluble forms. With higher soil temperatures between rain events, nutrient leaching from the forest floor increases as a result of increased microbial mineralization and nutrient release. (iii) Nutrient leaching losses are in part controlled by differential elemental accumulation by plants[18]. Exclusion of plant uptake from the forest floor results in relatively more leaching of highly mobile critical plant nutrients like potassium and nitrogen, as compared to other elements.

METHODS

Sample materials

Forest floor samples used in this laboratory study were obtained from field sites located in the subalpine zone of Mt. Moosilauke (71° 50′W, 44° 1′N) in the White Mountains of New Hampshire. Mt. Moosilauke (elev. 1462 m) is the westernmost of the White Mountain summits that extend above treeline, and has been the focus of a number of recent studies of ecosystem structure and function[6,7,15,18].

The forests of the subalpine zone are relatively short-statured and floristically simple. The dominant canopy species, *Abies balsamea*, is usually associated with the minor subdominants *Betula papyrifera* var. *cordifolia*, *Picea rubens*, and *Pyrus americana*[15]. The soils are predominantly Typic or Lithic Cryorthod and Borofolist soils[16], and have been described elsewhere[4]. The soils of this cool temperate environment are characterized by a prominent forest floor (averaging 12.2 cm in depth), the soil horizon of prime interest in this study.

Experimental design

Laboratory microcosm experiments were conducted in 1977 using soil column tension lysimeters and intact cylinders of forest floor. For these laboratory experiments, thirty-five intact blocks of forest floor were removed from two comparable subalpine forested stands between June 13–15, 1977. These cores were treated as described by Cronan[4] and were stored at 6°C. Within one week, thirty 12-cm diameter cores of forest floor had been installed in acid washed-distilled water rinsed plastic tension lysimeters[5], and had been positioned in a controlled environmental chamber programmed to simulate summer balsam fir zone conditions (6°C with a 12/12 light/dark cycle).

Beginning in the first week of July, the 30 lysimeters were subjected to a 3.5 cm, pH 4.0 simulated throughfall event (Table 1) every five days. For each lysimeter wetting, two 200 ml portions of throughfall were applied over the course of thirty minutes by an automatic pressurized rainmaker system[4]. Throughout the 30 min precipitation event, each of the lysimeters was evacuated with *ca* 0.3 bars of tension. The microcosms were each exposed to four of these preliminary, 'conditioning' throughfall events, in order to bring the forest floor cores to more or less stable behavior in their new controlled environment.

Experimental sampling was initiated in mid-July. In order to characterize the baseline, or pretreatment, leachate chemistry for each forest floor microcosm, lysimeter percolates were sampled for each of the first six pH 4.0, 6°C throughfall events (day 1–27). After the completion of six 'pretreatment period' simulated throughfall events, the 30 microcosms were segregated at random into six separate treatment groups, each containing five of the original lysimeters. The five microcosms assigned to the pH 4.0, 6°C treatment group continued to receive the unchanged pretreatment conditions and thus served as the control group for the microcosm experiment. In the same 6°C environmental chamber, five other microcosms were shifted to a pH 5.7 artificial throughfall, while five others were exposed to pH 3.5 artificial throughfall conditions. The fifteen remaining forest floor microcosms were moved to a chamber set at 24°C, and were segregated respectively into groups exposed to pH 5.7, 4.0, and 3.5 artificial throughfall. During the treatment period, the groups of microcosms all received six additional simulated throughfall applications over the course of 30 days (experiment day 28–57) using appropriate artificial throughfall solutions (Table 1). After six sample collections had been obtained under treatment conditions, the 30 microcosms were maintained for seven additional throughfall events (between day 58–92) under the same treatment conditions. Of the seven supplementary throughfall events, only the seventh was used for sample leachate collections.

It should be noted that the pH 4.0 and pH 3.5 treatment groups constituted an experiment in

Table 1. Composition of simulated canopy throughfall for the laboratory leaching experiments

Treatment	Concentration (micro-equivalents per liter)											
	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Total cations	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-	Total anions
pH 5.7	2	0	0	0	100	0	102	0	0	100	2	102
pH 4.0	100	25	10	20	4	5	164	125	20	19	0	164
pH 3.5	300	25	10	20	4	5	364	325	20	19	0	364

which microcosm leaching under simulated average ambient throughfall conditions was compared with leaching in response to a pH 3.5 throughfall regime of the hypothetical future. For that most acid treatment, the lysimeters at both temperatures first received two pH 3.7 events, followed by pH 3.5 throughfall events for the duration of the experiment. The pH 5.7 treatments were planned as a separate comparative experiment designed to examine forest floor leaching resulting primarily from soil-derived organic acids, rather than atmospheric mineral acids. As shown in Table 1, the pH 5.7 groups received an altogether different artificial throughfall from the other groups. The pH 5.7 artificial throughfall was a solution of distilled water to which 10^{-4} N NaCl had been added to produce an ionic strength roughly similar to the other treatments.

The final phase of the experiment involved trying to deplete the available (soluble and exchangeable) cation pool in the forest floor microcosms by exceeding the mineralization rate with excessive H-ion loading and exchange. The focal hypothesis for this experiment was that cation leaching losses are controlled by the availability of soluble and exchangeable cations, so that cation leaching losses decrease as the finite pool of available cations decreases. The two treatment groups exposed to pH 3.5 throughfall were selected for this experiment, because these lysimeters had already received the greatest H-ion inputs and would be most likely to exhibit cation depletion effects associated with H-ion saturation of exchange surfaces. Two days after the seventh supplementary throughfall event (day 94), the ten lysimeters receiving pH 3.5 throughfall were each given five sequential 3.5 cm applications of pH 3.5 throughfall over the course of approximately five hours. Leachates were sampled on the second and fifth throughfall applications. Under these conditions, the microcosm pools of available cations were presumably being leached without replenishment from biological mineralization.

