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Effects of *in vitro* acidification of a podzol on the chemistry of percolates and horizons

Robert Boutin and Gilles Robitaille

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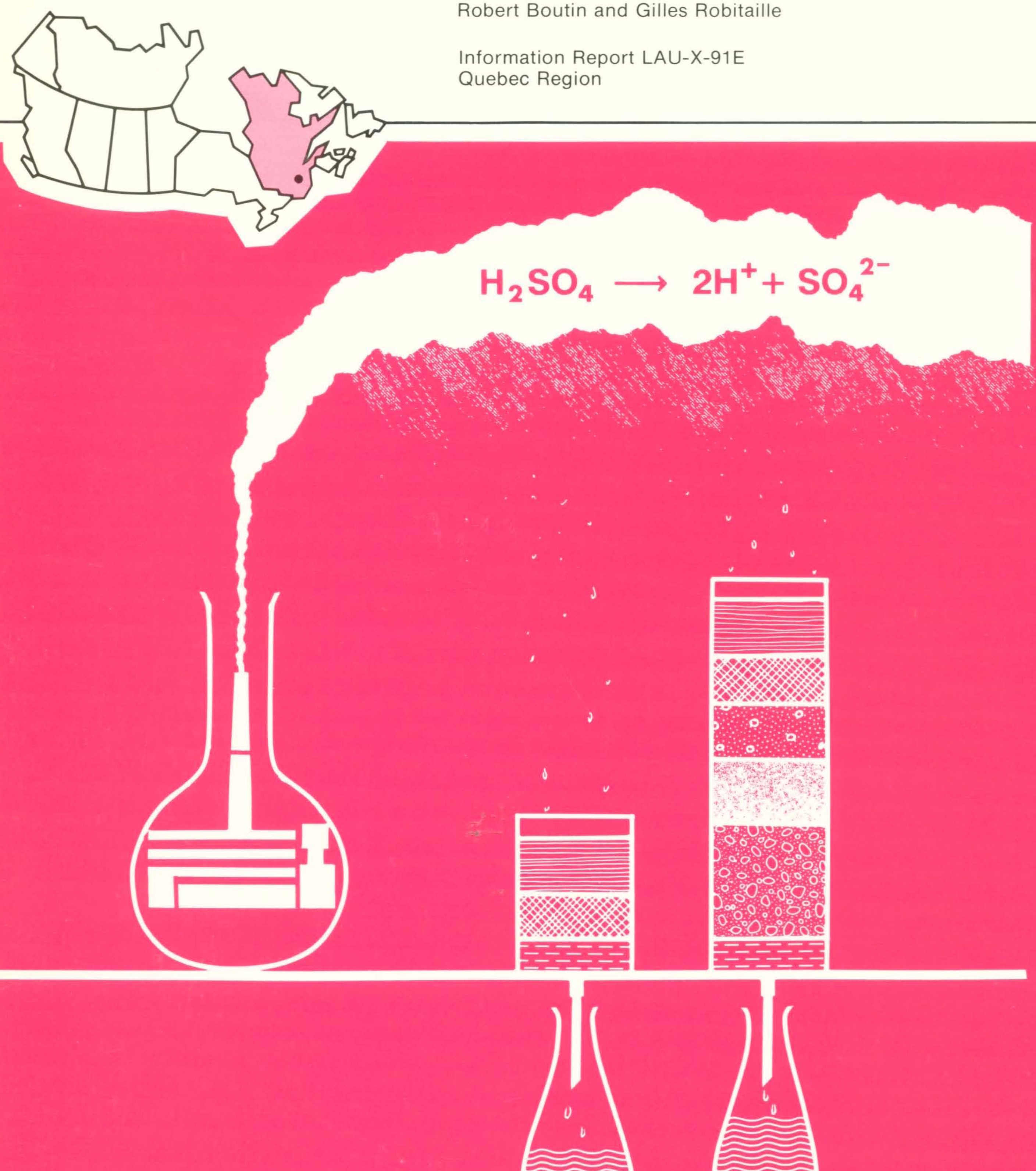

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ABSTRACT

Acidification of reconstituted soil columns from the LF, H, Ae, Bhf1, and Bhf2 horizons of a Ferro-Humic Podzol sampled at the Lake Laflamme Watershed (Montmorency Forest), enabled us to examine buffering processes occurring in organic and mineral horizons treated with H^+ and SO_4^{2-} at different concentrations. Endogenous acidification related to nitrification considerably narrowed the differences between the treatment effects. Treatment-related loss of exchangeable bases were confined to the LF horizon (and H horizon for exchangeable Mg). The same pattern of differences between the treatments was noted for the percolates.

More than 80 percent of the H^+ in the input was consumed by the processes of ammonification and ionic exchange with exchangeable Ca. Relative to the initial exchangeable content, leaching loss, and exchangeable fraction loss in the reference treatment (deionized water, pH 5.6) increased in the following order: K > Mg > Ca, the inverse of the respective initial concentrations on the exchange sites. The order was reversed when the effects of this treatment were compared with the effect of the most acidified treatment (pH 2.9). Because the leaching of K^+ was particularly enhanced by a substantial column of water and by the absence of root uptake, it was not possible to determine the specific effect of acidification on this element.

The dissolution of aluminium-containing minerals was by far the most significant buffering process in the spodic horizons. In all of the treatments, the process was greatly accelerated by nitrification and maintained by desorption of SO_4^{2-} and/or dissolution of hydroxyaluminosulfates for pH 2.9 and pH 3.3 treatments.

RÉSUMÉ

L'acidification de colonnes de sol reconstituées à partir des horizons LF, H, Ae, Bhf1 et Bhf2 d'un podzol ferro-humique échantillonné sur le bassin du lac Laflamme (Forêt Montmorency) nous a permis d'évaluer les mécanismes-tampon effectifs dans les horizons organiques et minéraux soumis à des apports de plus en plus grands de H^+ et SO_4^{2-}. L'acidification endogène ajoutée par la nitrification a réduit considérablement l'écart entre les effets des différents traitements. Les pertes en bases échangeables reliées aux traitements ont été confinées à l'horizon LF (et à l'horizon H dans le cas du Mg échangeable). Les différences entre les traitements ont suivi le même patron que dans le cas des percolats.

Plus de 80 % du H^+ ajouté a été consommé dans les horizons organiques principalement par les processus d'ammonification et d'échange ionique avec Ca échangeable. Les pertes par lessivage et les pertes des fractions échangeables dans le traitement de référence (eau déminéralisée, pH 5,6) ont été, relativement au contenu échangeable initial, plus importantes dans l'ordre suivant: K > Mg > Ca, soit l'inverse des concentrations respectives initiales sur les sites d'échanges. Cet ordre est inversé lorsque l'on compare l'effet de ce traitement avec celui du traitement le plus acide (pH 2,9). Le potassium étant très sensible au lessivage accru par la percolation d'une lame d'eau importante et par l'absence de prélèvement, il n'a pas été possible de dégager l'impact spécifique de l'acidification sur cet élément.

La dissolution de minéraux contenant de l'aluminium a été de loin le processus-tampon majeur dans les horizons spodiques et ce processus a été grandement accéléré par la nitrification dans tous les traitements et maintenu par la désorption de SO_4^{2-} et/ou la dissolution d'hydroxi-alumino-sulphates dans le cas des traitements acides à pH 2,9 et 3,3.

INTRODUCTION

Since the early 1980s, concern has been growing in Europe and North America over phenomena linked to the long-range transport of air pollutants (LRTAP). It is now known that atmospheric oxidation of $S0_2$ and NO_x from specific (industrial) and diffused (regional) pollution sources is responsible for the increase in H^+, SO_4^{2-}, and NO_3^- ion concentrations currently found in precipitation.

The chemical composition of precipitation changes on contact with the plant life, soils, and parent rock that characterize drainage basins. Conversely, all these elements of the biogeochemical cycle may be altered by significant changes in the chemical composition of precipitation. Forest canopies act as effective filters for the aerosols, dust, gases, and mists contained in the air and this interception process, which is more effective in conifers because of the persistence of the leaves and the greater leaf area, can contribute to a significant increase in total deposition on forest ecosystems (Matzner 1983; Skeffington 1983).

In addition to direct effects on the aerial portions of the trees which may result in accelerated leaching of bio-elements thereby causing changes in the rate and equilibrium of nutrient cycles, there may be indirect effects influencing the growth and maintenance of forest species through changes in the soil that should be specifically studied. Leaching from foliage is a process which may cause acidification of the soil (Miller 1984; Foster 1985) in the presence of increased cation reabsorption. The filtering action of the canopy only modifies the flow of acidifying elements in time and space, and this filtering role delays the process rather than countering it.

When studying the effect of acid deposition on the soil, two major types of change may be considered:

1. chemical processes such as cation exchange, anion sorption, mineral changes, and biological cycling of the elements, combine to alter the composition of the water before it flows into the rivers and lakes;

2. the nutrient status of the soil and its resulting capacity to support the growth of higher plants could undergo substantial changes following modification of the characteristics of the soil solution resulting from the buffering processes involved (Ulrich et al. 1980).

Acid soils, such as Ferric-Humo Podzols derived from granite parent rock, are considered highly sensitive to acid deposition. The pH (H_2O) of the upper organic horizons generally varies from 3.5 to 4.0 and increases with depth to roughly 5.5 at the interface between horizons B and C. With time, natural processes inevitably cause acidification of these soils which may be accelerated by acid deposition produced by human activity.

As part of the research to establish the biogeochemical cycle of the Lake Laflamme basin (Montmorency forest, Quebec), a study involving the *in vitro* acidification of a podzol reconstituted horizon by horizon was conducted in order to achieve the following objectives:

a) Determine the effect of an accelerated acid (H_2SO_4) load on the physical and chemical parameters of the soil and on the ion concentrations of the percolates from the organic and spodic horizons of a Ferro-Humic Podzol;

b) Identify the significant parameters and study their inter-relationships;

c) Further our knowledge of acidification-related changes occurring in the nutrient elements of a podzol in order to gain a better understanding of phenomena observed *in situ* (with or without treatment).

MATERIALS AND METHODS

Description of the sampling station

The biophysical characteristics of the Montmorency forest (where the soil samples were taken) have been described in detail by Jurdant and Bernier (1966). In this area of Quebec, the coldest temperatures (mean atmospheric temperature: 0.2°C) and the greatest levels of precipitation (1 424 mm year^{-1}, 33 percent in the form of snow) have been recorded for the region south of the 50th parallel. The cover consists of 90 percent balsam fir (*Abies balsamea* (L.) Mill.) mixed with white birch (*Betula papyrifera* Marsh.), white spruce (*Picea glauca* (Moench) Voss), and black spruce (*Picea mariana* (Mill.) B.S.P.), which colonizes primarily the poorly drained soils near the lake. The herb *Oxalis montana* Raf. forms the dominant subassociation. The organic and mineral material used for the *in vitro* acidification experiment was obtained from a profile dug in a slope with a southern exposure located 100 m from the rim of Lake Laflamme (47°17' N and 71°14' W; altitude of 795 m). The soil is a fragic Ferro-Humic Podzol (Canadian Soil Survey Committee 1978) developed from till made up primarily of charnockite. This moderately well drained sandy loam of the Laurentian series, along with the Des Neiges series (podzol occupying the steeper slopes), occupies roughly 50 percent of the basin area. Some of the physiochemical characteristics of the horizons from which the samples were taken are given in Table 1.

Table 1. Physicochemical characteristics of horizons reconstituted from a Ferro-Humic Podzol of the Laurentian series

Horizon	Thickness	Approx. density	pH (H_2O)	O.C.	Total N	C/N	C.E.C.[a]	Ca	Mg	K	B.S.
	cm	Mg m^{-3}		%	%		cmol(+)kg^{-1}				%
LF	5	0.090	4.3	48.0	2.16	22	123	24.5	2.58	2.12	23.7
H	4	0.113	3.7	38.3	1.67	23	114	10.5	1.40	1.20	11.7
Ae	5	0.962	4.2	1.09	0.06	18	4	0.31	0.06	0.06	10.8
Bhf1	6	0.584	4.2	8.83	0.39	23	56	1.44	0.13	0.09	3.0
Bhf2	10	0.697	4.7	5.98	0.25	24	50	0.69	0.07	0.03	1.6
Bf1	13	0.955	4.8	2.99	0.19	16	25	0.37	0.02	0.03	1.7
Bf2	9	1.231	5.0	2.47	0.12	21	18	0.33	0.01	0.03	2.1

[a] 1 *N* NH_4OAc method at pH 7.0.

Soil sampling and reconstitution

Samples from the forest floor were taken over an area of 1.5 m x 3 m after grasses and shrubs had been removed. The forest floor was subdivided into two distinct parts: 1) the LF layer consisting of litter (L) and the fermentation horizon (F), and 2) the humus-bearing horizon (H). Samples of the eluviated horizon (Ae) were then collected taking care to avoid mixing them with the overlying organic horizons and the underlying (illuviated) spodic horizons. The profile was described and samples of the spodic horizons, Bhf1, Bhf2, Bf1, and Bf2, were collected. Within 24 hours, the material from the seven sampled horizons was taken to the laboratory where it was sifted (6.3-mm mesh) and homogenized before storage in the dark at 1.6°C.

Reconstitution of each horizon was based on mean thickness values estimated from the description of 17 profiles at the drainage basin. The amount of moisture needed to reconstitute a given horizon to a specific thickness was determined by preliminary trials. A vibrator was used so that the reconstituted apparent density was as close as possible to the density observed *in situ.*

The horizons were reconstituted in 10-cm transparent acrylic cylinders with inside diameters of 10 cm. The cylinders were not covered with any opaque material and were perforated at the bottom. A 6-mm (inside diameter) drainage tube was connected to the bottom of each cylinder. The filter layer consisted of 200 g of silica (325 mesh) over 20 g fibre-glass. The silica and fiber glass had previously been washed with 1.0 *N* HCl, then intensively rinsed with demineralized water until only traces of the chloride ion remained. To avoid saturation, a vacuum of 0.01 MPa was applied to each of the columns. In order to study the transport of nutrient elements through the profile, the latter was reconstituted to two different levels, i.e., to horizon H (LF + H) and to horizon Bhf2 (LF + H + Ae + BLf_1 + BLf_2).

Experimental procedure

Twelve columns of each type were produced to give 3 replicates per treatment. Three of these solutions were acidified with H_2S0_4 in concentrations of 1250, 500, and 50 μmol (+) L^{-1} of H^+, respectively, for treatments with pH values of roughly 2.9, 3.3, and 4.3. The reference treatment consisted of demineralized water with a pH value of 5.6 (~2.5 μmol (+) L^{-1} of H^+). The solutions were applied by gravitational drip (the bottles, tubes, and flow regulators were the same as those used in medical practice for the administration of solutions) from above the soil surface at a rate of 62 mm (500 ml) per week for 24 weeks. All of the columns had previously been irrigated for 4 weeks with demineralized water. The weekly application lasted 4 to 6 hours. The volume and pH of the percolates were measured every week. All the other parameters were measured every week for the first 12 weeks, then every 2 weeks until the end of the treatment. The acidification experiment was conducted in a laboratory that was kept dark between working periods and maintained at a temperature of 15°C and relative humidity of 50 percent.

Chemical analyses

The SO_4^{2-}, NO_3^-, $H_2PO_4^-$, Na^+, NH_4^+, and K^+ concentrations in the percolates were determined by ion-exchange chromatography (Model 12 Dionex), whereas Ca^{2+}, Mg^{2+}, Mn^{2+}, and Al_t cation determinations were obtained by means of atomic absorption using a flame atomization system. The pH readings were recorded with a digital Radiometer pH meter equipped with a combined electrode.

After 24 weeks of weekly treatment, each horizon was separated and air dried before undergoing analysis. The following analyses were carried out on each horizon from each of the columns as well as on each of the initial horizons: C.E.C. and exchangeable cations using 1.0 *N* NH_40Ac (pH 7); organic carbon with the Walkey-Black method; total N with the Kjeldhal method; extractable phosphorus with 0.002 *N* H_2SO_4 using the Truog-1 method. The pH was determined with water in a 1:2 soil:solution ratio in the case of the mineral horizons and a 1:5 ratio in the case of the organic horizons.

In the present study, the concentration of a given ion was expressed by placing chemical symbols in brackets, e.g., $[SO_4^{2-}]$, whereas ion activity was designated by the use of parentheses, e.g. (Al^{3+}). However, for the purposes of simplifying the presentation of data, $[H^+]$ has been considered equal to H^+ activity, i.e., $(H^+) = 10^{(6\text{-pH})}$. Calculation of activity coefficients indicated that this represented a mean 5 percent underestimation of actual values.

Statistical analyses

In order to determine whether mean ion concentrations differed among treatments, one-way analysis of variance was used for each type of percolate. Two-way analysis of variance was also introduced (treatments (i=4) and types of columns (j=2)) to determine whether interactions occurred. When the hypothesis of homogeneity of variance could not be applied to variables, appropriate transformations were made, i.e., log $(x+1)$ or x^2 (Box and Cox 1964). The nonparametric Kruskal-Wallis test was introduced for non-normal variables. Multiple comparisons were made using the Student-Newman-Keuls (SNK) test in the case of analysis of variance without interaction and the method of least square means in the case of analysis of variance with interaction. Whenever nonparametric tests were applied, multiple comparisons were established using the tables drawn up by McDonald and Thompson (1967). In all of the tests, the null hypothesis (H_0), i.e., homogeneity of the means, was rejected when the probability was under 5 percent. Lastly, a study of correlations between variables was carried out using the Pearson coefficient of linear correlation. All of the calculations were made with SAS software (1985).

There was no significant difference between initial and collected volumes. It was therefore unnecessary to make a weighted calculation of mean concentrations and to convert concentration data (μmol (+ or -) L^{-1} into deposition data (kg ha^{-1}). For logistical reasons, the percolates for the 4th week were not subjected to analysis. Furthermore, pH data for percolate samples taken during odd-numbered weeks from the 12th to the 24th week were not analyzed since this single parameter, without an analysis of the principal ions, provided little additional information. The statistical analysis of percolate ion concentrations was therefore based on 17 weekly samplings, i.e., weeks 1 to 3, 5 to 12, 14, 16, 18, 20, 22, and 24.