Analysis of laboratory samples

Samples of soil solution were collected under tension in 500 ml glass side-arm flasks. Sample collection was terminated and lysimeter tension was released 30 min after the initiation of each precipitation event. After sample volume had been measured, a 250 ml subsample was placed in a clean polyethylene bottle. Samples were analyzed for pH (Fisher Accumet model 210) within several hours, and were vacuum-filtered through Whatman 44 paper within one to several days of collection. Until filtration, samples were stored in the dark at 6°C. Filtered samples were frozen until analyzed. Standard chemical methods described elsewhere[4,6] were used to analyze for Ca-ion, Mg-ion, K-ion, Na-ion, NH_4-ion, SO_4-ion, Cl-ion, and NO_3-ion. After 0.1 um filtration, small sample aliquots were analyzed for aluminum by the pyrocatechol violet method[8]. Organic anions were estimated by charge balance differences[6].

Various statistical tests were performed on the experimental data to test the significance of differences between the separate treatments. Initially, the data were surveyed for homoscedasticity using the F_{max} test[17]. These results indicated that the data would have to be transformed to permit an analysis of variance for the experimental results. Thus, the untransformed data were analyzed in pair-wise fashion with the non-parametric Mann-Whitney test. Within each group of five lysimeters, concentration data in pretreatment and treatment percolates were tested for significant 'before' and 'after' differences. Treatment effects were also evaluated by taking the net concentration changes for each element during the treatment period and comparing these values between treatment groups and with respect to the control group.

At the termination of the laboratory leaching experiments, each of the forest floor microcosms was mixed thoroughly, was subsampled, and was analyzed for total and extractable cations. These analytical methods have been described elsewhere[4].

Table 2. Comparative input-output solution chemistries for soil percolates derived from coniferous forest floors in the field[7] *versus* comparable forest floors in the laboratory (this study)

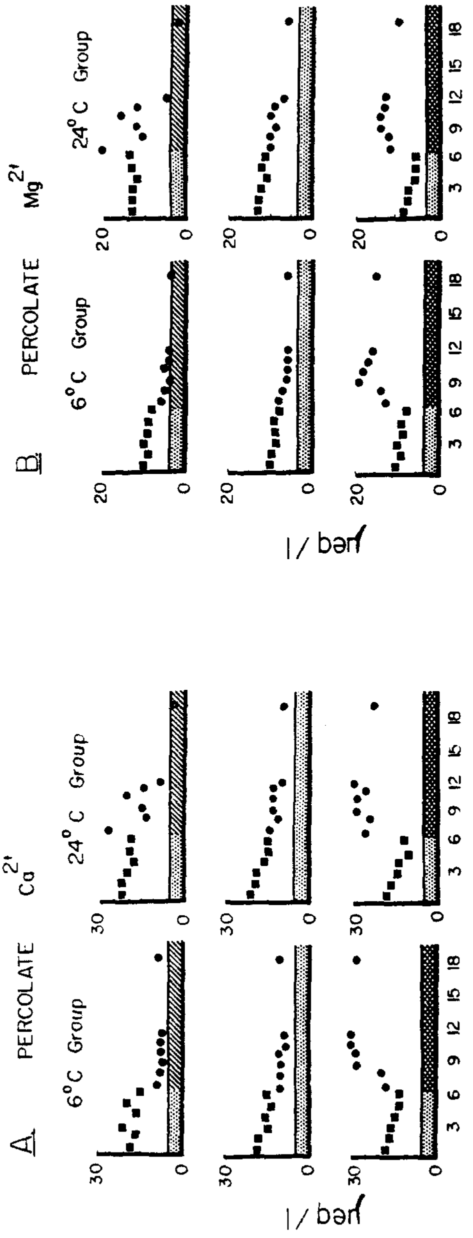
Sample	pH	Concentration (micro-equivalents per liter)													
		H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Al^{3+}	Total cations	SO_4^{2-}	NO_3^-	Cl^-	HCO_3^-	Total anions	Organic anions
Field study															
Canopy throughfall															
Mean	4.02	95	36	14	37	3	6	5	196	143	12	13	0	168	28[0]
Std. error	–	–	4	1	3	0.2	0.5	2	–	11	2	–	–	–	–
O_2 Horizon percolate															
Mean	4.04	91	25	15	16	7	5	54	213	137	8	16	0	161	52
Std. error	–	–	2	1	2	0.3	0.7	4	–	4	1	1	–	–	–
*Laboratory study**															
Artificial throughfall															
Mean	4.00	100	25	10	20	4	5	0	164	125	20	19	0	164	0
Microcosm percolate															
Mean	4.01	96	17	10	36	5	81	27	272	160	22	27	0	209	63
Std. error	–	–	0.4	0.3	1	0.1	5	2	–	2	1	4	–	–	–

[0] This value is calculated as the difference between summed inorganic cations and anions. It is slightly smaller than the figure reported in Cronan[7], because the cation data sets used in this paper do not include the small contributions from Fe and Mn.

* Mean data from the pretreatment period.

RESULTS AND DISCUSSION

The laboratory lysimeter experiments were conducted to investigate leaching losses from intact forest floor microcosms which lacked plants and which were subjected to various experimental treatments of temperature and throughfall chemistry. During the initial pretreatment period of the study, all of the 30 microcosms were maintained and were leached under identical simulated summer field conditions. With those environmental conditions, the baseline biogeochemical behavior of the microcosms could be directly compared with actual forest floor leaching patterns from the field[7]. The average leachate chemistries for the field and laboratory systems are compared in Table 2. While both field and laboratory forest floors received similar chemical inputs in throughfall, there were distinct differences in the leaching patterns for certain elements. In both systems, the free acidity of throughfall inputs remained virtually unchanged during percolation through the forest floor. Calcium concentrations in throughfall decreased by approximately one-third during percolation through both the laboratory and field forest floors. Because plants were absent from only the laboratory microcosms, this decrease presumably resulted primarily from ion exchange and/or microbial immobilization in both systems. Magnesium concentrations in throughfall remained relatively unchanged during percolation through the forest floors of both systems, indicating an approximate steady-state balance of processes in forest floors both with and without plants present. The behavior of potassium, ammonium, and nitrate was particularly distinctive for the laboratory and field systems. In the field, biological uptake processes tended to remove K-ion, NH_4-ion, and NO_3-ion from the soil solution of the rooting zone, resulting in lowered concentrations of these ions in the forest floor leachate. By contrast, the laboratory microcosms lacking plants exhibited marked increases in the forest floor leachate concentrations of K-ion and NH_4-ion, and showed an approximate steady-state balance for NO_3-ion. These patterns appear to imply the following: (i) that concentrations of potassium, ammonium, and nitrate in the forest floor solution are strongly influenced by plant uptake and recycling; (ii) that rates of ammonium release to the soil solution by ammonification and/or ion exchange may potentially be relatively high; and (iii) that although leachate ammonium concentrations increase in the absence of plants, nitrate concentrations do not increase correspondingly, perhaps because of an inhibition or lag in nitrification, or because of microbial immobilization. The laboratory data for sulfate and chloride suggest that these ions may also increase in concentration during water percolation through the forest floor. This implies that there may be


A
PERCOLATE Ca2+
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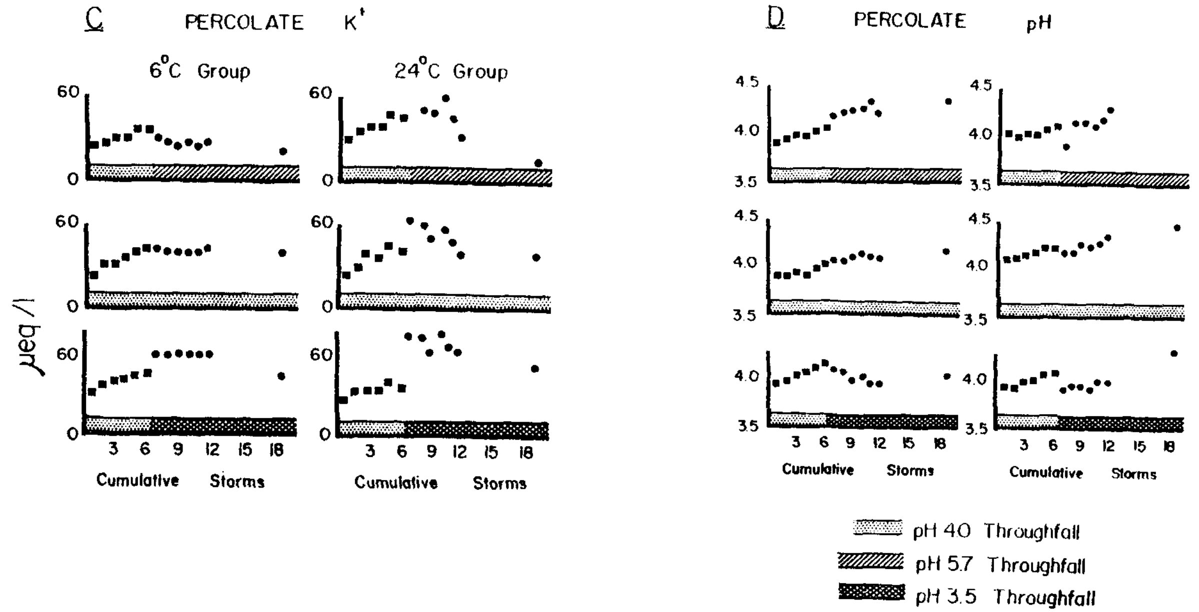

Fig. 1. Mean leachate chemistries for laboratory microcosms exposed initially to six pH 4.0, 6°C simulated throughfall events, followed by thirteen treatment level throughfall events. Each point represents the mean of five microcosm percolates for a given sampling date. *Squares* indicate pretreatment period leachates, while *circles* represent the treatment period leachate chemistry. The temperature headings indicate the incubation temperature of the treatment period. *Patterned bars* at the bottom of each graph show the throughfall conditions used during the pretreatment and treatment periods for each group of five microcosms. The point to the far right in each graph shows the concentration or pH at the thirteenth treatment period throughfall event.

release of adsorbed or organically bound sulfur and chloride in the forest floor which, in the absence of plant uptake and recycling, may lead to increased percolate concentrations of these ions. Finally, it can be noted that the forest floor percolate in both systems absorbs an appreciable quantity of dissolved aluminum and organic anions.

The main purpose in comparing the input-output leaching behavior between field and laboratory forest floors was to determine whether the laboratory microcosms represented a close proxy for the field system in controlled laboratory experiments. Having established the close similarity of the two systems under pretreatment conditions, it was assumed that subsequent experimental manipulations could be used with reasonable confidence to explore how the field system might respond to changes in various environmental factors. In the presentation which follows, results from all sic experimental treatments described in the methods are presented. It should be remembered that the pH 4.0 and pH 3.5 treatment groups are combined in one 2 × 2 design, while the pH 5.7 groups represent a separate, comparative experimental treatment in which the entire chemistry of simulated throughfall was altered (Table 1).