RESULTS AND DISCUSSION

Analysis of percolates

General

The effect of treatment on mean ion concentrations was much greater in the organic percolates (OP) (Table 2) than in the spodic percolates (SP) (Table 3). Concentrations of NO_3^- and H^+ did not vary with the treatment in the SP, whereas reduced nitrification and an increase in $[H^+]$ were recorded in the OP as a result of treatment. Significant treatment-related differences were recorded for $[SO_4^{2-}]$, $[Ca^{2+}]$, $[Mn^{2+}]$, and $[NH_4^+]$ in both types of percolates and for $[Mg^{2+}]$ in the OP only. The Mg^{2+} concentration seemed slightly higher in the percolates following treatment at pH 2.9 although the probability level was only 0.073. Irrespective of the type of percolate, the treatments did not produce any variations in the mean concentrations of $H_2PO_4^-$, Al_t, K^+, and Na^+. As we shall see later, the most acidic treatments, however, resulted in a greater concentration of Al_t in the SP at the end of the experiment. With the exception of $[K^+]$, concentrations were vastly different in the SP since the latter contained concentrations of Na^+ and Al_t that, respectively, were 2 and 10 times those occurring in the OP. In contrast, $H_2PO_4^-$ concentrations were 100 times lower than in the OP.

In this report, total aluminum concentrations are given in μmol (+) L^{-1} since all of the aluminum was arbitrarily considered to occur in Al^{3+} form. According to the equilibrium equations taken from Lindsay (1979), the weighted mean charge of Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$ ions in the SP equaled 2.9 provided that the AlF^{2+} and $AlSO_4^+$ complexes were not included in the calculations. The $[AlSO_4^+]$/[total Al] and $[AlSO_4^+]$/[total SO_4] ratios estimated from the data contained in Table 3 varied from 15 to 6 percent and from 20 to 25 percent

Table 2. Mean ion concentrations (μmol (+ or -)) in the organic percolates as a result of different treatments

		pH of treatments			
	p	2.9	3.3	4.3	5.6
SO_4^{2-}	<0.001	1336d+* (11)**	621c+ (10)	213b= (19)	156a= (17)
NO_3^-	<0.001	433a- (32)	586b- (19)	692c- (26)	770c- (27)
$H_2PO_4^-$	0.505	52a+ (4)	58a+ (7)	55a+ (9)	59a+ (4)
Total anions (TA)		1821 (45)	1265 (31)	960 (53)	985 (11)
Al_t***	0.365	100a- (23)	122a- (8)	120a- (11)	117a- (20)
Ca^{2+}	<0.001	508c- (20)	304b- (23)	278ab- (14)	247a- (23)
Mg^{2+}	0.001	80b+ (4)	58a+ (4)	60a+ (2)	54a+ (7)
Mn^{2+}	<0.001	41b+ (4)	19a+ (4)	18a+ (2)	15a+ (2)
K^+	0.055	87a+ (3)	79a+ (5)	73a= (5)	80a+ (3)
Na^+	0.381	12a- (2)	15a- (3)	12a- (1)	15a- (4)
NH_4^+	0.001	1118c+ (97)	893b+ (110)	605a+ (78)	744ab+ (15)
H^+	<0.001	192c+ (13)	101b= (5)	112b= (2)	82a- (7)
Total cations (TC)		2138 (79)	1591 (100)	1278 (76)	1354 (63)
TC - TA		316 (38)	326 (69)	319 (22)	368 (52)

* There is no statistical difference between mean values on the same line followed by the same letter. The symbol following each letter indicates whether the mean concentration in the organic percolates was lower (-), equal to (=) or higher (+) than the mean concentration in the spodic percolates (<0.05).

** Standard deviation.

*** The equivalent in aluminium was calculated on the assumption that all the aluminum was in trivalent form (Al^{3+}).

p Probability of acceptance of the nul hypothesis based on one-way analysis of variance.

Table 3. Mean ion concentrations (μmol (+ or -)) in the spodic percolates as a result of different treatments

		pH of treatments			
	p	2.9	3.3	4.3	5.6
SO_4^{2-}	0.016	724^{c}* (17)**	384^{b} (12)	213^{a} (10)	185^{a} (14)
NO_3^-	0.203	1670^{a} (108)	1678^{a} (54)	1802^{a} (36)	1747^{a} (90)
$H_2PO_4^-$	0.461	1a (2)	$<1^{a}$ (<1)	$<1^{a}$ (<1)	$<1^{a}$ (<1)
Total anions (TA)		2395 (93)	2062 (59)	2014 (41)	1932 (103)
Al_t***	0.163	1364^{a} (98)	1198^{a} (65)	1210^{a} (80)	1195^{a} (115)
Ca^{2+}	<0.001	559^{b} (3)	452^{a} (16)	422^{a} (13)	406^{a} (12)
Mg^{2+}	0.073	58^{b} (10)	45^{a} (4)	41^{a} (5)	42^{a} (7)
Mn^{2+}	<0.001	14^{b} (3)	4^{a} (2)	1^{a} (<1)	2^{a} (2)
K^+	0.704	80^{a} (12)	71^{a} (6)	75^{a} (2)	73^{a} (14)
Na^+	0.494	28^{a} (4)	26^{a} (1)	24^{a} (1)	26^{a} (3)
NH_4^+	0.043	193^{c} (47)	152^{b} (24)	142^{a} (23)	111^{a} (20)
H^+	0.578	98^{a} (7)	94^{a} (3)	97^{a} (1)	94^{a} (1)
Total cations (TC)		2394 (176)	2042 (93)	2012 (77)	1949 (170)
TC - TA		-1 (86)	-20 (92)	-2 (66)	18 (67)

* There is no statistical difference between mean values on the same line followed by the same letter (<0.05).

** Standard deviation.

*** The equivalent in aluminum was calculated on the assumption that all of the aluminum was in trivalent form (Al^{3+}).

p Probability of acceptance of the nul hypothesis based on one-way analysis of variance.

for treatments at pH 2.9 and pH 5.6, respectively. Assuming a valence of $^{3+}$ for total Al and of $^{2-}$ for total sulfate, it was estimated that the mean maximum error for the sum of SP cation and anion equivalents was 2 percent. If changes in the distribution of charges resulting from the formation of the $AlSO_4^+$ complex were not taken into account, the ionic balance remained virtually unchanged since the formation of one mole of $AlSO_4^+$ induced an equivalent loss of positive and negative charges. In the case of the OP, high concentrations of organic C prevented the formation of hydrated aluminum with a valence of less than 3 (James and Riha 1986). The ion concentrations given in Tables 2 and 3 therefore represent a valid approximation of charge distribution in this experiment.

The mean anion deficit in the organic percolates (317-368 μmol (-) L^{-1}), which in all likelihood was attributable primarily to soluble organic fractions (Cronan et al. 1978; Cronan 1980; Yavitt and Fahey 1984; Fahey and Yavitt 1988), represented 15, 20, 25, and 27 percent of the total anion charge for treatments at pH 2.9, 3.3, 4.3, and 5.6, respectively. This anion deficit was comparable to that measured *in situ* (roughly 320 μmol (-) L^{-1}) in the percolate samples taken under the H horizon during the first growing season following the installation of lysimeters (unpublished data). Under these conditions, however, which were more natural although influenced by installation-related disturbances, ion concentrations were much lower (comparable to treatments at pH 4.3 or pH 5.6). They were roughly 7 times lower for the anions and 3 times lower for the cations. Concentrations were much lower still once the initial disturbance no longer played a role (24 times lower for the anions and 6 times lower for the cations during the third sampling season). As a result, a very high percentage of cation leaching in the field (roughly 70 to 80 percent) involved organic anions or soluble organic complexes. The *in vitro* conditions in the present experiment reversed this process since 75 percent of the cations leached out with mineral anions.

Cronan et al. (1978) attributed 76 percent of cation leaching to SO_4^{2-} anions in percolates from the forest floor of a New Hampshire subalpine *Abies balsamea* stand. In the acid soils of cold temperate regions, leaching is thought to be primarily due to organic acids, whereas in the northeastern United States and northern Europe, H_2SO_4 is thought to be the chief causal agent (Abrahamsen et al. 1976). In southeastern Wyoming, organic and SO_4^{2-}ions are the principal anions encountered in percolates from the forest floor of *Pinus contorta* stand (Yavitt and Fahey 1984). Carbon-containing anions (organic anions and HCO_3^- when the pH is high) are thought to account for 30 to 70 percent of the total anion charge. Foster et al. (1986) observed that 50 percent of cation charges were balanced by NO_3^- and SO_4^{2-}anions in percolates from the forest floor of a mixed *Acer saccharum* and *Betula papyrifera* stand at Turkey Lakes, Ontario.

In the present experiment, the mineral anion input, resulting from internal oxidation of organic matter, therefore does not reflect mean *in situ* conditions, but may reflect conditions involving pronounced disturbances and/or considerable mineral deposition.

As a rule, the more acidic treatments produced OP of a lighter yellowish hue. Precipitation of humic acids as a result of increased acidity may account for the color changes, but Hay et al. (1985) have suggested fulvic acids as the causal agent. According to these authors, the carbon-fulvic acid/total organic carbon ratio in the organic percolates from monolith samples taken at Lake Laflamme was 63 percent. With acidification (pH 2.0 compared to pH 3.5), carbon-fulvic acid and total organic carbon levels dropped and the carbon-fulvic acid/total organic carbon ratio likewise decreased. The authors observed that little was known about the solubility of fulvic acids in diluted acids. A speciation study of aluminum in organic percolates from columns treated at pH 2.9 and pH 5.6 (unpublished data) indicated that 38 to 63 percent of the total aluminum was in organic form after 28 weeks of treatment. After 62 weeks, however, these values dwindled to between 0 and 44 percent. Therefore, leaching of soluble organic products resulting from the decomposition of organic matter occurred in large amounts at the onset of treatment, as indicated by changes in the total cation/total anion ratio (Figure 1), which was very high during the first week (2.4) but gradually decreased to a value of 1 towards the ninth week. This gradient was related to the change in coloration from the darker hues of the initial percolates to the lighter shades thereafter, reflecting the increasingly smaller percentage of charges supplied by organic anions.

In the SP, the mean cation charges were in a state of equilibrium with the mean anion charges (Table 3) and the total cation/total anion ratio (Figure 1) was more stable than in the OP. The anion deficits in one series of percolates (weeks 3, 5, 6, and 9) and the cation deficits in another series of percolates (weeks 1, 2, and 16-24) partially accounted for the equilibrium in mean concentration values. In short, with the exception of weeks 6 to 14 when the electric charges were in equilibrium in both the organic and spodic percolates, there was usually an anion deficit in the OP and a cation deficit in the SP. Rutherford et al. (1985) also recorded cation deficits on a general basis in SP from the same reconstituted podzol.

A visual appraisal failed to show any color changes in the SP during the course of the experiment. The liquid remained clear, indicating the effectiveness with which the mineral horizons retained the dissolved organic products from the organic LF and H horizons. This retention of organic substances indicated that water had percolated through the micropores thereby increasing the duration and area of contact and enhancing the chances of achieving a state of equilibrium with the mineral phases (Cozzarelli et al. 1987). Thus, the chemical characteristics of the SP differed completely from those of the OP.

The highest concentrations of SO_4^{2-} ions were found in the acid OP of treatments at pH 2.9 and pH 3.3, respectively, accounting for 62 and 39 percent of the total anion charge (Table 2). A predominance of NO_3^- ions occurred in the less acidic percolates of treatments at pH 4.3 and pH 5.6, representing 54 and 57 percent, respectively, of the total anion charge. In the SP (Table 3), NO_3^- was predominant in all of the treatments, representing 70 to 90 percent of the total anion charge from the most acidic treatment (pH 2.9) to the least acidic treatment (pH 5.6).

In the OP, the predominant cation was NH_4^+, representing 47 to 56 percent of the total cation charge. In the SP, Al_t was the predominant cation, accounting for 57 to 61 percent of the total cation charge. In both types of percolates, Ca^{2+} was the second-most prevalent ion, representing 18 to 24 percent of the total cation charge in the OP and 21 to 23 percent in the SP. Ammonification and leaching of Ca^{2+} in the organic horizons plus the dissolution of Al containing minerals in the spodic horizons were considered the most effective processes here for consuming the H^+ protons added in the treatments and/or produced by internal oxidation of organic matter. In the mineral horizons, far more Al was leached out than basic cations. This may be explained by low base saturation of these horizons (<10-15 percent), which did not allow for an effective exchange with H^+ (Reuss and Johnson 1985).

Although there were significant treatment-related gradients for several ions, only the mean SO_4^{2-} and H^+ ion concentrations in the OP differed in the treatment at pH 4.3 as compared to reference values. Partial inhibition of nitrification and enhanced Ca^{2+} leaching in the OP became significant only with treatments at pH values of 3.3 and lower, whereas only with the treatment at pH 2.9 did $[Ca^{2+}]$ increase in the SP as did $[Mg^{2+}]$ and $[Mn^{2+}]$ in both types of percolates.

Figure 2 shows the anion and cation concentrations of the principal major ions the 6th, 12th (maximum ion concentrations in the SP), and 24th weeks (maximum effect of treatments in the SP). The following observations may be made from this figure:

1) Irrespective of the treatment, time, and type of percolate, inorganic nitrogen represented a very significant portion of the charges. NO_3^- and NH_4^+ was influenced by the treatments in the OP, whereas in the SP, NO_3^- accounted for virtually all of the inorganic N and was not influenced by the treatments;

2) The adsorption of added sulfate was nil in the organic horizons, but pronounced in the spodic horizons at the onset of treatment;

3) The effect of the treatment became noticeable only toward the end of treatment in the SP. Aluminum nitrate was gradually replaced with aluminum sulfate and a significant Al_t concentration gradient was established;

4) The most acidic treatments appreciably increased the leaching of Ca^{2+} in the organic horizons.

Detailed analysis of ion concentrations

SO_4^{2-} and H^+

Treatment-added SO_4^{2-} ions were not retained in the organic horizons (Figure 3a). They were completely recovered in the OP along with a fraction resulting from oxidation of organic S during decomposition of organic matter. The latter process seemed to be slowed down by treatment acidity since SO_4^{2-} was estimated at 86, 121, 163, and 156 μmol (-) L^{-1} (Table 2) for treatments at pH 2.9, 3.3, 4.3, and 5.6, respectively. The relatively constant and high mineralization of organic S may be attributed to the presence of an open incubation system in which the horizons were periodically leached (Maynard et al. 1984). Maximum SO_4^{2-} concentrations occurred during the third week in percolates from treatments at pH 3.3, 4.3, and 5.6, i.e., simultaneously with maximum NH_4^+ (Figure 3b), K^+ (Figure 3c), and $H_2PO_4^-$ (Figure 3d) concentrations. This coincidence indicates that maximum mineralization was achieved at the onset of treatment. The literature contains numerous reports of the poor SO_4^{2-} absorption capacity of surface organic horizons (Cronan 1980; Fernandez 1987; Johnson and Todd 1983).

Analysis of the SP revealed significant adsorption of added SO_4^{2-} until week 6 for the treatment at pH 2.9 and until week 7 for the treatment at pH 3.3 (Figure 3a). Thereafter, adsorption rapidly decreased until week 11 when concentrations reached a plateau maintained until week 16. In treatments at pH 2.9 and pH 3.3, SO_4^{2-}, concentrations rose above those encountered in the treatment solution, beginning at the 20th and 18th weeks, respectively. Assuming that there was no desorption of initially adsorbed SO_4^{2-} and that there was uniform mineralization of organic S in all of the treatments in the Ae, Bhf1, and Bhf2 horizons (i.e., 29 μmol (-) L^{-1}, or the difference in mean SO_4^{2-} concentrations between the spodic and organic percolates in the treatment at pH 5.6), mineralization of organic sulfur in all of the LF, H Ae, Bhf1, and Bhf2 horizons respectively supplied 115, 150, 192, and 185 μmol (-) L^{-1} of SO_4^{2-} in the SP for treatments at pH 2.9 to pH 5.6. Once this endogenous production of soluble SO_4^{2-} was subtracted, it was possible to estimate that 51, 53, and 58 percent of SO_4^{2-} added by treatments at pH 2.9, 3.3, and 4.3, respectively, would be retained in the mineral horizons after 24 weeks of input, i.e., after percolation of a column of water of almost 1500 mm.

It should be noted that the term "retention" would be more appropriate here to describe the different contributing processes that help to reduce the solubility of SO_4^{2-} during percolation in the mineral horizons. In damp acid soils, SO_4^{2-} solubility may be regulated both by mechanisms involving adsorption by positively charged Fe and Al oxides and by processes in which Fe and Al hydroxysulfates are precipitated and dissolved (Adams and Rawajfih 1977). The possibility that different forms of aluminum hydroxysulfate may be produced has been explored in the section dealing with changes in aluminum concentrations.

A comparison of concentrations in organic and spodic percolates in relation to time and treatment indicated that, as time progressed, concentrations in the SP were equal to, if not greater than, those in the OP in the less acidic treatments. This excess SO_4^{2-} in the spodic percolates may be explained by the desorption of adsorbed SO_4^{2-} from the added and/or initially present SO_4^{2-} as well as by the oxidation of organic S within the mineral horizons.

Unlike SO_4^{2-} ions, the initial proton charge of the treatments was considerably modified during percolation through the LF and H horizons (Table 2). At pH 2.9 and pH 3.3, the mean H^+ concentration in the OP was 192 (pH 3.72) and 101 (pH 4.00) μmol (+) L^{-1}, respectively, i.e., 15 and 20 percent of the H^+ concentration in the input solutions. The percolates from treatments at pH 4.3 and pH 5.6, on the other hand, were more acidic than the input solutions, producing respective mean values of 112 (pH 3.95) and 82 (pH 4.09) μmol (+) L^{-1}.