In order to rule out the possibility that pretreatment and treatment leachate differences resulted from differences in percolate volumes, a general test was performed on mean pretreatment and mean treatment percolate volumes for each lysimeter. Results from a Mann-Whitney test between 30 pretreatment and 30 treatment means showed no significant difference ($P = 0.27$) for percolate volumes. It is thus assumed that concentration changes observed in different treatments resulted from changes in ion leaching.

In Fig. 1a-c, the pretreatment and treatment temporal patterns of leachate chemistry are illustrated for three major metallic nutrient cations – calcium, magnesium, and potassium. All treatment groups except the lysimeters exposed to pH 3.5 throughfall showed significantly decreased leachate calcium concentrations during the treatment period (Table 3). The low pH treatments at both temperatures showed significant increases in calcium concentrations, particularly as the pH was dropped a second time from 3.7 to 3.5 (at day 42).

With magnesium, the pH 5.7, 6°C group and the two pH 4.0 groups exhibited significant decreases in leachate concentrations between the pretreatment and treatment periods (Table 3, Fig. 1b). The pH 5.7, 24°C group maintained approximately consistent outputs throughout the first twelve rain events. Meanwhile, the two low pH groups showed significant ($P < .001$) increases in magnesium concentrations in response to the treatment. Again, the cool temperature group exhibited a stair-step incremental response as the throughfall pH was first dropped to 3.7 and then to 3.5.

Table 3. Statistical comparisons for the different groups of microcosms

A. Mean percent change in leachate concentrations for the treatment period compared to the pretreatment period. The asterisks indicate the results of Mann-Whitney two-tailed tests for significant differences between the pretreatment mean concentration and the treatment mean leachate concentration for each treatment group. (* designates $P < .05$, ** indicates $P < .01$, and *** represents $P < .001$).

Group	Ca^{2+}	Mg^{2+}	K^{+}	Al^{*}_{td}	NH_4^+	SO_4^{2-}	NO_3^-
pH 5.7, 6°C	−58%***	−50%***	−16%***	+12%	+33%	−63%**	−65%**
pH 5.7, 24°C	−19%*	−8%	+45%**	+82%*	+134%**	−44%***	−25%*
pH 4.0, 6°C	−38%***	−30%***	+24%***	+5%	+41%**	−19%**	−5%
pH 4.0, 24°C	−22%***	−25%***	+54%***	+33%	+208%***	+2%	+124%
pH 3.5, 6°C	+63%**	+78%***	+59%***	+34%	+118%**	+97%***	+6%
pH 3.5, 24°C	+87%***	+75%***	+100%***	+82%	+234%***	+143%***	+10%

B. Mann-Whitney tests for significant differences between separate treatment group and control group leachate concentrations. Concentration data for each of the six treatment dates and each of the five lysimeters per group were converted to net concentration changes by subtracting the appropriate mean pretreatment element concentration from each percolate data point. The two-tailed probabilities for these comparisons are indicated below.

Difference comparison	Ca^{2+}	Mg^{2+}	K^{+}	Al_{td}	NH_4^+	SO_4^{2-}	NO_3^-
pH 5.7, 6°C *vs* pH 5.7, 24°C	.05	.05	.005	ns	.002	.05	.05
pH 4.0, 6°C *vs* pH 4.0, 24°C	.05	ns	.01	ns	.05	ns	.002
pH 4.0, 6°C *vs* pH 3.5, 6°C	.001	.001	.001	ns	.02	.001	.05
pH 4.0, 6°C *vs* pH 3.5, 24°C	.001	.001	.001	ns	.002	.001	.05
pH 3.5, 6°C *vs* pH 3.5, 24 °C	ns	ns	.001	ns	.002	ns	ns
pH 4.0 *vs* pH 3.5	.001	.001	.001	ns	.02	.001	ns
6°C *vs* 24°C	.05	ns	.001	ns	.002	.10[0]	.002

* Total dissolved inorganic aluminum.

[0] This difference comparison was also made using ratios of the element concentration during each treatment period collection divided by the mean pretreatment concentration for the given microcosm. The results from that Mann-Whitney comparison showed a significant difference ($P < .002$) between sulfate concentrations in percolates at 24°C *versus* 6°C.

Leachate potassium concentrations for the low temperature, pH 5.7 group dropped when the throughfall pH was raised from 4.0 to 5.7 and throughfall inputs of K-ion dropped to zero. However, the warm temperature pH 5.7 group, the two pH 4.0 groups, and the two pH 3.5 throughfall groups all exhibited significant increases ($P < .001$) in percolate concentrations during the treatment period (Table 3, Fig. 1c). Finally, all 24°C treatment groups showed noticeably more variability in potassium concentrations during the treatment exposure to warmer temperatures.

During the pretreatment period, all microcosms received pH 4.0 artificial throughfall, and percolate mean pH's ranged between approximately 3.9 to 4.2

Table 4. Comparison of throughfall input and lysimeter output element concentrations during pretreatment and treatment periods. Concentrations are expressed in microequivalents per liter

Group	Pretreatment		Treatment		Pretreatment		Treatment		Pretreatment		Treatment		Pretreatment		Treatment	
	Input	Output	Input	Output	Input	Output	Input	Output	Input	Output	Input	Output	Input	Output	Input	Output
	pH				Ca^{2+}				Mg^{2+}				Al^{3+}			
pH 5.7, 6°C	4.00	3.98	5.70	4.24	25	19	0	8	9.5	10	0	5	0	16	0	18
pH 5.7, 24°C	4.00	4.02	5.70	4.11	25	21	0	17	9.5	13	0	12	0	22	0	40
pH 4.0, 6°C	4.00	3.94	4.00	4.09	25	16	25	10	9.5	10	9.5	7	0	18	0	19
pH 4.0, 24°C	4.00	4.16	4.00	4.24	25	18	25	14	9.5	12	9.5	9	0	45	0	60
pH 3.5, 6°C	4.00	4.04	3.52	4.00	25	16	25	26	9.5	9	9.5	16	0	37	0	47
pH 3.5, 24°C	4.00	3.99	3.52	3.93	25	15	25	28	9.5	8	9.5	14	0	17	0	31
	K^+				Na^+				NH_4^+				Total cations			
pH 5.7, 6°C	20	32	0	27	4	5	93	18	5	85	0	113	164	272	102	247
pH 5.7, 24°C	20	40	0	58	4	5	93	30	5	65	0	152	164	261	102	387
pH 4.0, 6°C	20	34	20	42	4	6	4	6	5	95	5	134	164	294	164	299
pH 4.0, 24°C	20	37	20	57	4	5	4	7	5	65	5	200	164	251	164	405
pH 3.5, 6°C	20	39	20	62	4	6	4	6	5	68	5	148	164	264	364	405
pH 3.5, 24°C	20	34	20	68	4	5	4	5	5	101	5	337	164	282	364	600
	SO_4^{2-}				Cl^-				NO_3^-				Organic anions			
pH 5.7, 6°C	125	163	0	61	19	27	93	17	20	20	0	7	0	62	0	108
pH 5.7, 24°C	125	157	0	88	19	27	93	117	20	20	0	15	0	57	0	167
pH 4.0, 6°C	125	166	125	134	19	27	19	50	20	18	20	17	0	83	0	98
pH 4.0, 24°C	125	155	125	158	19	27	19	40	20	33	20	74	0	36	0	133
pH 3.5, 6°C	125	159	325	313	19	27	19	39	20	16	20	17	0	62	0	36
pH 3.5, 24°C	125	160	325	389	19	27	19	60	20	20	20	22	0	75	0	129

(fig. 1d). The remarkable aspect of the pH behavior was that although the forest floors showed a range of percolate pH's, individual microcosms tended to exhibit very consistent pH buffering. Some microcosms would repeatedly drop the input pH below 4.0, while others would consistently raise the pH to a given level. In the treatment period, the pH 4.0 groups at both temperatures showed slight gradual increases in pH. The two groups receiving pH 5.7 throughfall exhibited mean percolate pH's ranging from 3.9 to 4.8 for individual treatment period collections, thus illustrating the internal capacity of the forest floor to acidify 'pure water' inputs. In the low pH groups, throughfall inputs of sulfuric acid were tripled in dropping to pH 3.5 during the treatment period. Although mean percolate pH's declined in these groups, the microcosms all showed great buffer intensities, with comparatively small percolate pH changes relative to the strong acid inputs. Thus, most of the added input of mineral acidity was consumed in ion exchange reactions and/or by organic buffering agents.

In Table 4, an overall summary is presented of the comparative ion inputs and outputs for the six groups of microcosms during the pretreatment and treatment periods. As indicated by the data, the forest floor microcosms exhibited the potential for dramatic changes in leachate chemistry in response to changes in the acidity of throughfall inputs and temperature-related changes in decomposition-mineralization conditions. The salient results to emerge from the experiments were as follows.

(i) In undisturbed forest floor microcosms lacking plants, there were significant differences ($P < .001$) in leaching of calcium, magnesium, and potassium between lysimeters exposed to pH 4.0 versus pH 3.5 simulated throughfall (pooled at both temperatures). A drop in throughfall pH from 4.0 to 3.5 (a tripling in H_2SO_4 concentration) produced 63–87 % higher calcium, 75–78 % higher magnesium, and 59–100 % greater potassium concentrations in treatment versus pretreatment percolates. Compared to the control, the pH 3.5 treatment groups showed 160–180 % higher calcium, 100–129 % greater magnesium, and 48–62 % higher potassium concentrations. Furthermore, ammonium losses in leachate were also significantly higher ($P < .02$) than the control for the pH 3.5 treatment groups at both temperatures.

(ii) Compared to the simulated 6°C summer average forest floor temperature regime, the warmer 24°C regime promoted accelerated leaching of calcium, potassium, ammonium, sulfate, and nitrate, presumably as a result of increased biological mineralization. Results indicated that there were significant differences in percolate concentrations for Ca-ion ($P < .05$), K-ion ($P < .001$), NH_4-ion ($P < .002$), SO_4-ion ($P < .002$), and NO_3-ion ($P < .002$) between the low temperature versus higher temperature microcosms (pooled for pH 4.0 and 3.5). Yet, at the low pH treatment, the increase in H_2SO_4 inputs appeared to overshadow the temperature effect on calcium and magnesium leaching. Hence, there was no significant diference in leaching of these two cations between the 6°C and 24°C pH 3.5 groups. There was, however, a significantly greater (Table 3) increase in potassium and ammonium concentrations from the 24°C than the 6°C pH 3.5 group (suggesting that potassium and ammonium losses are relatively more strongly influenced by temperature-related biological processes than by physical-chemical H^+ exchange and weathering).

(iii) Under simulated field conditions (*e.g.* 6°C, pH 4.0 artificial throughfall), but in the absence of plant uptake, laboratory microcosms showed net leaching of the critical nutrients potassium and ammonium. Microcosms also exhibited net leaching of sulfate and limited net leaching of nitrate. In contrast, field percolates show a dramatic net removal of potassium and limited net removal of ammonium and nitrate from throughfall inputs. Sulfate concentrations in field percolates are generally similar to concentrations in throughfall.

(iv) Under pretreatment conditions, the three major essential metallic cations behaved in the following manner: calcium concentrations in percolates were lower than throughfall inputs, suggesting calcium retention; magnesium inputs and outputs for the forest floor were in approximate steady-state; and potassium concentrations in percolates increased over throughfall inputs to the forest floor. This implies that in the absence of plant uptake, the relative tendencies for 'immobilization' or forest floor retention decrease in the order Ca > Mg > K.