The higher acidity recorded in the percolates from treatment at pH 4.3 (as compared to percolates from treatment at pH 3.3) (Figure 3e) was associated with lower NH_4^+ production (Figure 3b). Since ammonification involves H^+ consumption, lower consumption in the horizons treated at pH 4.3 may have increased percolate acidity. Maximum H^+ concentrations were recorded between the 11th and 14th weeks, attaining 260 (pH 3.59), 135 (pH 3.87), 164 (pH 3.79), and 116 (pH 3.94) μmol (+) L^{-1}, respectively, for treatments at pH 2.9 to pH 5.6. With the exception of the treatment at pH 2.9 (beginning at the 10th week), the OP proved to be less acidic than the initial H horizon (pH (H_2O)=3.7; $[H^+]$=200 μmol (+) L^{-1}; Table 1).

Having achieved equilibrium in organic horizons (0-20 cmol HNO_3 kg^{-1}) from four forest soils in New York State, James and Riha (1986) recorded consumption of 67 to 96 percent of added H^+ ions. As there was no compensation for 38 to 79 percent of this loss by an increase in soluble metals, they attributed a significant portion of H^+ consumption to the protonation of weak organic acid anions in solution and in solid phases. In our experiment, however, ammonification apparently played a major role. James and Riha (1986), for their part, made no mention of significant NH_4^+ production. The difference in findings is probably related more to differences in experimental procedures than to the specific characteristics of the horizons studied.

The different treatments did not have a significant effect on the mean H^+ concentration in the SP (Table 3) which ranged from 94 (pH 4.03) to 98 (pH 4.01) μmol (+) L^{-1}. These percolates, however, collected from under the Bhf2 horizon, proved far more acidic than the initial horizon itself which had a pH value (H_2O) of 4.7 (Table 1). This acidification was related to nitrification which occurred in all of the columns and was unrelated to treatment (Tables 2 and 3; Figure 3f).

Changes in $[H^+]$ in the SP were characterized by:

1) A sharp drop from the onset of treatment to week 5 (Figure 3e), i.e., 116 ± 6 to 82 ± 7 μmol (+) L^{-1}. The percolates from treatment at pH 2.9 yielded minimal values of 72 μmol (+) L^{-1} (pH 4.14) which were associated with maximum NH_4^+ values (Figure 3b);

2) In less acidic treatments (pH 4.3 and 5.6), a sharp rise reaching at week 8 the level of concentrations at the onset of the experiment. In the case of the more acidic treatments (pH 2.9 and 3.3), the increase was slower to occur, taking up to 12 and 14 weeks;

3) A subsequent drop related to a progressive decline in nitrification (Figure 3f) followed by the development of a significant gradient related to the effect of the treatments. The mean pH values for the percolates obtained from weeks 18 to 24 were 4.04, 4.13, and 4.14, respectively, for treatments at pH of 2.9 to pH 5.6.

Like Lilieholm and Feagley (1988) and Morrison (1981) in their acidification experiments, we observed that the pH values for the percolates from the treatments at pH 2.9 and pH 3.3 were higher than the pH values for the added solutions, indicating that the simulated acid rain, which corresponded to 30 years of H^+ deposition on the Lake Laflamme basin (for treatment at pH 2.9), had little effect on the soil's buffer capacity. In addition to this exogenous supply, there was also a nitrification-related endogenous supply of H^+ which was considered equal to another 30 years of H^+ deposition.

Orthophosphates ($H_2PO_4^-$)

Mean $H_2PO_4^-$ concentrations in the OP were not influenced by the treatments and ranged from 52 to 59 μmol (-) L^{-1} (Table 2). Concentrations reached peak values, i.e., 45 to 163 μmol (-) L^{-1}, within the first 6 weeks (Figure 3d) and dropped sharply to 20 ± 5

μmol (-) L^{-1} in the 7th week. Concentrations subsequently stabilized at higher values beginning at the 16th week (40 to 73 μmol (-) L^{-1}). Changes in $H_2PO_4^-$ concentrations were highly characteristic and no other ion displayed a similar pattern, except in reverse in the case of H^+ (Figure 3e), Ca^{2+} (Figure 3g), Mg^{2+} (Figure 3h), and Mn^{2+} (Figure 3i).

Traces of $H_2PO_4^-$ in the SP (Table 3) indicated that virtually all of the ion was retained by adsorption on the Fe and Al oxides present in the mineral horizons. Our results agree with those of Haynes and Swift (1986) who, as compared to control values, did not detect any loss of supplementary phosphate in the leachates of a silty loam (eutric Cambisol; FAO) following treatment at pH 6.0 to pH 3.5.

NO_3^- and NH_4^+

The acid treatments partially inhibited nitrification within the organic horizons. The NO_3^- concentration in the percolates of treatments at pH 2.9, 3.3, and 4.3 rose to 56, 76, and 90 percent respectively, of the NO_3^- concentration in the percolates from the reference treatment (pH 5.6). The nitrification rates defined by the $[NO_3^-]/([NO_3^-] + [NH_4^+])$ ratio were 0.28, 0.40, 0.53, and 0.51, respectively, for treatments at pH 2.9 to pH 5.6.

There have been several reports of decreased NO_3^- concentrations following acidification (Bienkowski et al. 1986; Haynes and Swift 1986; Lodhi 1982; Strayer et al. 1981). In the present study, however, acidity did not prove to be very effective in dramatically lowering NO_3^- production. Even though the mean pH of the OP ranged from 3.7 to 4.1, mean NO_3^- production was 433 to 770 μmol (-) L^{-1}. In the SP in which the mean pH remained around 4.0, NO_3^- concentrations exceeded 1 700 μmol (-) L^{-1}. Stroo et al. (1986) attributed nitrification in an acid medium to acidity-tolerant heterotrophic organisms. It is thought that other heterotrophic organisms are capable of causing the non-assimilative reduction of NO_3^- to NH_4^+ (Yavitt and Fahey 1984). The simultaneous or alternate action of these organisms with antagonistic effects (oxidation and reduction) in conjunction with the constraints of acid charges, may account for the variations recorded in the NH_4^+/NO_3^- ratio in the OP.

Although NH_4^+ concentrations were higher in the more acidic treatments, this was not the result of increased ammonification, but rather of reduced nitrification since the mean amount of inorganic N leached from the organic horizons remained constant, yielding cumulative values of 17.7, 16.5, 14.2, and 16.8 mmol, of N per column for the duration of the experimental period for treatments at pH 2.9 to pH 5.6, respectively (Figure 4), i.e., an approximate mean value of 300 kg N ha^{-1}. This mineralized nitrogen, estimated from percolate concentrations, represented roughly 18 percent of the initial N pool in the LF and H horizons. This is an extremely high mineralization coefficient considering that the reported annual mean value under *in situ* conditions is 2 to 10 percent (Bartholomew 1965).

It should be noted, however, that the total nitrogen concentration in the organic horizons remained the same before and after treatment. This phenomenon may be explained by the loss of C as a gas (CO_2) or by the leaching of soluble organic forms (Well and Jorgensen 1975). Cronan (1980), Yavitt and Fahey (1984), and Moore (1987) also reported that [NH_4^+] increased with the acidity of simulated rain. Moore (1987) mentioned, moreover, that mineralization remained at the same level for all treatments.

The mineralization coefficient of columns treated at pH 4.3 tended to be lower than those treated at pH 3.3 or pH 5.6 (Figure 4). Bitton et al. (1983) measured the *in situ* effect of acidification on a Florida entisol. Findings indicated a 50 to 63 percent decrease in acid treatment-related nitrification (pH 3.0 and 3.7) as compared to the control (pH 4.5). In addition, similar to our own findings, they observed that the mineralization coefficient was lower in soils treated at an intermediate pH (pH 3.7) than in soils treated with a less acidic pH of 4.5 (-50 percent) or a more acidic pH of 3.0 (-58 percent). The authors suggested that nitrogen mineralization was influenced by protease activity.

In the spodic columns, the total amount of leached inorganic N in each column remained constant, i.e., 22.2 ± 0.5 mmol (Figure 4). Irrespective of the treatment, the nitrification rate was very high and roughly constant (90 to 94 percent) although slightly lower in the more acidic treatments. Subtraction of inorganic nitrogen from the organic horizons (16.3 mmol) yielded a value for total mineralized nitrogen within the Ae, Bhf1 and Bhf2 horizons, i.e., 5.9 mmol. This value corresponded to 3 percent of the total N pool contained in these three horizons. This mineralization coefficient represents an overestimation since we did not take into account organic nitrogen leached from the organic horizons and mineralized in the mineral horizons.

Changes in NO_3^- and NH_4^+ concentrations (Figures 3f and 3b) indicated that the maximum values were achieved more rapidly in the OP (weeks 3 to 8 for NO_3^- and weeks 2 to 5 for NH_4^+) than in the SP (weeks 10 to 16 for NO_3^- and weeks 8 to 12 for NH_4^+) except in the case of NH_4^+ in the SP treated at pH 2.9. In this instance, the maximum concentration was reached in the 5th week. The latter finding suggests that two processes may have come into play either separately or simultaneously:

1) the momentary action of a process involving the inhibition of nitrification which may have been triggered in the mineral horizons under the influence of the most acidic treatment (pH 2.9);

2) the shift of NH_4^+ on the exchange sites by cations leached from the higher horizons.

Hern et al. (1985) also recorded high NO_3^- peaks in an experiment involving acidification of a Humo-Ferric Podzol (Turkey Lakes, Ontario). These peaks appeared in the surface percolates (12 and 25 cm) after the addition of a 650-mm column of water and 60 cm below the surface after the addition of an 850-mm column of water. These columns of water corresponded roughly to those yielding maximum NO_3^- concentrations in our experiment.

It is interesting to note that part of the nitrogen leached from the organic horizons was retained in the mineral horizons between weeks 3 and 11 (Figure 4). The absence of root uptake under conditions which were unfavorable to denitrification combined with the soil's very weak capacity to adsorb nitrates promoted intensive leaching of this anion which occurred in the spodic percolates in concentrations that were never less than those encountered in the organic percolates (Figure 3f). At the onset of treatment, therefore, ammonium nitrogen was retained in the mineral horizons since only a portion of the NH_4^+ leached from the organic horizons was nitrified.

The relatively large flow of mineral nitrogen in this experiment calls for a more thorough study of the production and consumption of H^+ by processes involved in the mineralization and oxidation of organic matter. The data presented in Table 4 were calculated from stoichiometric equations compiled by van Breeman et al. (1983) and from the mean ion concentrations in Tables 2 and 3. Since the amount of nitrates produced in the mineral horizons ($[NO_3^-]_{sp}$-$[NO_3^-]_{op}$) was always greater than the NH_4^+ leached from the organic horizons, it was assumed that the latter ion was completely nitrified in the mineral horizons (process (4)). Thus, H^+ production as a result of mineralization and oxidation of organic N (process (1)) within the mineral horizons was equal to the relationship $[NO_3^-]_{sp}$ - $[NO_3^-]_{op}$ - $[NH_4^-]_{op}$. The processes associated with the mineralization of organic P and the mineralization and oxidation of organic S (process (2)) in the organic horizons were also taken into account to demonstrate the significance of processes involved in the transformation of nitrogen forms. While organic acids, e.g., oxalic acid, which are intermediate byproducts of decomposition, may be an important source of H^+, they were not considered here.

The consumption of H^+ due to ammonification in the organic horizons treated at pH 2.9 and pH 3.3 exceeded the production of H^+ arising from the complete oxidation of organic N, P and S. This resulted in potential pH values of 3.15 and 3.43, respectively, for treatments with initial pH values of 2.9 and 3.3. Conversely, H^+ production was greater than H^+ consumption in treatments at pH of 4.3 and pH 5.6. In this case, the potential pH arising from the summation of these processes was 4.35 and 3.61, respectively.

The potential proton charge ratio, which was 500:200:20:1 in the input solutions, dropped to 2.9:1.5:1.5:1 when the above-mentioned processes were taken into account. The latter ratio

Table 4. Production and consumption of H^+ by processes involved in the mineralization and oxidation of organic matter during experimental *in vitro* acidification of a Ferro-Humic Podzol

Treatment		Organic horizons (LF, H)			Mineral horizons (Ae, Bhf1, Bhf2)		
		Input	Cumulative	Potential pH*	Input	Cumulative	Potential pH
		µmol(+) L^{-1}			µmol(+) L^{-1}		
pH 2.9	(1)	1250	1250	2.90	192	192	3.72
	(2)	433	1683	2.77	119	311	3.51
	(3)	148	1831	2.74	-	-	-
	(4)	-1118	713	3.15	-193	118	3.93
	(5)	-	-	-	2236	2354	2.63
pH 3.3	(1)	500	500	3.30	101	101	4.00
	(2)	586	1096	2.96	199	302	3.52
	(3)	179	1265	2.90	-	-	-
	(4)	-893	372	3.43	-152	150	3.82
	(5)	-	-	-	1786	1933	2.71
pH 4.3	(1)	50	50	4.30	112	112	3.95
	(2)	692	742	3.13	505	617	3.21
	(3)	218	960	3.02	-	-	-
	(4)	-605	355	3.45	-142	475	3.32
	(5)	-	-	-	1210	1685	2.77
pH 5.6	(1)	2.5	2.5	5.60	82	82	4.09
	(2)	770	773	3.11	233	315	3.50
	(3)	215	988	3.00	-	-	-
	(4)	-744	244	3.61	-111	204	3.69
	(5)	-	-	-	1488	1692	2.77

(1)	Treatment input	
(2)	Mineralization and oxidation of N: $R\text{-}NH_2 + 2O_2 \rightarrow R\text{-}OH + NO_3^- + H^+$	org. col.: $[H^+] = [NO_3^-]_{op}$** spod. col.: $[H^+] = [NO_3^-]_{sp}$*** $- [NO_3^-]_{op} - [NH_4^+]_{op}$
(3)	Mineralization of organic P: $R\text{-}H_2PO_4 + H_20 \rightarrow R\text{-}OH + H_2PO_4^- + H^+$ and mineralization and oxidation of S: $R\text{-}SH + 3/2\ H_20 + 7/2\ 0_2 \rightarrow R\text{-}OH + SO_4^{2-} + 2H^+$	org. col.: $[H^+] = [SO_4^{2-}]_{op} + [H_2PO_4^-]_{op}$ spod. col.: (undetermined)
(4)	Mineralization of organic N: $R\text{-}NH_2 + H_20 + H+ \rightarrow NH_4+ + R\text{-}OH$	org. col.: $-[H^+] = [NH_4^+]_{op}$ spod. col.: $-[H^+] = [NH_4^+]_{sp}$
(5)	Nitrification of NH_4^+: $NH_4^+ + 20_2 \rightarrow NO_3^- + H_2O + 2H^+$	org. col.: (undetermined) min. col.: $[H^+] = 2 \times [NH_4^+]_{op}$

* pH values were calculated from H^+ concentrations and not from H^+ activity. The values are consequently slightly lower than theoretical values (max. -0.05 pH unit).

** op: organic percolates.

*** sp: spodic percolates.

is a far more accurate reflection of the mean H^+ ion concentration ratio in the organic percolates which is 2.3:1.2:1.4:1. In addition, in the mineral horizons, nitrification of NH_4^+ leached from the organic horizons was responsible for a very high endogenous production of H^+, i.e., 71 to 96 percent of the effective proton charge, depending on the treatment. The resulting potential pH values ranged from 2.63 to 2.77, whereas the pH values for the organic percolates ranged from 3.72 to 4.09. The effective proton charge ratio shrank further to 1.4:1.1:1:1. The experimental conditions produced highly significant endogenous acidification which considerably reduced the differences between the findings recorded in the different treatments.

This phenomenon has been reported by several authors (Hern et al. 1985; Freiesleben and Rasmussen 1986; Skeffington and Brown 1986; Boutin and Robitaille 1987; Brown 1987). Unlike Hern et al. (1985) and Brown (1987), however, we do not believe that root activity alone could withdraw the large amounts of inorganic N produced by mineralization from the soil solution. Kelly and Strickland (1987) recorded high concentrations of NO_3^- in the percolates collected in the microcosms 100 cm below the surface after a 28-month stabilization period followed by an 8- to 10-month percolation period. All of the microcosms were completely covered with 3-year-old *Pinus virginiana* and *Liriodendron tulipifera* seedlings.

Ca^{2+}, Mg^{2+}, K^+, and Na^+

The treatments at pH 2.9 and pH 3.3 yielded greater Ca^2+ concentrations in the OP compared to the reference treatment at pH 5.6 (Table 2). The [Ca^{2+}] in the OP was multiplied by a factor of 2.1 for treatment at pH 2.9 and by 1.2 for treatment at pH 3.3. The concentration multiplication factors were 1.4 and 1.1, respectively, in the SP. It should be noted that these factors are similar to the effective proton charge ratio calculated above. In the reference treatment, Ca^{2+} losses in the OP represented 60 percent of the losses in the SP, whereas under the influence of treatment at pH 2.9, the percentage rose to 90 percent. The difference between the treatments at pH 5.6 and 2.9 was therefore more pronounced in the organic than in the spodic percolates, indicating greater Ca^{2+} retention in the mineral horizons with the more acidic treatments. The increase in exchangeable Ca in the mineral horizons treated at pH 2.9 substantiated these findings when compared to horizons treated at pH 5.6. This calcium retention was probably due to sulfate adsorption by the sesquioxides as a result of an increase in negative charges (Johnson and Cole 1977; Cronan 1980).

Peak Ca^{2+} concentrations were recorded in the 12th week in both the organic and spodic percolates treated at pH 2.9 (Figure 3g). Up to the 12th week, the increase in Ca^{2+} concentrations in the OP corresponded to a decrease in NH_4^+ concentrations (Figure 3b) which reached minimal values toward the 12th week. The subsequent decrease in or stabilization of the Ca^{2+} concentration seemed to be related to the decrease in NO_3^- concentrations (Figure 3f). Within the organic horizons, Ca^{2+} leaching dynamics were therefore strongly influenced by the scope of the ammonification and nitrification processes. If experimental conditions had been less favorable to mineralization of organic N, less $(NH_4)_2SO_4$ would have been formed and a greater portion of the added SO_4^{2-}would have percolated in H_2SO_4 or $CaSO_4$ form. The latter is the product of ion exchange between H^+ in solution and exchangeable Ca.

Only the treatments at pH 2.9 increased the amount of Mg^{2+} leached as compared to the reference treatment at pH 5.6. The OP, increased 1.5-fold and in the SP increased 1.4-fold (Table 2). As with Ca^{2+}, Mg^{2+} was leached primarily during the first twelve weeks, paralleling a decrease in NH_4^+ concentrations (Figures 3b and 3h). Part of the Mg2+, which was leached from the LF and H horizons was retained in the mineral horizons. The Mg^{2+} concentrations ranged roughly from 80 to 120 μmol (+) L^{-1} between the 5th and 18th weeks in the OP of columns treated at pH 2.9, whereas all of the concentrations were below 80 μmol (+) L^{-1} in the SP (Figure 3h). This Mg^{2+} retention was also recorded in columns treated with demineralized water.

In both the organic and spodic percolates, there was no significant difference between the treatments of mean concentrations of the monovalent K^+ and Na^+ cations (Figures 3c and 3j). Because of similarities with the NH_4^+ ion (valence, crystallographic radius, mobility; Bohn et al. 1979), K^+ concentrations in the organic and spodic percolates underwent the same type of changes observed in NH_4^+ concentrations. As with the latter cation at the onset of treatment, there was partial K^+ retention in the mineral horizons. The Na^+ concentrations, on the other hand, underwent different changes. The ion is more mobile than K^+ and NH_4^+ and was not retained in the mineral horizons. Sodium concentrations were higher in the SP (26 μmol (+) L^{-1}) than in the OP (13 μmol (+) L^{-1}).

It seems contradictory that K^+ was not more extensively leached by the more acidic solutions when we consider the mobility of potassium. As we shall see later, however, this is not the case since the greatest drop in concentrations following percolation of the input solutions, as compared to initial values, was recorded in exchangeable K. In an experiment involving the decomposition of *Picea abies* needles, Hovland et al. (1980) noted that K^+ was more mobile than Mg^{2+} and Ca^{2+}, but that the amount of K^+ leached paralleled the volume of the input solutions. They found, on the other hand, that Ca^{2+} and Mg^{2+} were more susceptible to an increase in acidity. In our experiment, the leaching of K^+ was favored by a large column of water as well as by the absence of roots. Rains and Bledsoe (1976) demonstrated that K^+ loss was halved when a brown podzol (mixed mesic Dystric Xeropsamment), sifted and reconstructed into a column, was covered with seedlings.

According to Cronan (1980), if the pH of rain decreases from 4.0 to 3.5 in an subalpine *Abies balsamea* stand, potentially negative effects on the nutrient status of K^+ will occur in less than 10 years. The author also reported that this effect could be considerably reduced by removal by the roots and mineral alterations.

Mn^{2+} and Al_t

Only in the percolates from columns treated at pH 2.9 was there a significant increase in mean Mn^{2+} concentrations (Tables 2 and 3; Figure 3i). Mean concentrations for treatments at pH 3.3, 4.3, and 5.6 ranged from 15 to 19 μmol (+) L^{-1} in the OP and from 1 to 3.5 μmol (+) L^{-1} in the SP, whereas under the influence of treatment at pH 2.9, they rose to 41 and 14 μmol (+) L^{-1}, respectively. In the OP, changes in $[Mn^{2+}]$ were similar to those encountered in $[H^+]$. Findings indicate that there was considerable manganese retention in the mineral horizons. Relatively high Mn^{2+} concentrations in the OP probably reflect manganese cycling by the organic material making up these horizons (James and Riha 1986). Of all the elements studied, relatively more Mn^{2+} was leached than any other element as a result of treatment at pH 2.9 as compared to the reference treatment. These findings agree with those of Skiba and Cresser (1986) which were obtained after leaching of the organic horizons of a *Picea sitchensis* stand. They differed, however, from the findings of James and Riha (1986) who observed that the addition of acid had little effect on the solubilization of manganese. In the latter, however, the organic horizons were in a state of equilibrium rather than leached.

Concentrations of Al_t in the OP were independent of treatment acidity. The concentrations were initially high (230 to 270 μmol (+) L^{-1}) but decreased as the amount of water added increased (Figure 3k). The rise in pH values of the percolates in the experiment conducted at pH 2.9 in no way influenced Al_t concentrations or mean treatment concentrations (Table 2). During an acidification experiment conducted on soil columns extracted from the same station, Hay et al. (1985) demonstrated that total organic C concentrations were higher at the beginning (120 mg L^{-1}), but thereafter decreased until the end of treatment (40 mg L^{-1}). Skiba and Cresser (1986) and Evans (1986) observed the positive correlation between total organic C and Al_t. These findings, along with our own observations on the changes in percolated color and in aluminum concentrations, clearly show that aluminum in the organic horizons migrates to the mineral horizons primarily in organic form.

In the SP, there was a strong linear relationship (Figure 5) between mean NO_3^- and Al_t concentrations for weeks 1 to 12. Subsequently, reduced nitrification (Figure 3f) was attended by a parallel decrease in $[Al_t]$ in the percolates from columns treated at pH 4.3 and 5.6. The $[Al_t]$, however, remained high in the more acidic percolates (Figures 3e and 3k) because of the pH and because the SO_4^{2-} was hardly absorbed any longer in the Bhf1 and

Bhf2 horizons. Leaching of Al in nitrate form was therefore gradually replaced by leaching of the sulfate form in columns treated with high H_2SO_4 concentrations (pH 2.9 and 3.3).

Solubility diagrams were constructed in order to determine the mineral phases regulating Al solubility in the mineral horizons (Figures 6, 7a, 7b, and 8). The activities calculated in each of the percolates were graphed with the solubility curves for natural and synthetic gibbsite, $Al(OH)_3$; jurbanite, $AlOHSO_4.5H_20$; and balsaluminite, $Al_4(SO_4)(OH)_{10}.5H_20$. Since all of the solutions were supersaturated in relation to alunite ($KAl_3(SO_4)_2(OH)_6$), the latter was not shown. The activity of Al^{3+} and SO_4^{2-} was calculated from Lindsay's chemical equilibrium equations (1979). The formation of complexes with F^- was considered negligible since total Al concentrations were very high compared to total F concentrations. Total aluminum measured by atomic adsorption (Al_t) was considered totally monomeric and inorganic. This may result in an overestimation of (Al^{3+}) and consequently an underestimation of the pK value for the solubility products (Freiesleben 1988). Some solutions may therefore appear supersaturated in relation to a given mineral, although this is not the case. Furthermore, as Manley et al. (1987) observed, the experimental procedures for determining the thermodynamic constants and the composition of water still lack the precision needed to develop quantitative equilibrium models for mineral-water interactions. McKeague (1979) stated that in order to understand the dynamics of pedogenesis, it was necessary to have solid data on solution volume and concentrations, speciation, and time-related changes in solutions percolating through the soil. Soils are typically in a state of disequilibrium. Equilibrium diagrams may act as a guide, and any interpretation should be considered semi-quantitative.

The thermodynamic constants used in this study as well as the corresponding references are shown in Table 5. Since the laboratory temperature was 15°C, a correction was made in pK values using van't Hoff's equation (Stumm and Morgan 1981), stipulating that the variation in the standard heat content for the reaction (ΔH°_r) is independent of temperature, i.e.,

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^o{}_r}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad [1]$$

where K_2 and K_1 represent equilibrium constant values at temperatures T_2 and T_1 and where R is the gas constant.

Time-related changes in $pAl(OH)_3$ are illustrated in Figure 6. The effect of the treatments was insignificant. Mean $pAl(OH)_3$ values ranged from 33.74 (treatment at pH 2.9) to 33.65 (treatment at pH 5.6) for the entire 24 weeks and from 33.47 to 33.39 for weeks 14 to 24. In the initial percolates, the solutions were generally undersaturated in relation to natural gibbsite (pK_s = 33.6 at 15°C), but seemed to enter into equilibrium with the gibbsite from the 5th week on. Beginning with the 12th week, supersaturation was recorded, indicating that a more unstable mineral regulated Al^{3+} activity.

The first 12 weeks corresponded to a period of very intense microbial activity that was reflected in the sudden rise in inorganic N concentrations. The soil solution was constantly modified by the addition of ions from decomposing organic matter and from partial equilibrium with the mineral phase. With the rapid increase in microbial activity, the soil

Table 5. Thermodynamic constants used in this study

Reaction	pK_s		$\Delta H°_r$	References
	25°C	15°C	cal mol^{-1}	
Hydroxide ligands				
$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$	4.99	5.37	14 775	a
$Al^{3+} + 2H_2O \rightarrow Al(OH)_2^+ + 2H^+$	10.13	10.51		a
Sulfate ligand				
$Al^{3+} + SO_4^{2-} \rightarrow AlSO_4^+$	-3.20	-3.14	2 290	a
Gibbsite				
$Al(HO)_3(s) \rightarrow Al^{3+} + 3OH^-$				
natural	33.23	33.60	14 470	a
synthetic	33.89	34.27		a
Jurbanite				
$AlOHSO_4 \rightarrow Al^{3+} + SO_4^{2-} + OH^-$	17.23	17.03	-7 698	b,c
	17.80	17.60		c,d
Basaluminite (crystalline form)				
$Al_4 (SO_4) (OH)_{10} \rightarrow 4AL^{3+} + SO_4^{2-} + 10(OH)^-$	117.7	118.6f		e

a Nordstrom et al. (1984); b van Breemen (1973); c Freiesleben (1988); d Nordstrom (1982); e Adams and Rawajfih (1977); f Nothing was found in the literature concerning the standard entholpie of basaluminite. The pK_S value at 15°C may be estimated, however, by adding 0.9 to 117.7 (0.9 = 3* (33.60 - 33.23) + (17.03 - 17.23)).

solution could not enter into equilibrium with the mineral phase. This became possible only when the activity had significantly abated. If $pK_s = 33.6$ (at 15°C) represented the true state of equilibrium of the soil type studied, determination of Al^{3+} using the equation (Lindsay 1979)

$$(Al^{3+}) = 10^{(8.4\ -\ 3pH)} \qquad [2]$$

obviously resulted in a serious overestimation of (Al^{3+}) during the period when microbial activity rapidly increased.

In the equilibrium diagrams 7a and 7b, pAl + 3pOH is represented as a function of 2pH + pSO_4 (van Breemen 1973; Freiesleben 1988) for both the least acidic (pH 4.3 and 5.6) and most acidic (pH 2.9 and 3.3) treatments. The points on the upper part of these graphs were obtained in the percolates in the early stages of treatment (undersaturation in relation to natural gibbsite), whereas the points in the lower left hand side of Figure 7a resulted from an increase in SO_4^{2-} concentrations following initial retention in the mineral horizons.

Unlike van Breemen (1973), Freiesleben (1988), and Courchesne (1988), we were unable in this experiment to produce a significant alignment of the points on one or the other of the equilibrium curves because there was an insufficient range of pH and SO_4 concentration values. In the experiment conducted by Courchesne (1988), however, the solutions seemed to stabilize on the jurbanite curve ($pK_s = 17.8$) only after a relatively longer extraction period (24 hours instead of 5 minutes or 6 hours). Similarly, our results also indicated a tendency toward stabilization (which was not necessarily a state of equilibrium), but over a much longer period of time because of the processes triggered by microbial decomposition. Mean $pALOHSO_4$ values for weeks 14 to 24 (Figure 8) were 17.01 ± 0.10, 17.32 ± 0.09, 17.68 ± 0.06, and 17.80 ± 0.09, respectively, for treatments at pH 2.9 to pH 5.6. In van Breemen's (1973) study, Al^{3+} and SO_4^{2-} activity seemed to be regulated by jurbanite ($pK_s = 17.03$ at 15°C) in the solutions from the most acidic treatments, whereas in the experiment conducted by Nordstrom, regulation by jurbanite ($pK_s = 17.60$ at 15°C) occurred in the solutions from the least acidic treatments. These findings suggest that increasingly unstable minerals, in this case jurbanite and basalumite, may be precipitated out.

Coefficients of linear correlation

Table 6 contains the coefficients of linear correlation between the ion concentrations in the organic and spodic percolates. In the OP, the positive correlation of SO_4^{2-} with H^+ and NH_4^+ and the negative correlation of SO_4^{2-} with NO_3^- indicated the inhibitory effect of added H_2SO_4 on nitrification. In the spodic percolates, these correlations were not significant, suggesting that treatments had little effect on the mineralization and oxidation of the N containing molecules in the mineral horizons.

The correlations SO_4^{2-} - Mg^{2+} and SO_4^{2-} - Mn^{2+} were similar in the organic and spodic percolates, whereas the SO_4^{2-} - Ca^{2+} correlation was 0.62 in the OP and only 0.09 ($p > 0.05$) in the SP. The strongest anion correlation in the SP was NO_3^- - Al_t ($r = 0.83$), which illustrates the effect of internal nitric acid production on Al dissolution. That the SO_4^{2-} - Al_t correlation was weaker in the SP ($r = 0.45$) was probably because of interactions between nitrification and the adsorption of SO_4^{2-}. There was no anion - Al_t correlation in the OP.

The SO_4^{2-} - K^+ correlation were not significant, whereas the NO_3^- - K^+ correlations were significant in both the OP ($r = 0.55$) and the SP ($r = 0.71$). These correlation indicated that NO_3^- would be more effective in leaching K^+, since the monovalent charge of each might favor their association. This was also observed in the case of NH_4^+ and K^+ which displayed strong correlations in both types of percolates (OP: $r = 0.86$; SP: $r = 0.74$), which suggests that these two monovalent cations shared certain characteristics with respect to their electric bonds with anions (Hakamata 1983). Only in the OP were K^+ - Na^+ and NH_4^+ - Na^+ correlations included in this category since the r values were 0.76 and 0.70, respectively.

Strong correlations between bivalent metal cation concentrations were recorded only in the OP. The correlations Ca^{2+} - Mg^{2+}, Ca^{2+} - Mn^{2+}, and Mg^{2+} - Mn^{2+} were 0.81, 0.88, and 0.74, respectively, in the OP. In the SP, these correlations were (in the same order): 0.02, 0.33, and 0.37. These differences suggest that the processes involved in the alteration, leaching, and retention of bivalent cations are specific, depending on the type of horizon.

Soil analyses

Exchangeable bases

Ca^{2+}, Mg^{2+}, and K^+ losses from the LF and H horizons, on the one hand, and from the Ae, Bhf1, and Bhf2 horizons, on the other, as a result of leaching were compared with treatment-induced changes in the exchangeable fraction (Tables 7, 8, and 9). Leaching from the mineral horizons was estimated from the difference between the respective concentrations in the organic and spodic percolates.

In comparison to initial values, all of the treatments resulted in a significant increase in exchangeable Ca in the H horizon (Table 10), whereas there was a significant drop in the LF horizon for treatments at pH 3.3 and pH 2.9. Because of exchangeable Ca losses in the LF horizon, the total exchangeable Ca gain for all of the organic horizons gradually decreased as the treatment pH rose (from 2.92 to -0.07 cmol $(+)kg^{-1}$) (Table 7). The total amount of Ca produced by mineralization of organic matter (leached Ca + gain in exchangeable Ca) in the

Table 6. Pearson coefficents of linear correlation between ion concentrations in the organic percolates (1) and spodic percolates (2)

	H^+	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Mn^{2+}	Al_t
SO_4^{2-}	(1) 0.62	-0.33	0.39	0.62	0.34	0.11	0.00	0.53	-0.08
	(2)-0.11	0.10	-0.06	0.09	0.38	0.02	-0.27	0.64	0.45
H^+		-0.24	-0.22	0.81	0.64	-0.37	0.48	0.83	-0.51
		0.30	0.17	0.57	0.57	0.02	0.26	0.04	0.18
NO_3^-			0.25	-0.13	0.22	0.55	0.24	-0.20	0.07
			0.37	0.34	-0.03	0.71	-0.33	0.19	0.83
NH_4^+ -				0.16	-0.27	0.86	0.70	-0.34	0.51
				0.36	-0.19	0.74	-0.13	0.07	0.12
Ca^{2+}					0.81	-0.26	-0.39	0.88	0.45
					0.02	0.35	0.15	0.33	0.21
Mg^{2+}						-0.16	-0.33	0.74	-0.46
						-0.15	0.16	0.37	0.06
K^+							0.76	-0.46	0.55
							-0.25	0.19	0.55
Na^+								-0.56	0.62
								-0.03	-0.45
Mn^{2+}									-0.57
									0.33

$r_{(203)}[0.05] = 0.137$
$r_{(203)}[0.01] = 0.180$
$r_{(203)}[0.001] = 0.231$

LF and H horizons was 7.28, 7.19, 6.97, and 9.03 cmol (+) kg^{-1} for treatments at pH 5.6 to pH 2.9. "Mineralization" is used in the broad sense and includes the destruction of plant and microbial cells (Yavitt and Fahey 1984). In the same order as above, losses due to leaching were equal to 60, 69, 78, and 101 percent of the Ca produced by mineralization. In other words, the chances of achieving a balance between exchangeable Ca loss in the LF horizon and exchangeable Ca gain in the H horizon were enhanced with increased treatment acidity. In the Ae, Bhf1, and Bhf2 horizons, the amount of Ca leached was lower than the loss of the exchangeable fraction. This resulted in a negative value for weathering (this process was considered negligible in the organic horizons because of the low mineral content) and mineralization, which suggests reverse processes, i.e., precipitation of a calcium salt and metabolic absorption. Precipitation of $CaSO_4$ in the horizons treated at pH 2.9 may have been one of the causes of reduced weathering (-0.05 + 0.005 cmol (+) kg^{-1}) compared to the other treatments.