(v) The throughfall treatments with pH 5.7 distilled water containing 100 ueq/1 NaCl showed that a) the forest floor has a substantial ability to acidify water inputs either through organic acid leaching or through cation exchange involving Na-ion and H-ion, and b) ion exchange processes involving the neutral salt sodium chloride apparently resulted in net leaching of several cations (*e.g.* Ca-ion, Mg-ion, and perhaps K-ion, H-ion, and NH_4-ion) and marked decreases in percolate sodium concentrations.

Evidence for controls on the leaching process

One of several alternate hypotheses proposed at the start of this investigation was that cation leaching losses from the forest floor are controlled by the availability of these cations. Partial support for this idea comes from the observation that forest floor percolates tend to have a large amount of free and total acidity in proportion to the comparatively low concentrations of basic cations in solution; this may imply that there is a limited supply of exchangeable cations capable of participating in ion exchange neutralization reactions with H-ion. Feller[9] also invoked this type of cation availability hypothesis to explain why winter percolates became progressively more dilute in his British Columbian research sites. To test this hypothesis for the fir zone forest floor, cation depletion experiments were incorporated into the microcosm studies. It was assumed that by interfering with replenishment of available cations from biological mineralization, leachate concentrations might decrease as the finite available cation pool decreased in size. In this study, the problem was approached by staging precipitation events in rapid succession with no intervals between storms for decomposition activities.

Fig. 2a shows a hypothetical curve predicting gradual decreases in percolate

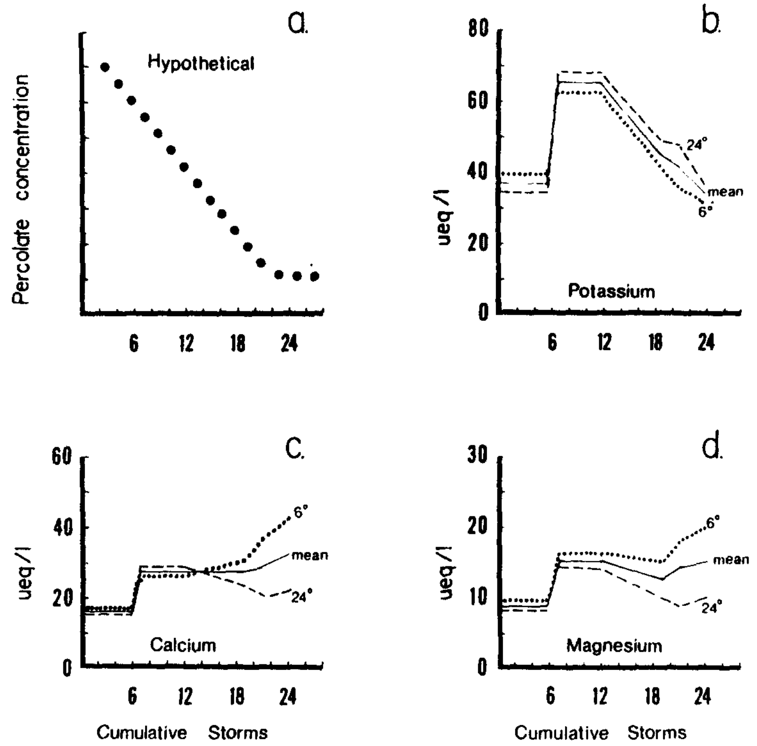

Fig. 2. Laboratory microcosm test for decreases in cation leaching resulting from depletion of the available cation pool. Graph A shows the hypothetical decreases in percolate cation concentrations predicted for the case when successive storm events deplete the available cation pool in the forest floor. *Graphs B-D* show observed laboratory microcosm mean percolate concentrations during the pretreatment period, treatment period, and during the final five successive storm events in the warm and cool pH 3.5 treatment groups.

cation concentrations as successive rain storms 'out-run' the rate of net mineralization and deplete the available pool of soluble and exchangeable cations. In Fig. 2b-d, percolate concentrations of calcium, magnesium, and potassium are shown for the two pH 3.5 treatment groups during the entire course of the experiment. From these data, it appears that the average concentrations of calcium and magnesium did not follow the model, but remained relatively constant during the cation depletion test. In contrast, potassium concentrations decreased rather dramatically after the first six treatment precipitation events, suggesting that the hypothesis might potentially help to explain potassium leaching behavior. In this particular case, potassium supplies evidently became sufficiently exhausted over a short period of time to cause a dramatic decrease in leachate potassium concentrations.

The microcosm leaching data were used to explore a number of other questions related to the control of leaching losses. The experimental results indicated that warmer temperatures tend to increase leachate concentrations of several ions; however, it remained unclear what temperature-related mechanism was important. One approach that was used was to focus on the following hypothesis: if the important temperature effect is to accelerate organic decomposition and mineralization of cations, then one might expect structural elements like calcium to increase in concentration in solution at a relatively faster rate than non-structural electrolyte cations like potassium. This hypothesis would predict that leachate Ca^{2+}/K^{+} and Mg^{2+}/K^{+} ratios should increase in those microcosms that were moved into the warmer chamber for the treatment period. In actuality, the ratios dropped consistently at both temperatures in the pH 5.7 and 4.0 treatments, while the two low pH groups showed no apparent changes in ratios. Thus, the results tended not to support the hypothesis.