All of the treatments caused a significant reduction in exchangeable Mg levels in the LF, Bhf1 and Bhf2 horizons as compared to initial values (Table 11), whereas in the H horizon, the concentrations were slightly higher for the treatments at pH 3.3 to pH 5.6 and slightly lower for the treatment at pH 2.9. As in the case of the percolates, differences between treatments became apparent in the organic horizons at pH 2.9 only. Losses due to leaching in the organic horizons (from 0.97 to 1.44 cmol (+) kg^{-1}) (Table 8) were partially compensated by losses in the exchangeable fraction (0.25 to 0.56 cmol (+) kg^{-1}). Thus, 66 percent of the excess Mg leached in the treatment at pH 2.9, as compared to the treatment at pH 5.6, is thought to have come from the exchange sites. Mineralization accounted for the remainder. A similar proportion, i.e., 63 percent, was recorded for Ca. The limited leaching of Ca and Mg in the H horizon may be related to storage of these elements in rhizomorphic fungal tissue (Yavitt and Fahey 1984). In the mineral horizons, the mechanisms involved in the precipitation and absorption of Mg seemed to be the same as for Ca.

Similar to $[K^+]$ in the percolates, there was little variation in exchangeable potassium levels between treatments, but a considerable drop was recorded in relation to initial values (Table 12) in the organic horizons, whereas there was only a slight decrease in the Ae and Bhf1 mineral horizons attended by a slight increase in the Bhf2 horizon. Losses in exchangeable K in the organic horizons ranged from 62 to 74 percent of leaching losses (Table 9) whereas for Mg, these percentage ratios were 26 to 39 percent. With the exception of the treatment at pH 4.3, which resulted in similar leached and exchangeable K losses from the mineral horizons, potassium leached from the organic horizons was generally retained in the mineral horizons ($[K^+]_{sp} - [K^+]_{op} < 0$). This retention was not compensated by an increase in the exchangeable fraction. Exchangeable sodium levels were not determined. There is reason to believe, however, that sodium behaves like K (absence of any treatment-induced effect on $[Na^+]$ in the percolates) and that, like potassium, it does not undergo any significant changes on the exchange sites following acidification (Lee 1985).

Leaching losses in the OP from columns treated with demineralized water represented 84, 49, and 25 percent of the initial exchangeable K, Mg, and Ca fractions, respectively (Table 13). These values rose to 95, 72, and 52 percent under the influence of treatment at pH 2.9. Whereas the exchangeable Ca in the LF and H horizons increased by 17 percent in the reference treatment, exchangeable Mg levels decreased by 13 percent and exchangeable K levels, by 59 percent. Treatment at pH 2.9 did not modify the initial exchangeable Ca level,

Table 7. Leached and exchanged calcium concentrations after 24 weeks of treatment (cmol (+) kg^{-1})

	pH of the treatments			
	5.6	4.3	3.3	2.9
LF and H Horizons				
- loss through leaching	4.36	4.97	5.43	9.10
- loss (-) or gain (+) in the exchangeable fraction	+2.92	+2.22	+1.54	-0.07
- mineralization	7.28	7.19	6.97	9.03
Ae, Bhf1, and Bhf2 Horizons				
- loss through leaching	0.16	0.14	0.14	0.05
- loss (-) or gain (+) in the exchangeable fraction	-0.42	-0.40	-0.40	-0.36
- weathering and mineralization	-0.26	-0.26	-0.26	-0.31

Table 8. Leached and exchanged magnesium concentrations after 24 weeks of treatment (cmol (+) kg^{-1})

	pH of the treatments			
	5.6	4.3	3.3	2.9
LF and H Horizons				
- loss through leaching	0.97	1.08	1.04	1.44
- loss (-) or gain (+) in the exchangeable fraction	-0.25	-0.34	-0.30	-0.56
- mineralization	0.72	0.74	0.74	0.88
Ae, Bhf1, and Bhf2 Horizons				
- loss through leaching	-0.008	-0.013	-0.009	-0.015
- loss (-) or gain (+) in the exchangeable fraction	-0.018	-0.016	-0.018	-0.020
- weathering and mineralization	-0.026	-0.029	-0.027	-0.035

Table 9. Leached and exchanged potassium concentrations after 24 weeks of treatment (cmol (+) kg^{-1})

	pH of the treatments			
	5.6	4.3	3.3	2.9
LF and H Horizons				
- loss through leaching	1.40	1.31	1.42	1.58
- loss (-) or gain (+) in the exchangeable fraction	-0.98	-0.97	-1.00	-0.98
- mineralization	0.42	0.34	0.42	0.60
Ae, Bhf1, and Bhf2 Horizons				
- loss through leaching	-0.005	0.002	-0.008	-0.008
- loss (-) or gain (+) in the exchangeable fraction	-0.007	-0.002	-0.009	-0.007
- weathering and mineralization	-0.012	0.000	-0.017	-0.015

Table 10. Exchangeable calcium (cmol (+) kg^{-1}) before and after treatment

		pH of the treatments			
Horizon	Initial values	5.6	4.3	3.3	2.9
LF	24.50	24.0a	24.2a	21.1ab	19.9b
H	10.50	16.8a	15.2a	16.9a	14.9a
Ae	0.3	10.29a	0.28a	0.28a	0.35a
Bhf1	1.44	0.50a	0.51a	0.51a	0.53a
Bhf2	0.69	0.25b	0.28b	0.28b	0.32a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

Table 11. Exchangeable magnesium (cmol (+) kg^{-1}) before and after treatment

Horizon	Initial values	pH of the treatments 5.6	4.3	3.3	2.9
LF	2.58	1.84a	1.73a	1.84a	1.54a
H	1.40	1.63a	1.56a	1.54a	1.31b
Ae	0.06	0.06a	0.06a	0.06a	0.06a
Bhf1	0.13a	0.11ab	0.12a	0.11ab	0.10b
Bhf2	0.07	0.04a	0.04a	0.04a	0.04a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

Table 12. Exchangeable potassium (cmol (+) kg^{-1}) before and after treatment

Horizon	Initial values	pH of the treatments 5.6	4.3	3.3	2.9
LF	2.12	0.71a	0.74a	0.71a	0.69a
H	1.20	0.64a	0.64a	0.61a	0.66b
Ae	0.06	0.04a	0.04a	0.04a	0.04a
Bhf1	0.09	0.08ab	0.08a	0.09ab	0.08b
Bhf2	0.03	0.05a	0.04a	0.05a	0.05a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

but resulted in a 28 percent loss of exchangeable Mg. The losses of exchangeable K were the same as those recorded at pH 5.6.

Losses due to leaching and exchangeable base losses in the organic horizons treated with demineralized water were directly related to the mobility of the cations (K > Mg > Ca) and inversely related to the saturation of the exchangeable fraction (K < Mg < Ca). This order of mobility is consistent with the organic exchange surfaces (Brown 1987). Similar findings were obtained with cations leached from *Picea abies* needles treated with H_2SO_4 (Hovland et al. 1980). Additional acidification as a result of treatment seemed to be the most effective in leaching Ca, followed by Mg, then K, i.e., the order of the proportions on the exchange sites, as observed by Haynes and Swift (1986) in their acidification experiment. In the mineral horizons, exchangeable fraction losses occurred in the reverse order, i.e., losses of 14, 23, and 58 percent of exchangeable K, Mg, and Ca, respectively, following treatment with demineralized water. These losses were little influenced by the more acidic treatments.

The absence of roots, disturbance during reconstruction of the horizons, high temperatures, acceleration of mineralization with resulting nitrification, and percolation of a large column of water all contributed to substantially increasing the amount of bases leached. This reduced the differences between treatment-induced effects, especially in the case of K^+, which was so easily leached from organic horizons treated only with demineralized water that the most acidic treatment had virtually no effect. Brown (1985, 1987) also recorded the same finding in monoliths containing humic podzol horizons as compared to *in situ* specimens. In this instance, the total K concentration was decreased by 66 percent in both the reference and acid treatments.

pH, base saturation, extractible P, and Total N

Comparison between pH values before and after treatment revealed significant acidification, but between the treatments themselves, there were no significant differences (Table 14) except in the case of the H and Ae horizons in which the less acidic treatments tended to cause a slight drop in pH. Thacker et al. (1987) did not observe any differences in pH values between the treatment at pH 3.5 and the treatment at pH 5.7 in horizon samples taken from the same station and treated in the laboratory. In their study, unlike ours, the pH of the initial soils was not altered by leaching (except for their most acidic treatment at pH 2.0). It should be mentioned that Thacker et al. (1987) added 10 000 mm of water, i.e., six times the total amount of water used in our experiment. While non-significant at the statistical level, the pH gradient in the spodic horizons revealed a tendency toward increased acidity with the more acidic treatments. There was a correlation between this increase and pH levels and total Al concentrations in the SP (Figures 3e and 3K).

Table 13. Leached and exchanged base concentrations after 24 weeks of treatment (cmol (+) kg^{-1})

		Initial values	Exchangeable fraction: loss (-) or gain (+)		Leached fraction	
			pH 5.6	pH 2.9	pH 5.6	pH 2.9
K	o.h.*	1.66 (100)***	-0.98 (-59)	-0.98 (-59)	1.40 (84)	1.58 (95)
	m.h.**	0.050(100)	-0.007(-14)	-0.007(-14)	-0.005(-10)	-0.008(-16)[t]
Mg	o.h.	1.99 (100)	-0.25 (-13)	-0.56 (-28)	0.97 (49)	1.44 (72)
	m.h.	0.080(100)	-0.018(-23)	-0.020(-25)	-0.008(-10)	-0.015(-19)
Ca	o.h.	17.5 (100)	+2.92 (17)	-0.07 (<1)	4.36 (25)	9.10 (52)
	m.h.	0.72 (100)	-0.42 (-58)	-0.36 (-50)	0.16 (22)	0.05 (7)

* organic horizons.

** mineral horizons.

*** percentage value in relation to the initial exchangeable fraction.

[t] a negative leached fraction indicates that the concentration in the spodic percolates is lower than in the organic percolates.

Table 14. pH (H_2O) of the horizons before and after treatment

Horizon	Initial values	pH of the treatments: 5.6	4.3	3.3	2.9
LF	4.30	3.60a	3.63a	3.57a	3.60a
H	3.70	3.56ab	3.53b	3.57a	3.57a
Ae	4.20	3.89b	3.90b	3.92ab	3.96a
Bhf1	4.20	4.00a	3.98a	3.93a	3.91a
Bhf2	4.70	4.38a	4.37a	4.26a	4.23a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

Due to the preponderance of exchangeable Ca, base saturation paralleled exchangeable Ca levels. This meant both a significant difference between treatments in the LF horizon only (Table 15) and an increase in base saturation in the H horizon with a drop in the Bhf1 and Bhf2 horizons when pre- and post-treatment values were compared. Thacker et al. (1987) also observed that base saturation was higher in untreated soils in the LF layer and underwent a greater decrease in absolute terms under the influence of the most acidic treatment.

Compared to the treatment at pH 5.6, the treatment at pH 2.9 resulted in a virtual 100 percent increase in extractible P obtained by the Truog method in the LF horizon (Table 16). The increase was also significant, although less so, in the H horizon. The treatments did not have any effect on extractible P in the mineral horizons. Compared to initial levels, the treated H and Ae horizons underwent the greatest change, with approximate increases of 200 and 300 percent, respectively. Organic and mineral P transport following leaching of the organic layers may account for this accumulation.

CONCLUSIONS

The findings of this acidification study may be summarized as follows:

Organic percolates and horizons

- Non-retention of SO_4^{2-};
- Consumption of over 80 percent of added H^+ following percolation in the LF and H horizons;
- Dominant buffer processes: ammonification and ion exchange with exchangeable Ca;
- Acid treatments at pH 2.9 and 3.3 partially inhibited nitrification, but produced no changes in net mineralization;
- Treatments at pH values of 3.3 and 2.9 increased the amount of Ca^{2+} leached, but only treatment at pH 2.9 increase Mg^{2+} leaching. The amount of K^+ leached was not increased by the acid treatments.
- Differences between treatments with regard to exchangeable base losses occurred in the LF horizon only (and in the H horizon in the case of exchangeable Mg). The same pattern of differences was observed as in the percolates;

Table 15. Base saturation (%) before and after treatment

		pH of the treatments			
Horizon	Initial values	5.6	4.3	3.3	2.9
LF	23.7	19.8a	20.8a	17.4b	16.5b
H	11.7	14.5a	13.6a	14.7a	13.0a
Ae	10.8	8.7a	8.8a	7.9a	10.2a
Bhf1	3.0	1.1a	1.1a	1.1a	1.2a
Bhf2	1.6	0.8b	0.8ab	0.8ab	0.9a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

Table 16. Extractible phosphorus (mg 100 g^{-1}) before and after treatment

		pH of the treatments			
Horizon	Initial values	5.6	4.3	3.3	2.9
LF	15.1	15.9b	15.4b	19.7b	27.2a
H	8.0	14.9b	13.5ab	16.6a	16.2a
Ae	0.45	1.26a	1.21a	1.44a	1.64a
Bhf1	0.20	0.30a	0.25a	0.22a	0.25a
Bhf2	0.10	0.10a	0.09a	0.04a	0.08a

There is no statistical difference between the mean values in each horizon that are followed by the same letter ($p < 0.05$).

- Percolation of acidified or demineralized water increased the amount of exchangeable Ca in the H horizon, but this increase was nullified for treatment at pH 2.9;

- Compared to initial exchangeable values, the greatest losses due to leaching and exchangeable fraction losses after percolation of non-acidified demineralized water were recorded in the following order: K > Mg > Ca, i.e., the opposite of initial concentrations on the exchange sites. The order was reversed when the reference treatment was compared with the most acidic treatment;

- After 24 weeks of treatment under the conditions of this experiment (input of 1 500 mm), mineralization within the LF and H horizons constitued the most important source of soluble Ca and Mg in the percolates, irrespective of treatment. Ion exchange was the main source of K lost in the leachates;

- Since K proved highly susceptible to intense leaching following the addition of a substantial amount of water which percolated through the LF and H horizons and since there was no removal of K by plant roots, it was not possible to measure the real effect of acidification on this element. As a result, in order to determine the effect of acidification on K leaching, testing must be done on minimally disturbed soil with a root system. This calls for *in situ* experiments. We advise against the use of monoliths. In planned laboratory experiments, seedlings or young trees should be used, but it must be realized that these conditions may be far from those encountered in the field. All of these considerations on the status of K suggest that regulation of this element is determined far more by the water circulation system than by the quality of the water;

- $H_2PO_4^-$ concentrations in the percolates were independent of treatment. Acidification resulted in an increase in extractible P obtained with 0.002 *N* H_2SO_4.

Spodic percolates and horizons

- There was a 50 percent retention of SO_4^{2-}. Between the 18th and 20th weeks of treatment (input of 1 100 to 1 200 mm of water), concentrations in the percolates from columns treated at pH 2.9 and 3.3 were above those occurring in the output solutions.

- Nitrification was high and occurred independently of treatment;

- The most important buffer process involved the dissolution of Al containing minerals. Higher concentrations of Al were recovered at the end of treatment and this was related to the pH gradient of the percolates. Low basic saturation accounted for the preponderence of this buffer process;

- On the basis of the equilibrium diagrams, gibbsite, jurbanite, and basaluminite may have been precipitated out. Increasing mineralization during the first half of the experiment was a contributing factor in slowing the tendency toward a more stable zone.

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APPENDIX

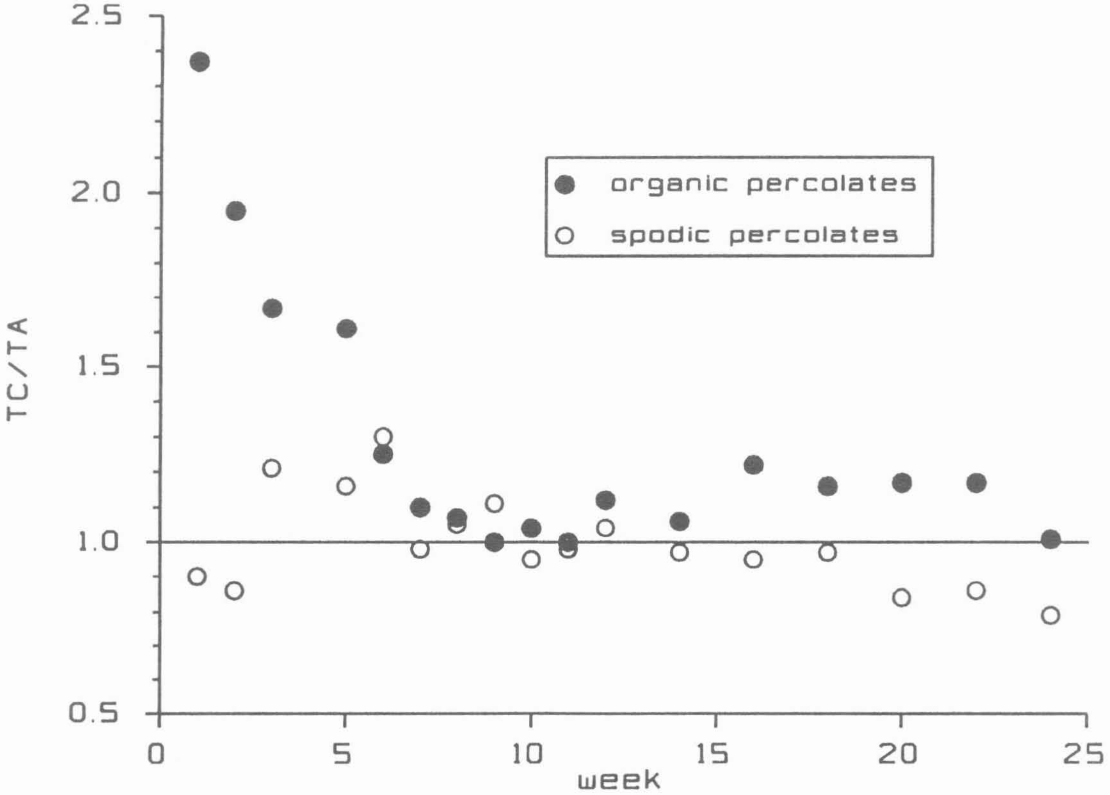

Figure 1. Total cation (TC)/total anion (TA) ratio in the organic and spodic percolates.

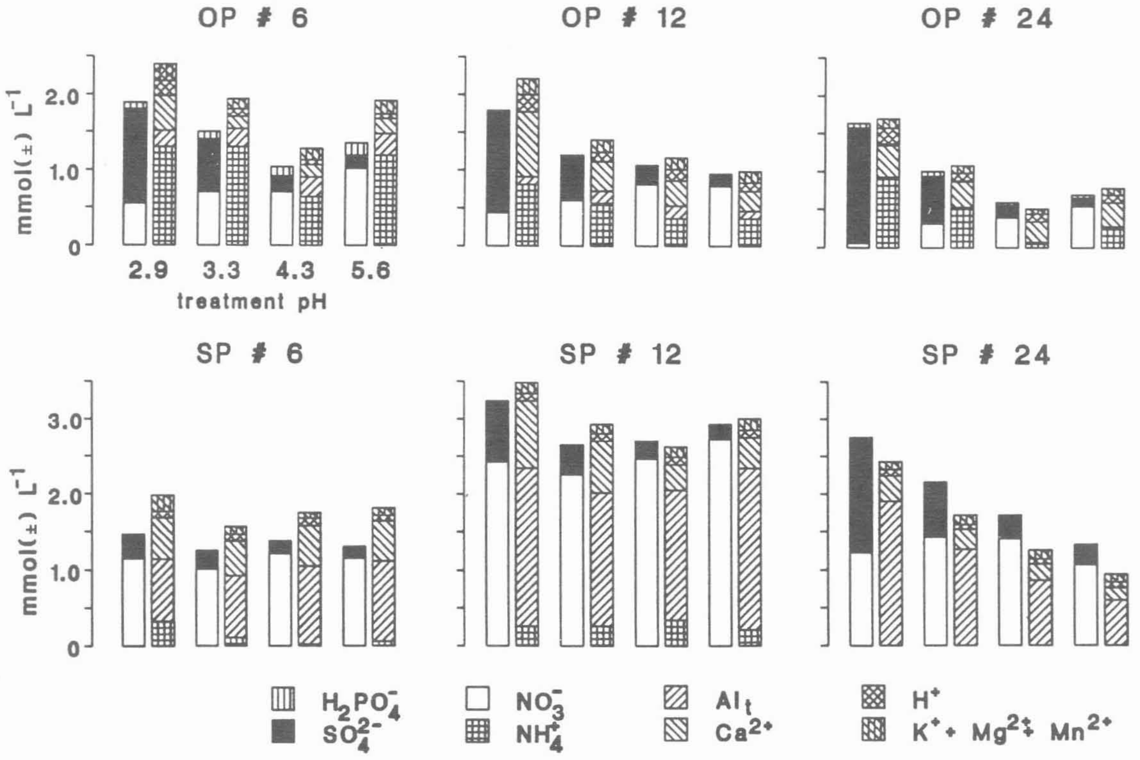

Figure 2. Ion concentrations in the organic (OP) and spodic percolates (SP) collected after 6, 12, and 24 weeks of treatment.