Other alternative hypotheses were also explored in an attempt to elucidate the possible mechanisms through which temperature influences ion leaching. Unfortunately, it was not possible to substantiate any one simple explanation for the temperature-related increase in leaching. In general, the experimental data indicated that increased temperatures accelerate decomposition-mineralization processes and either directly or indirectly result in an enrichment of both cation and anion concentrations in the leachate solution. With respect to cations, the increased leaching at higher temperatures may have resulted from one or more of the following mechanisms: i) an increase in cation mineralization and concomitant increase in the abundance of exchangeable basic cations; ii) increased mineralization release of water soluble salts (*e.g.* $MgSO_4$) which are directly leachable; and/or iii) accelerated mineralization release of mineral and organic acids capable of leaching cations from the relatively large existing pool of exchangeable nutrients.

Evidence for the last mechanism comes from the observation that compared to the pH 5.7, 6°C treatment, the leachate from the pH 5.7, 24°C treatment showed a lower pH (4.11 *vs* 4.24), and higher concentrations of sulfate (88 *vs* 61), chloride (117 *vs* 71), nitrate (15 *vs* 7), organic anions (167 *vs* 108), and total cations excluding H-ion (309 *vs* 189). Thus, the warmer treatment appeared to favor both increased mineralization release of organic and mineral acids and increased leaching of cations. This same line of logic is supported by examining the case of a model microcosm. In this experimental study, each microcosm contained approximately 60–100 gm dry weight of forest floor material. Based upon extraction data, each microcosm thus contained roughly 2000 to 7000 ueq of exchangeable calcium. At pH 4.0, every precipitation event introduced approximately 40 ueq of sulfuric acid to react with the forest floor available cation pool. Comparing the available pools of cations (as exemplified by calcium) and mineral free acid, it seems evident that the abundance of free H-ion is more likely to limit the replacement of adsorbed cations than is the fluctuating size of the relatively large available cation pool. Hence, several lines of inquiry suggest that increased cation leaching resulting from temperature-accelerated decomposition is not as strongly dependent upon increased cation mineralization as it is upon increased release of soil-derived acids capable of participating in exchange reactions.

Leaching fluxes relative to pools and other ecosystem transfers

Experiments described in this paper and by others[1,12] have shown that acid precipitation may cause increased leaching of essential nutrient cations from soils. One potential long-term consequence of such a trend of accelerated leaching is a reduction in soil fertility and plant productivity in forest ecosystems exposed to chronic acid rain. In view of this concern, it would be instructive to evaluate the laboratory microcosm leaching results in relation to the overall cation economy of the balsam fir ecosystem and with respect to the predicted long-term fertility of this acid rain impacted system.

Using the laboratory microcosm as a model system, one can examine the potential significance of accelerated leaching rates on the nutrient status of the fir zone forest floor. The mean dry weight of the microcosms was approximately 72 g. Mean total calcium concentration in the microcosm forest floor samples was 7.25 meq/100 gm, or 5.2 meq of total calcium per microcosm. With the pH 3.5 throughfall treatment, each microcosm containing about 5000 micro-equivalents of total calcium lost approximately one ueq/l of Ca^{2+} (over and above throughfall inputs), or about 0.4 μeq of Ca^{2+} per precipitation event. Over the course of eighteen pH 3.5 events, the lysimeters each received *ca* 63 cm or about 1/3 to 1/4 of the annual fir zone total precipitation. This removed *ca* 7–10 ueq of calcium, which could ideally amount to 21 to 40 ueq over an annual cycle of such precipitation events (assuming that each volume of rain and snow produced these same leaching responses). This upper limit of calcium removal would be 0.8% of the total forest floor calcium pool per year in the absence of net plant uptake and recycling.

Similar calculations were made for magnesium, potassium, and nitrogen to estimate the percentage of the forest floor pool of each element that could potentially be leached if all of the year's precipitation percolated through the forest floor, and if the mean pH of the year's throughfall averaged 3.5 instead of 4.0. Under these conditions of extreme acidity, increased infiltration, and negligible plant uptake, the following projections resulted: i) a maximum of 3% of the total forest floor magnesium pool could be removed per year; ii) a maximum of 85% of the total forest floor potassium pool could conceivably be removed per year (if the high rates of potassium leaching continued without depletion effects); and iii) a maximum of 6–16% of the total forest floor nitrogen pool could be removed per year as inorganic nitrogen.

While the preceding calculations provide an interesting indication of the potential effects that an increase in acid precipitation might exert on systems like the balsam fir zone, the experimental results unfortunately do not permit the problem to be evaluated in a whole ecosystem context with due consideration given to the moderating effects of the plant community and the mineral soil buffering capacity. To extrapolate with some accuracy to the field situation, one would have to model net leaching resulting from the combined influences of variable sulfuric acid leaching, variable plant nutrient uptake and accumulation, and variable mineral soil weathering and buffering. The experimental system used in this study was too simple to permit that degree of extrapolation. Further whole-system experiments will be needed for a thorough evaluation of the problem. At present, the experiments have indicated that potassium may be the nutrient most likely to exhibit depletion effects and to influence plant productivity in the balsam fir subalpine ecosystem.