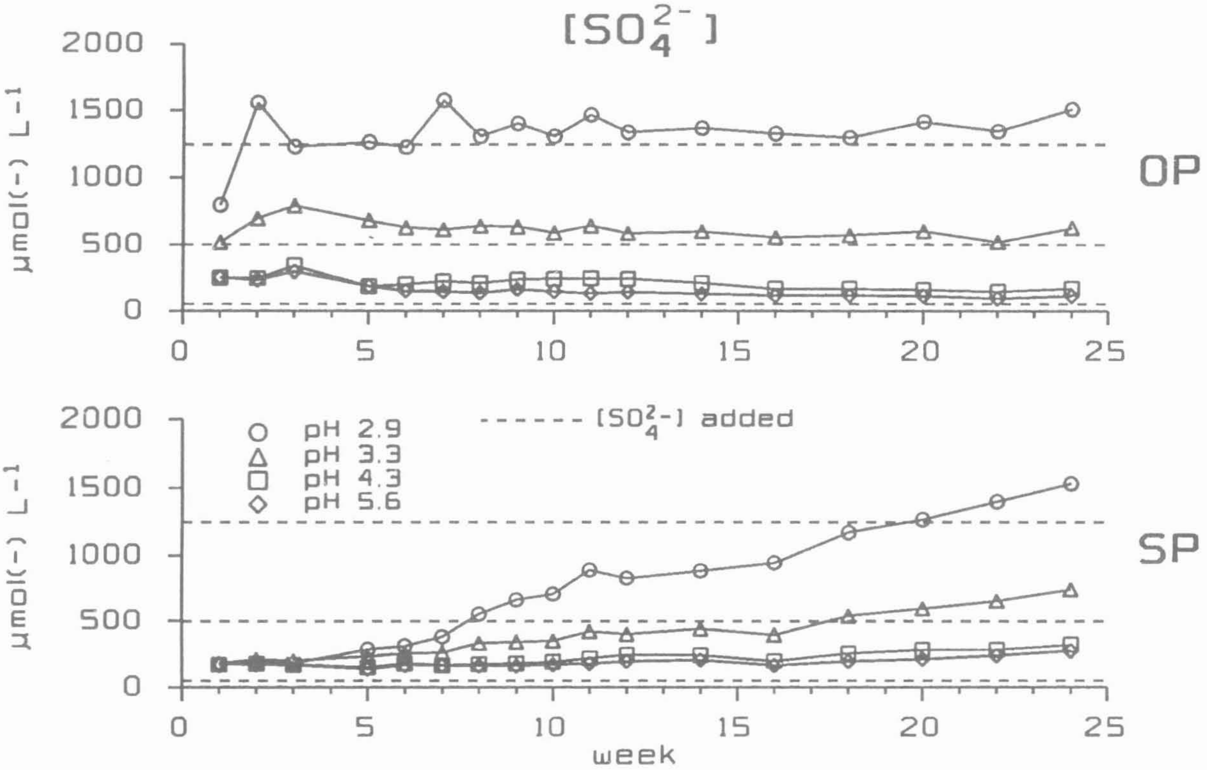

Figure 3a [SO$_4^{2-}$]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

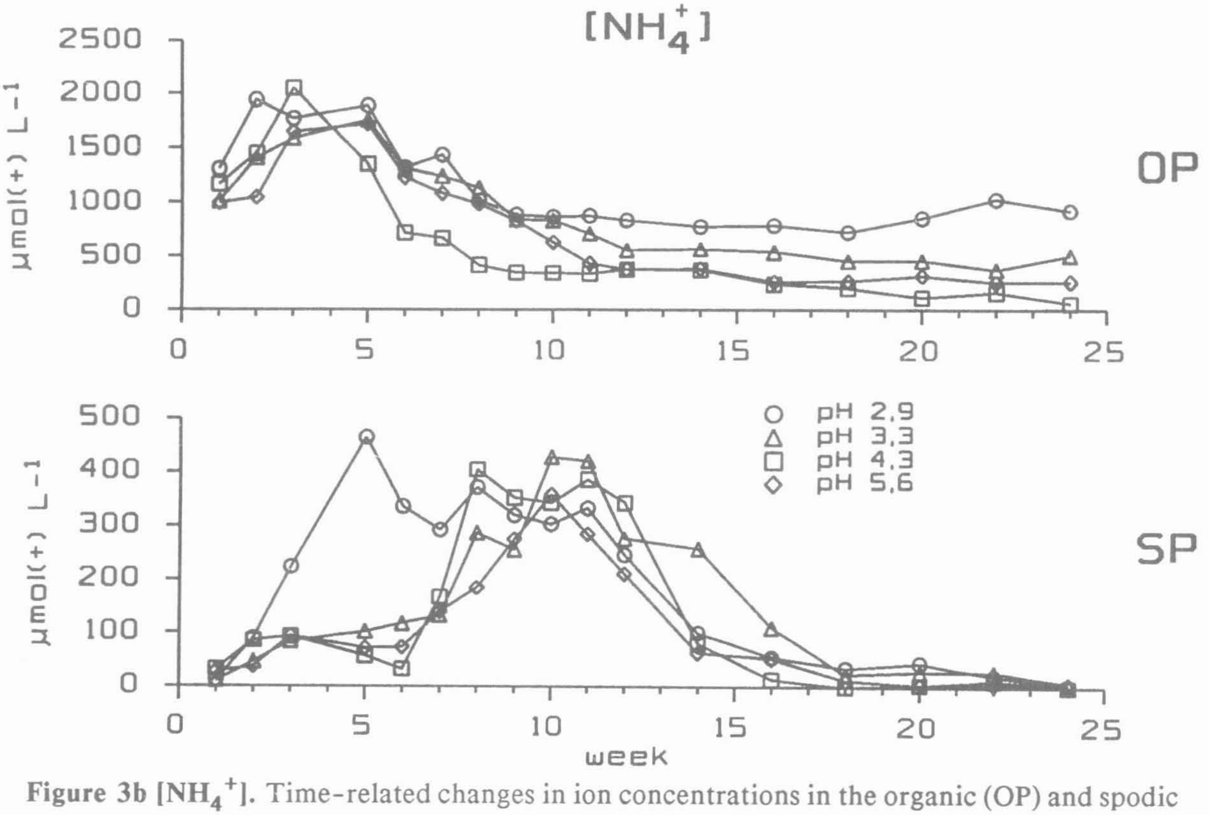

Figure 3b [NH$_4^+$]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

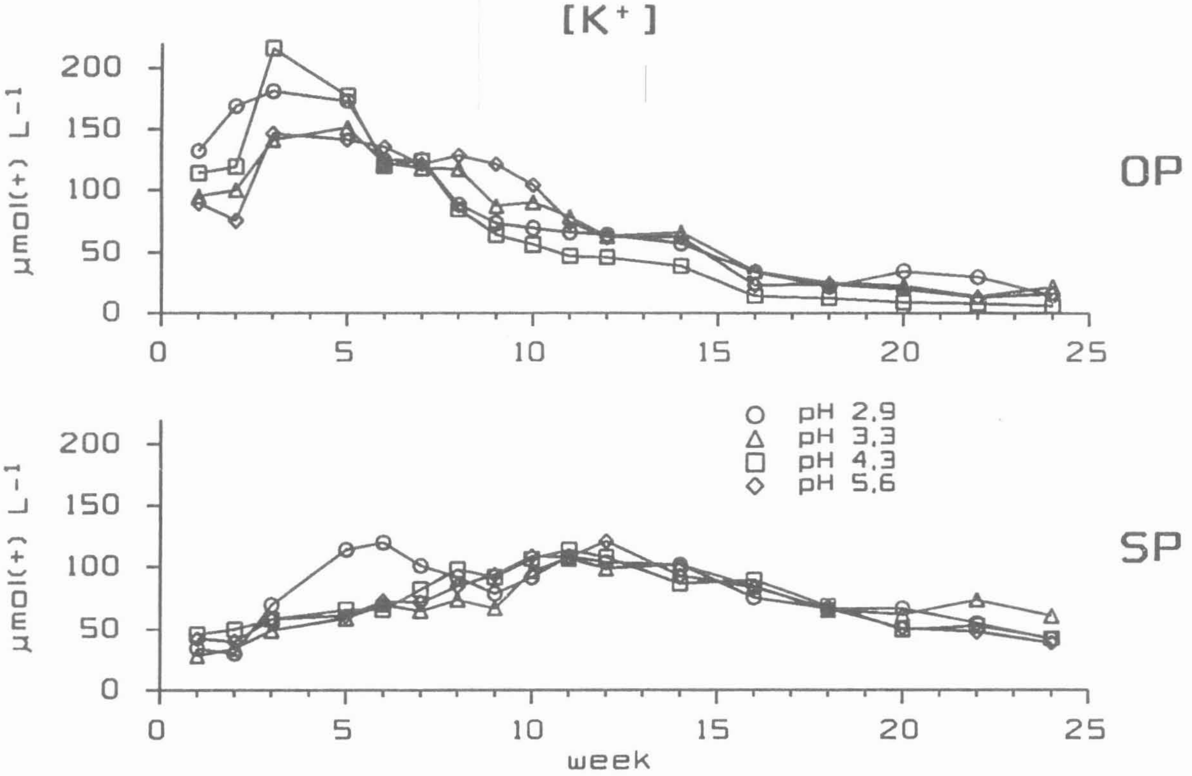

Figure 3c $[K^+]$. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

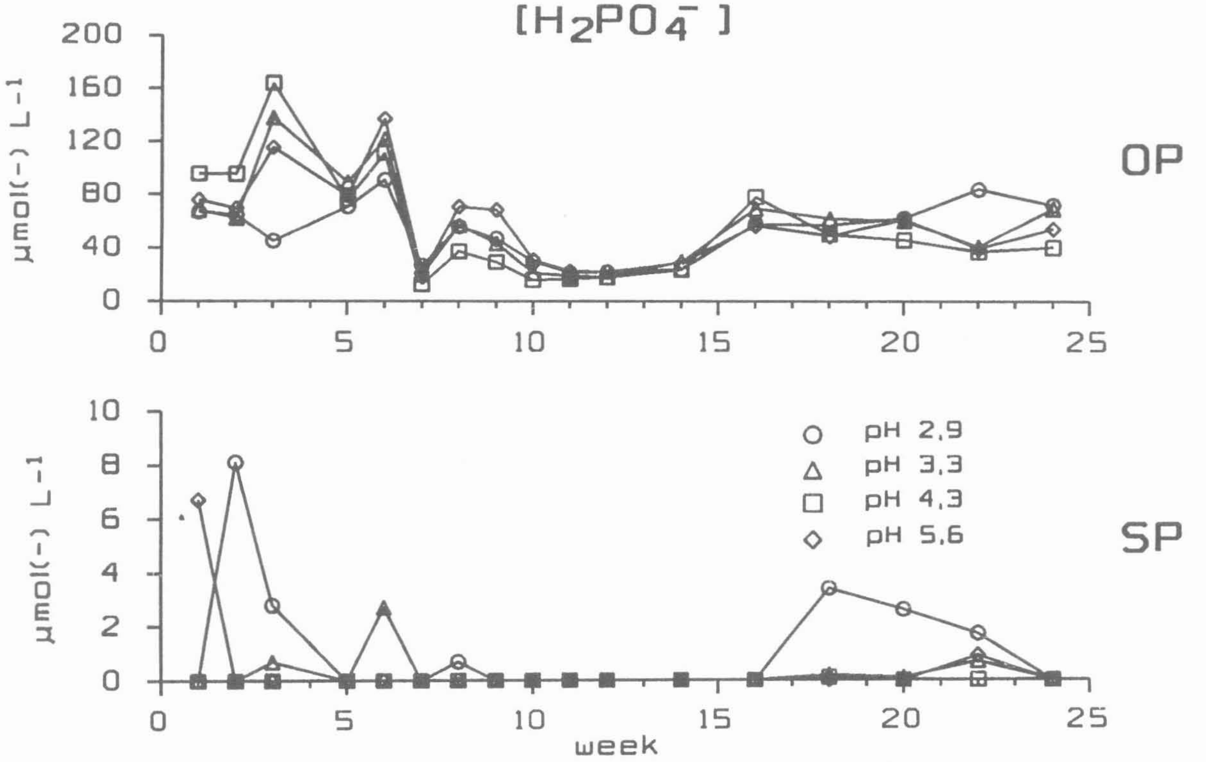

Figure 3d $[H_2PO_4^-]$. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

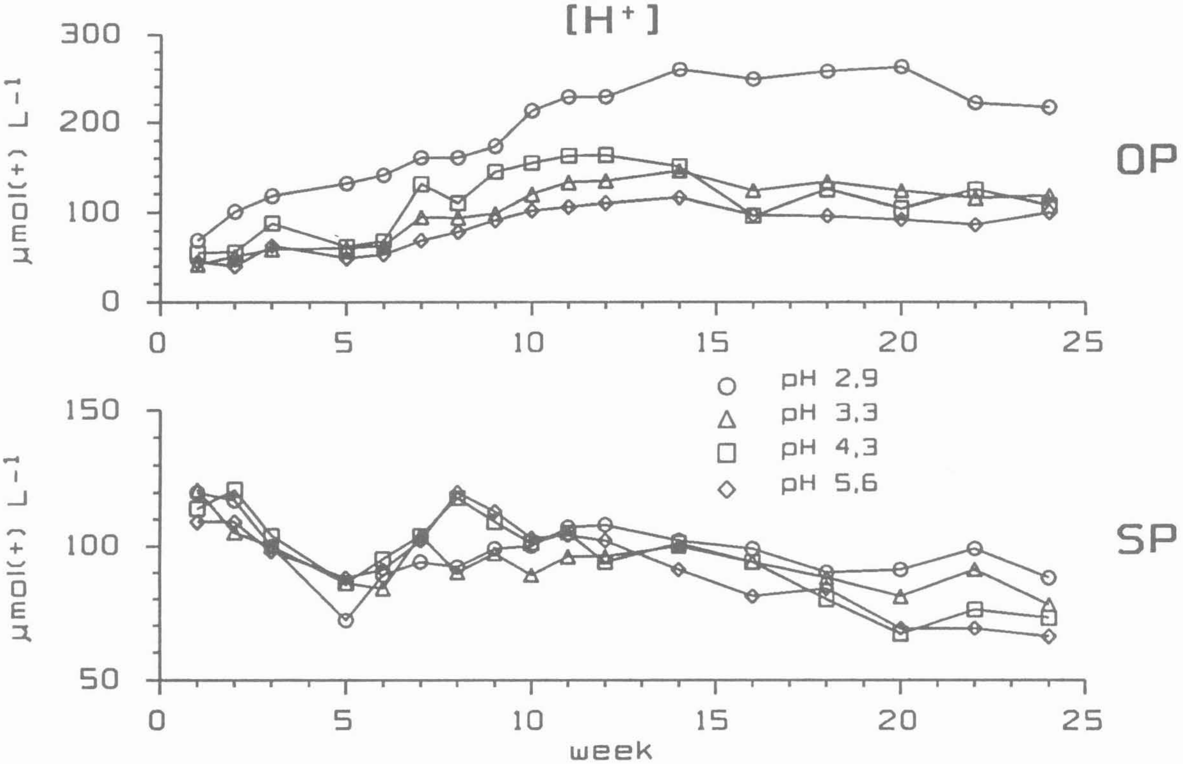

Figure 3e [H$^+$]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

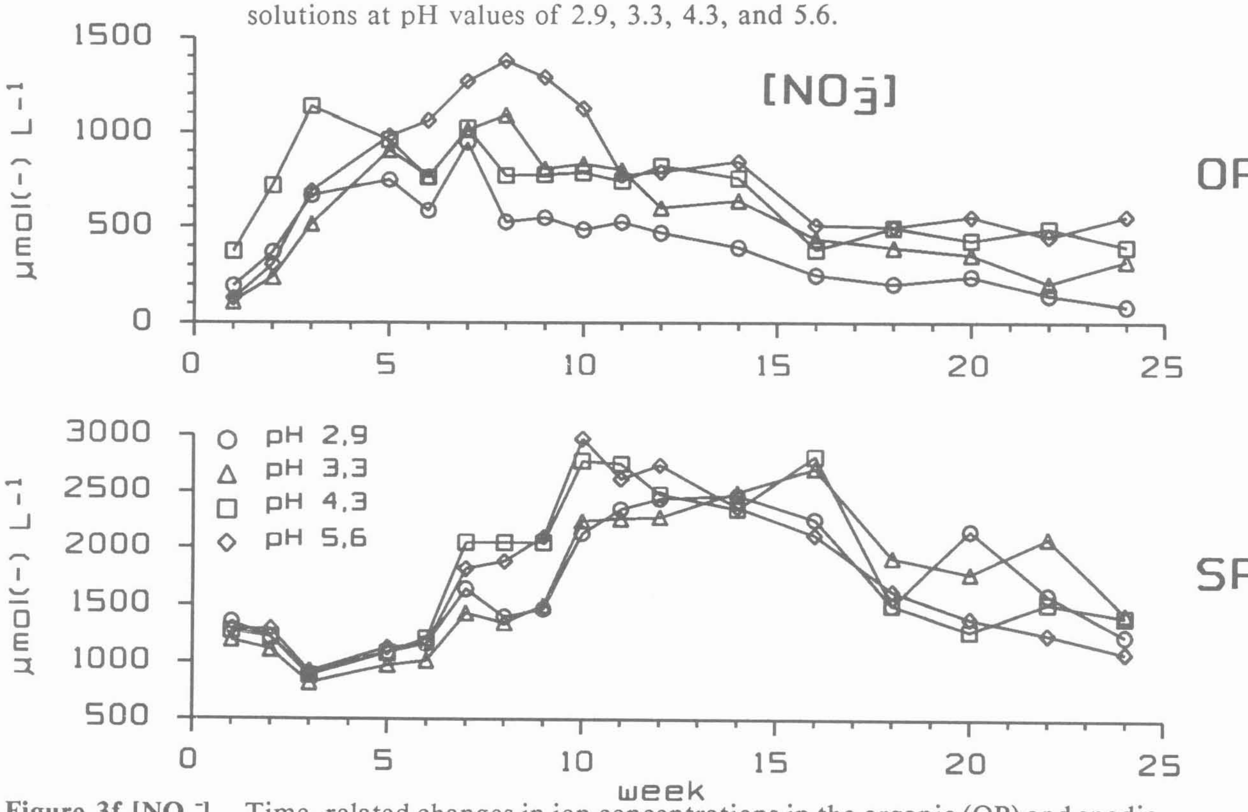

Figure 3f [NO$_3^-$]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

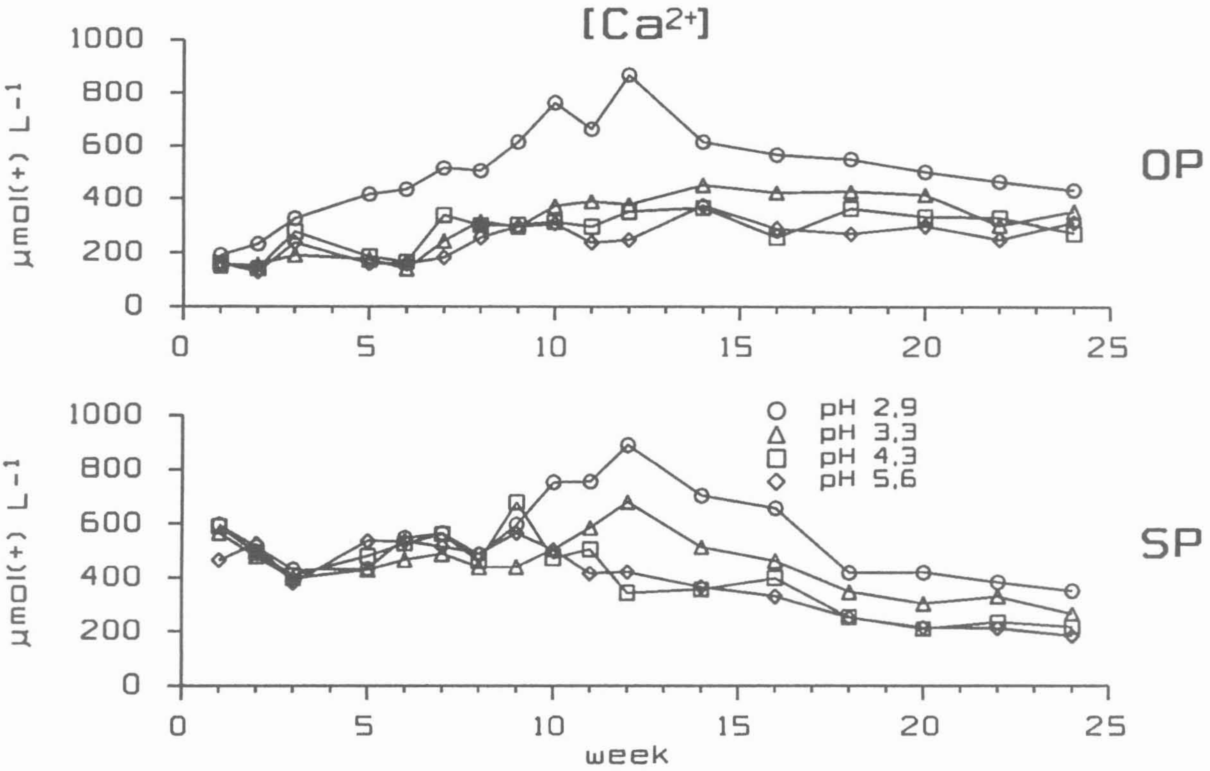

Figure 3g [Ca^{2+}]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

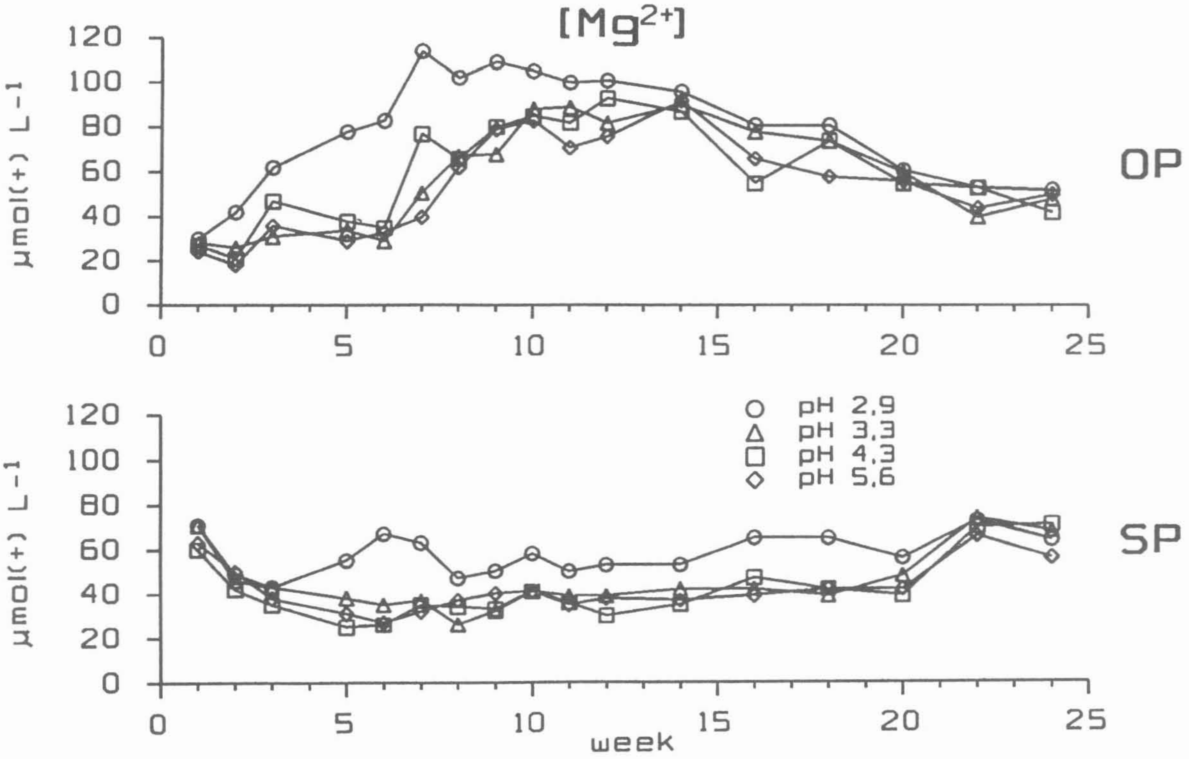

Figure 3h [Mg^{2+}]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

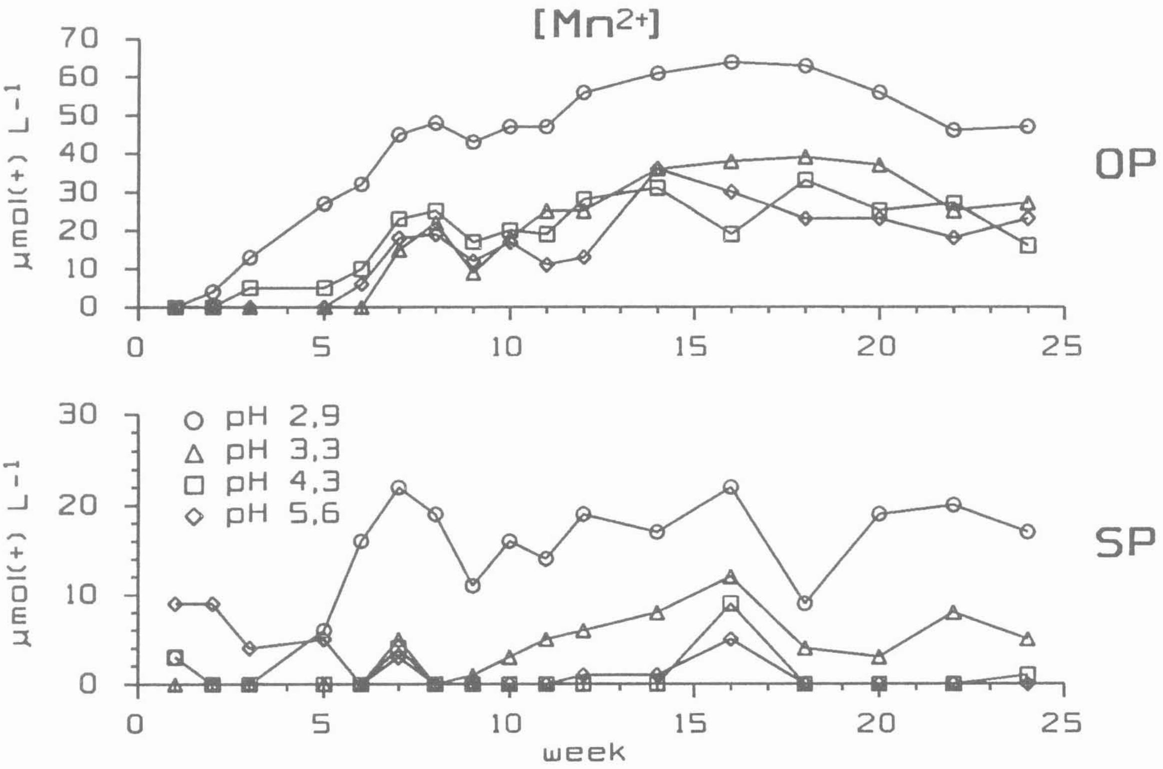

Figure 3i [Mn^{2+}]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

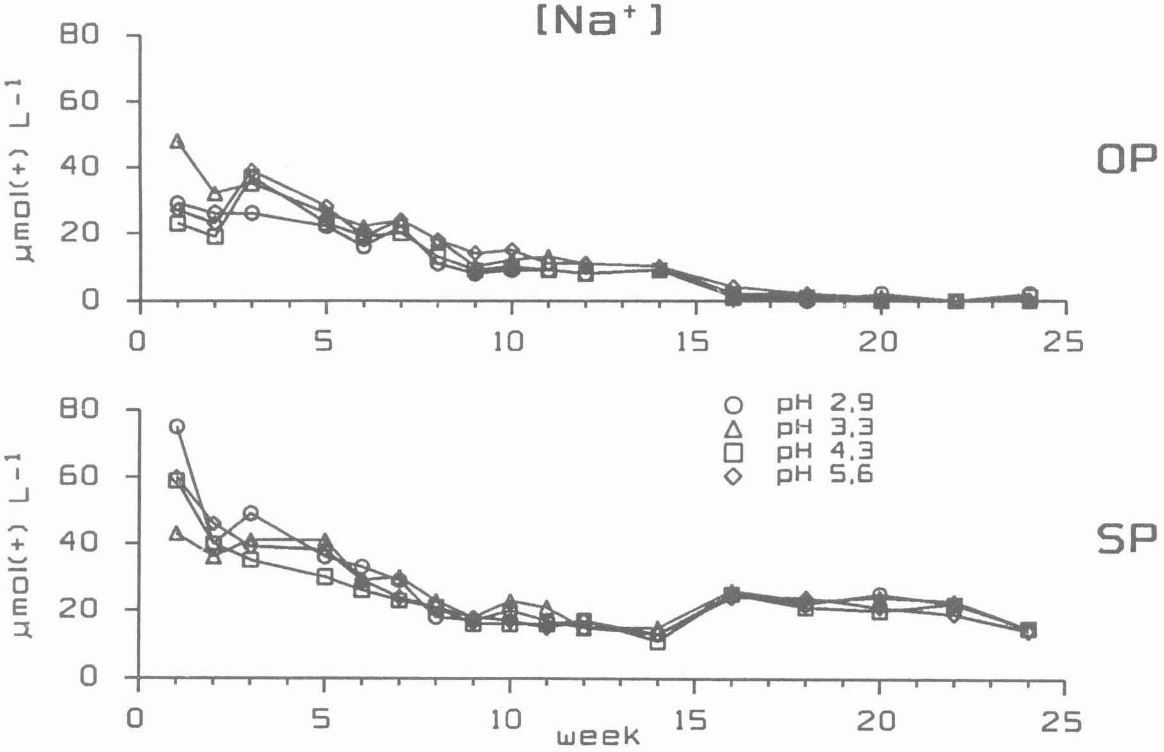

Figure 3j [Na^{+}]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

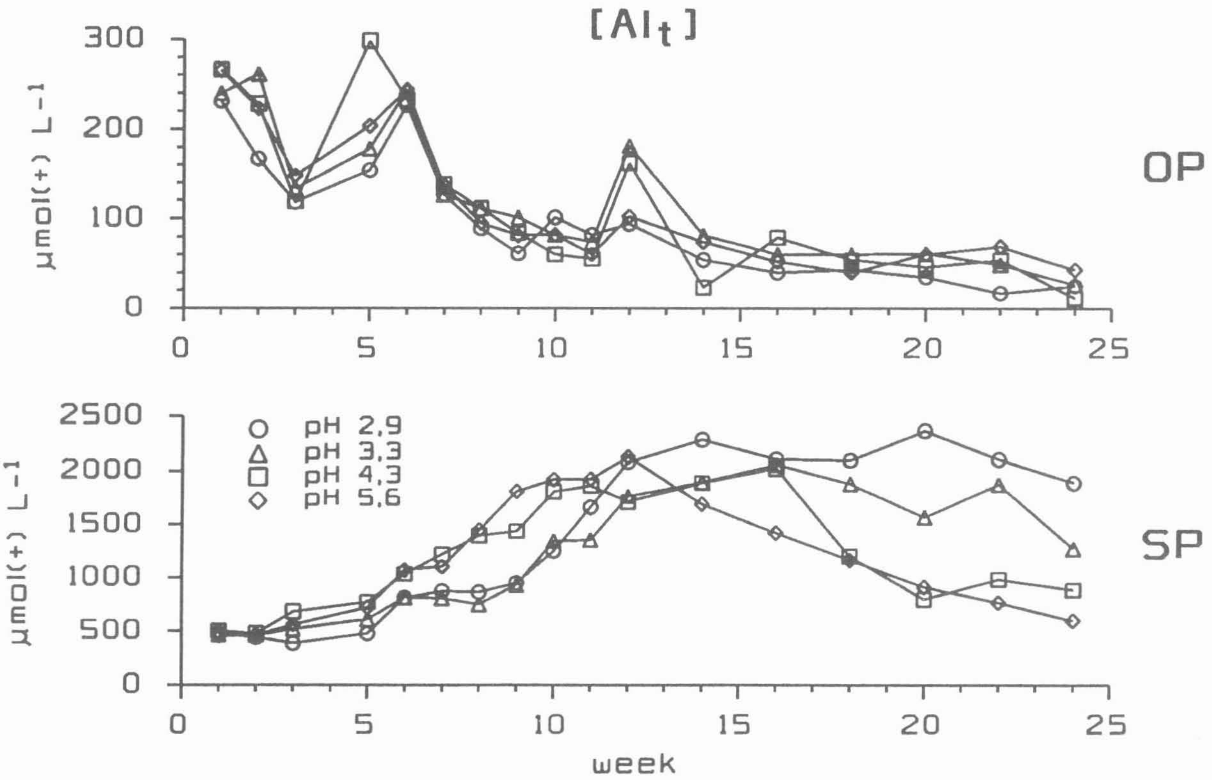

Figure 3k [Al$_t$]. Time-related changes in ion concentrations in the organic (OP) and spodic percolates (SP) of a reconstructed Ferro-Humic Podzol treated with acid solutions at pH values of 2.9, 3.3, 4.3, and 5.6.

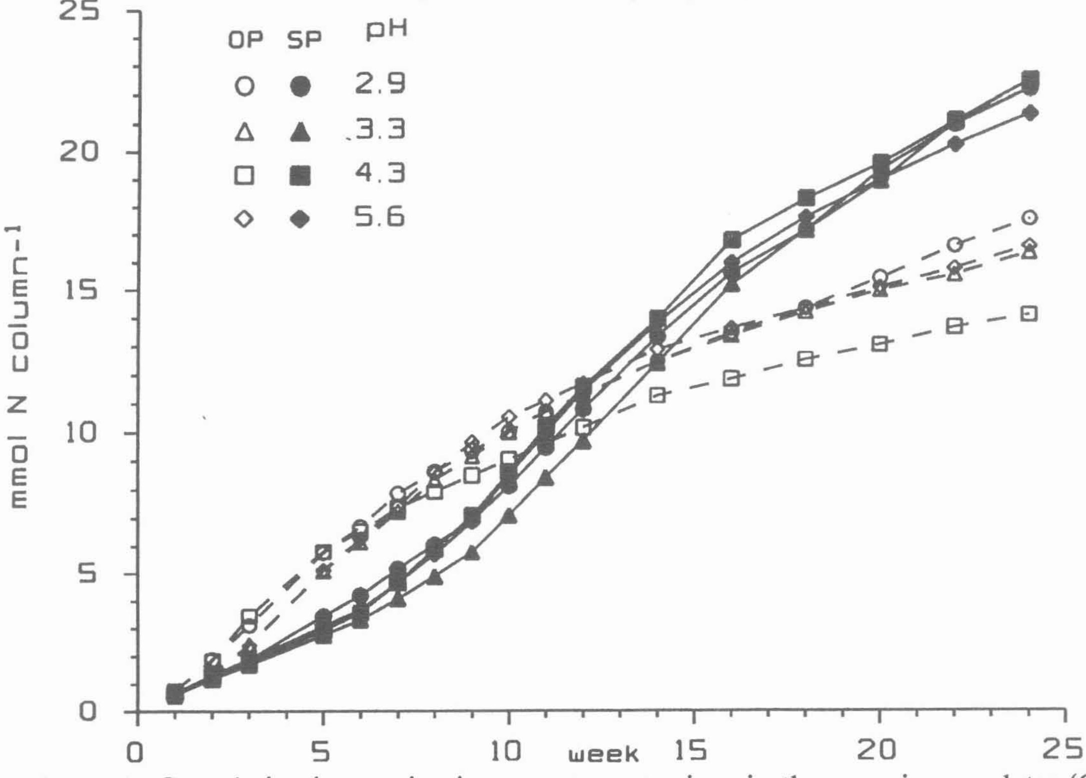

Figure 4. Cumulative inorganic nitrogen concentrations in the organic percolates (OP) and spodic percolates (SP) from a podzol as a function of pH values from simulated rain.

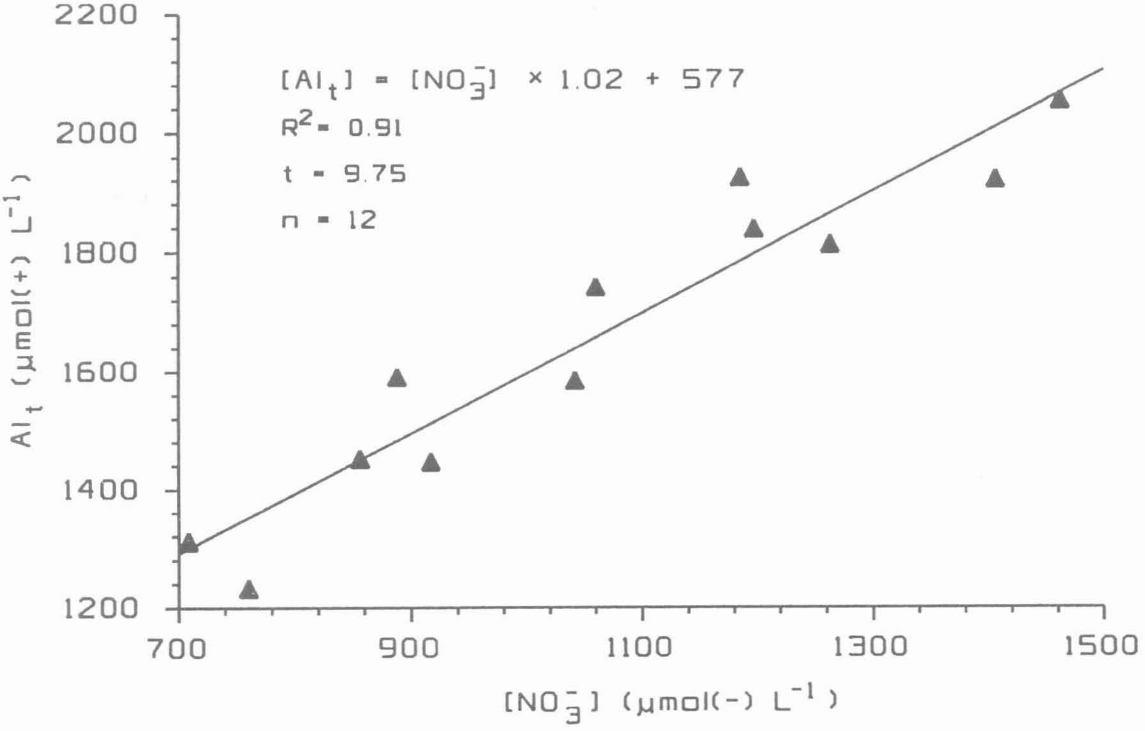

Figure 5. Total percolated aluminum as a function of percolated nitrates in the spodic percolates collected from weeks 1 to 12.

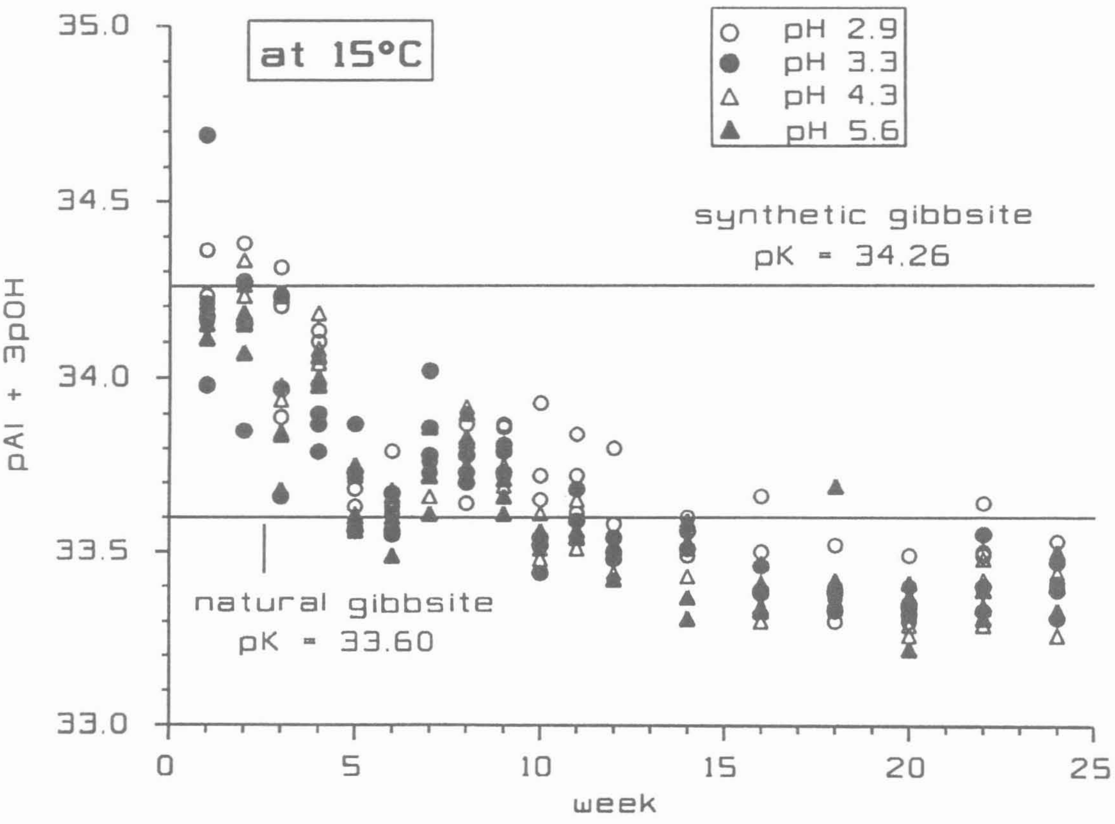

Figure 6. Changes in pAl + 3pOH in the spodic percolates.

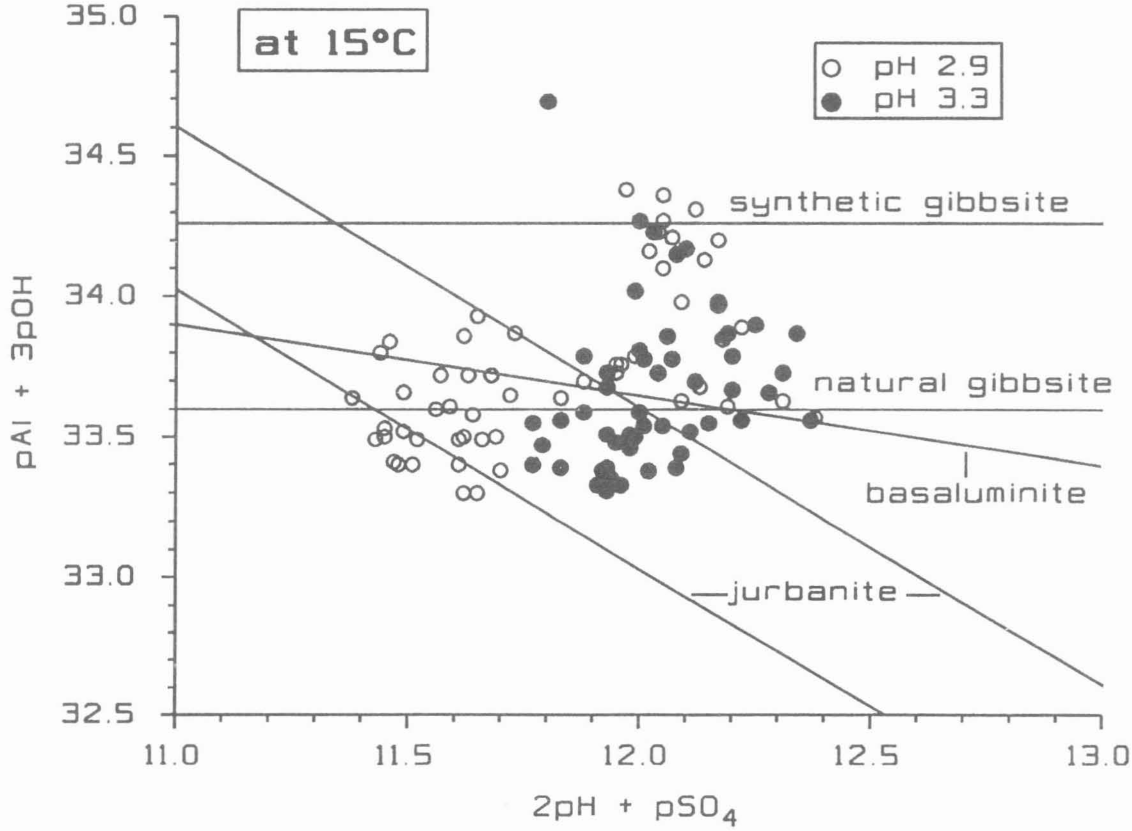

Figure 7a. pAl + 3pOH as a function of 2pH + pSO_4 in the spodic percolates. Treatments at pH 2.9 and pH 3.3.

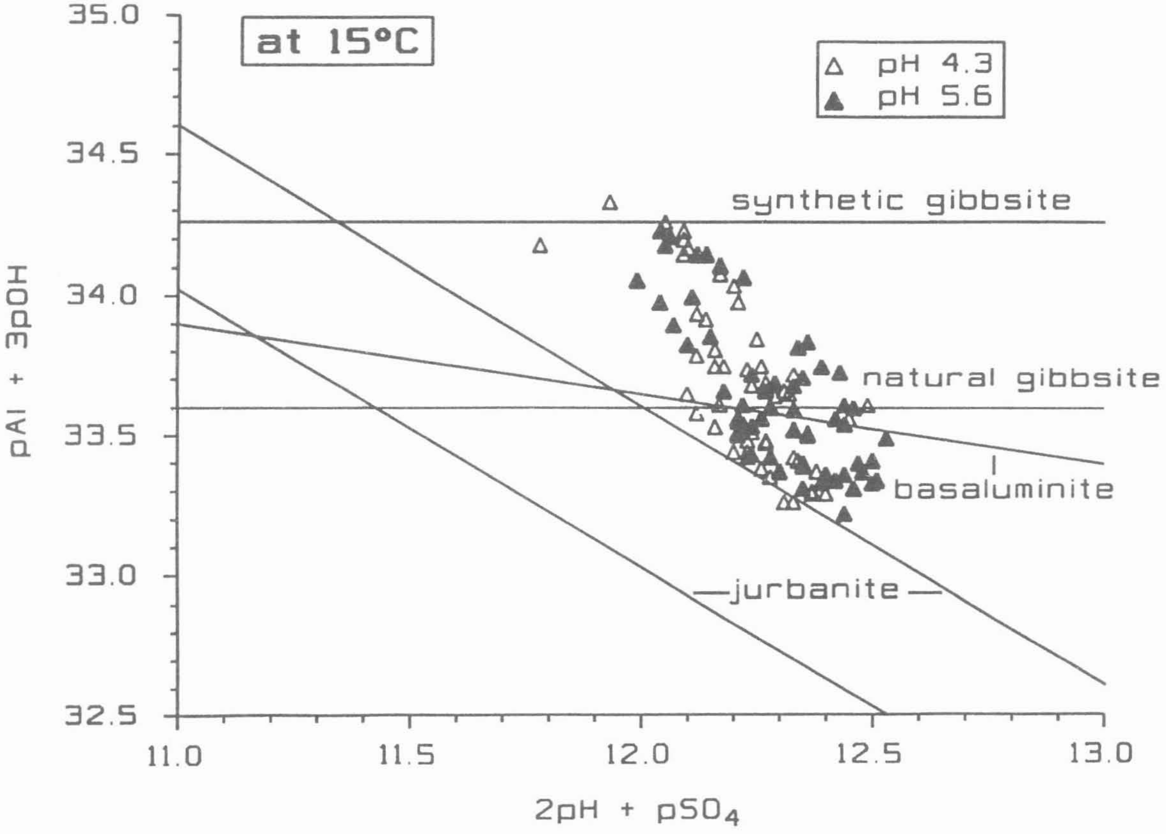

Figure 7b. pAl + 3pOH as a function of 2pH + pSO_4 in the spodic percolates. Treatments at pH 4.3 and pH 5.6.

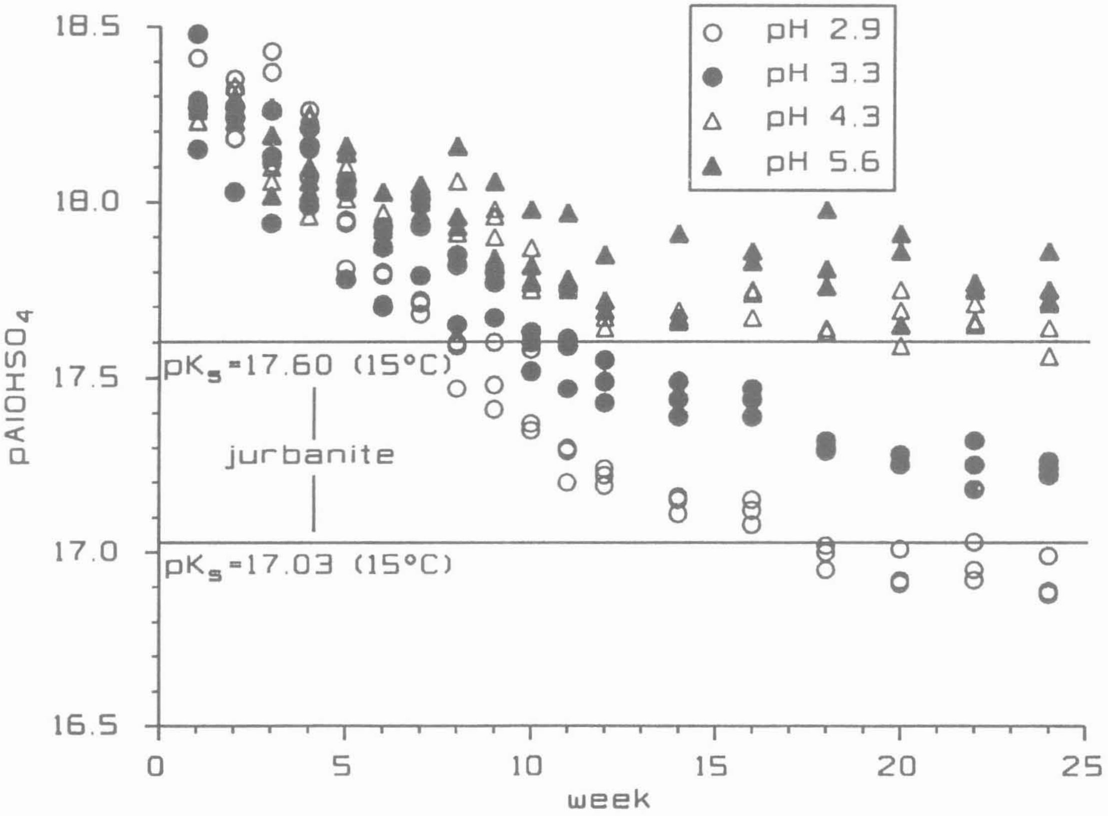

Figure 8. Changes in pAlOHSO$_4$ in the spodic percolates.

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