Relationship to other studies

Interesting comparisons can be made between these fir zone experimental results and several published experimental studies concerned with the effects of acid precipitation and other factors on ion transport. Overrein[12] exposed lysimeters containing relatively undisturbed podzolic forest soils to simulated rain events with varying precipitation chemistries. As in this study, he observed a sharp increase in calcium leaching as the pH of precipitation inputs approached levels below 4.0. In comparison, lysimeters leached by distilled water, pH 4.3 water, and pH 4.3 rain showed generally similar low level cation leaching losses. Wiklander[21] conducted experiments to examine the role of neutral salts in reactions between acid precipitation and soils. His studies were thus somewhat analogous to the distilled water-NaCl treatments in this fir zone experimental study. In acid soils, he found that neutral salt inputs can participate in exchange reactions which result in a lowered solution pH, but an increase in soil base saturation. Similar results were observed in this study, wherein the pH 5.7 treatment microcosms showed leachate pH's in the 3.9–4.8 range and forest floor bulk dry weight sodium concentrations that were three times higher than the other treatment groups at the end of the experiment. From his results, Wiklander reached two conclusions: i) to the extent that precipitation-borne H_2SO_4 flushes through the soil while meteoric cations are retained, there can be an increase in soil base saturation, and ii) studies examining soil leaching by anthropogenic H_2SO_4 which do not consider the natural atmospheric deposition of neutral salts will be likely to exaggerate the harmful effect on acid soils. Other important Scandinavian experimental studies were conducted in Norway by Abrahamsen *et al.*[1]. Their field lysimeter investigations with podzol-brown earth and iron podzol soil samples showed the following results: i) the application of acid rain with $\mathrm{pH} \leq 4$ to podzol soils significantly increased the acidity of the leachate and resulted in direct increases in the leaching of aluminum; ii) over the course of two years, podzols exposed to rain with $\mathrm{pH} < 4$ showed decreases in exchangeable Ca, Mg, and Mn; and iii) with increasing acidity of rain inputs, the podzol lysimeters exhibited net losses of Ca, Mg, Al, Mn, Na, K, and Fe, while podzol-brown earth lysimeters showed net losses of Ca, Mg, and Al under similar conditions. When the 'rain' pH was dropped from 5.7 to 4.0, the net loss of Ca and Mg increased 50–110% in the podzol lysimeters. Then, when the rain pH was lowered from 5.7 to 3.0, net losses of Ca and Mg increased 130–239%. One of the interesting outcomes from their comparative study was that their results conflicted somewhat with Wiklander's[20,21]. Wiklander concluded that the adverse effect of acid precipitation is likely to be less in very acid soils, such as podzols, than in slightly acid and neutral soils. Yet, Abrahamsen *et al.*[1] found that the effects of acid rain inputs were greater in the more acid, less cation-rich podzol soil.

In Washington state, Johnson and Cole[10] performed sulfuric acid leaching experiments using field plots of an Everett series Inceptisol. Their results showed that acid 'rain' inputs produced a great removal of cations from the O and A horizons, but that most of the ions were retained in the B horizon as a result of sulfate adsorption on mineral soil sesquioxides. Such findings raise important considerations for the work described in this paper and other studies. To the extent that a mineral soil contains anion adsorption sites, there would be a capacity for ecosystem moderation or buffering of increased cation losses from surface horizons.

Wood and Bormann[22] conducted experiments to examine foliar and soil leaching in laboratory potted soil systems containing pine seedlings. With plants present, they found that leaching of magnesium and calcium steadily increased as the 'rain' acidity increased through the pH range 5.6–2.3. However, in the same systems, potassium losses did not increase until the 'rain' pH was lowered to 3.0 or below.

Rains and Bledsoe[14] performed studies to examine the effects of Douglas fir seedlings on the transfer of nutrients through soil columns containing sieved brown podzolic soil. As would be predicted from the fir zone study, they found that potassium concentrations in leachates from columns without seedlings were almost twice the level of leachates from columns with trees. They also found that the quantity of potassium leached from columns lacking seedlings was the same in warm and cold temperature treatments, while calcium leaching was lower in the cold temperature treatment. Such results agree with the hypothesis set forth in this study concerning temperature effects upon leaching rates of structural versus electrolyte cations. Curiously, the results from the fir zone forest floor experiments did not support this hypothesis.

In summary, the studies described in this report were conducted to examine the influence of different environmental variables upon the chemistry of soil leachate solutions. Forest floor microcosms exposed to simulated field conditions behaved very much like field plots under the same environmental conditions; however, there were predictable differences in leaching losses from laboratory and field systems for those ions which are strongly controlled by plant uptake. In general, the exclusion of plant uptake from microcosms resulted in increased leaching of potassium, ammonium, nitrate, and sulfate. As the acidity of throughfall inputs to the microcosms increased, the forest floors exhibited increased leaching losses of calcium, magnesium, potassium, and ammonium. These increases appeared to result primarily from mass action ion exchange. The fact that aluminum losses did not increase correspondingly suggested that there may be a kinetic lag in the mobilization and leaching of aluminum. When microcosms were exposed to warmer temperatures, percolates showed increased leaching losses of calcium, potassium, ammonium, sulfate, nitrate, and organic anions. Experiments conformed that each ion in solution may exhibit very individualistic behavior, responding differentially to one or more environmental variables.

The studies also provided information concerning the potential impact of acid precipitation on soils of the balsam fir zone. At present in the balsam fir zone, it appears from field and laboratory data that the nutrient recycling processes of the intact forest ecosystem minimize the soil leaching threat by acid precipitation during the growing season. Nevertheless, if mean rain pH's in the Northeast were to drop from 4.0 to 3.5, there would be a potential for marked changes in the fir zone forest floor nutrient status. Depending upon the ameliorating effects of plant uptake and nutrient replenishment from weathering, the increased leaching of calcium and magnesium would pose depletion problems on a time scale of 10 to 100 years. Accelerated potassium leaching could potentially be detrimental on a time scale of a few years. At the present time, the real leaching threat of acid precipitation in the mountains of New England may manifest itself during the spring and autumn periods when plant uptake is low; in late successional stages when plant uptake is declining; or following disturbance to the plant community (*e.g.* wind storm). In order to assess the ultimate impact of acid rain upon soil fertility, it has become clear that one must consider not only the potential acceleration of leaching that may result from atmospheric inputs of H_2SO_4 and HNO_3, but also the compensating processes which may counteract the adverse effects of increased leaching. These processes include the deposition of meteoric nutrient elements from the atmosphere[21], accelerated weathering of mineral material, ion adsorption by soil materials, and biological processes of nutrient release and accumulation.

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