ACID RAIN: SCIENTIFIC AND TECHNICAL ADVANCES

Edited by R. Perry
R.M. Harrison,
J.N.B. Bell
and J.N. Lester

ACID RAIN: SCIENTIFIC AND TECHNICAL ADVANCES

EFFECTS OF ENDOGENOUS AND EXOGENOUS SOURCES OF ACIDIFICATION ON THE CHEMICAL PROPERTIES OF A PODZOL.

R. Boutin & G. Robitaille

Laurentian Forestry Centre, Canadian Forestry Service, B.O. Box 3800, Sainte-Foy, Québec, CANADA G1V 4C7

ABSTRACT

An *in vitro* acidification experiment was performed on reconstituted profiles of a orthic ferro-humic podzol. Endogenous production of protons associated with nitrification was responsible for a significant drop of pH and exchangeable bases in the organic horizons LF and H. This process was more effective in leaching K than Mg and Ca as a percentage of the initial level. The converse was true for acidification by exogenous sources; compared to the control (pH 5.6), acidified water (pH 4.3 to pH 2.6 with a 2/1 equivalent ratio of H_2SO_4/HNO_3) induced a significant gradient of Ca and Mg losses while K losses were significant only at pH 2.6. In the mineral horizons, bases were not substantially depleted and the acid treatments induced a significant drop of pH related to an increased concentration of Al in soil solution.

INTRODUCTION

Northeastern North America receives a substantial acid deposition which may affect forest growth and productivity. Most of the area covered by this region receives $S-SO_4^{2-}$ in excess of the forest requirement (1). An excess of nitrogen is rarely encountered (2) except in specific situations such as heavy ammonia deposition from manure in forest stands near intensively managed farm lands (3). Late autumn fertilization by high nitrate deposition in elevated mountain ecosystems, downwind from coal power plants may also occur (4).

Sulphuric and nitric acid from atmospheric deposition constitute most of the exogenous part of the total acid load on soils. Simultaneously, endogenous sources of H^+ occur in soils due to nitrification, cation uptake, carbonic and organic acid formation and humification (5,6). The relative importance of these different sources of acidity have to be known because the general mechanism of soil acidification must be understood before establishing the impact related to the anthropogenic acidification.

Acid deposition and internal acid formation have the potential to leach cations out of the rooting zone and to mobilize Al^{3+} from polymeric hydroxy-Al which may be toxic for fine roots and cause forest dieback (7). Potassium deficiencies in leaves of Acer saccharum Marsh. (8) and K and Mg deficiencies in Pinus resinosa Ait. plantations (9,10) on fluvio-glacial deposit have been reported in the Appalachian region and in the lowlands of the St. Lawrence River in the province of Quebec. Calcium deficiencies have not been reported but concentrations are low. Podzol is the major group of soil on well drained glacial till, that supports most of the commercial forest of Quebec. Under balsam fir-white birch stands of the Laurentian highlands, north of Quebec city, high precipitation and low mean annual temperature enhance the pedogenetic process of podzolisation and give rise to very acid podzols.

These podzols are characterized by an important accumulation of organic matter (up to 10 cm) which constitute the top organic horizons L, F and H. Despite the low

pH (H_2O) of these horizons (3.5 to 4.5), this is where most of the feeding roots are found. However, some penetrate the spodic B horizons where organic products and Fe-Al oxydes accumulate. Reasons for this preference are a relatively high pool of available nutrients in the organic layers coupled with the protective effect of chelation by soluble organic molecules which pull out free Al^{3+} ions from soil solution.

Aluminum toxicity caused by the low pH (often around pH 4.0) in the first centimeters of the Bhf horizon is reputed to discourage roots from penetrating further down the profile. This mechanism may play a major role in forest dieback related to biological stress induced by multiple factors. For example, not enough soluble Al^{3+} for toxicity to roots may be present in mineral horizons, at the beginning of aluminum buffer range (= pH 4.4) (11). However, a slight shift of pH toward pH 4.0 could bring the Al concentration to a level toxic to feeding roots. Even when these roots account for only a small proportion of the total root system, their mortality may induce a significant stress in the case of drought because there is a reduced possibility for uptake of water and nutrients from the less dry mineral horizons. The study of acidification on a podzol should be concentrated on the organic layers but specific effects on the mineral horizons have to be considered.

This paper presents some results from an in vitro acidification experiment performed on reconstituted profiles of an orthic ferro-humic podzol. Exchangeable bases (Ca, Mg and K), exchangeable acidity (H and Al) and pH were measured in the organic and mineral horizons, before and after percolation of deionized and acidified water. This experiment is complementary to the in situ acidification experiments and to the monitoring of soils and waters of the lake Laflamme watershed, Montmorency forest, Quebec. This study site is one of the three major sites chosen by the Canadian Forestry Service (CFS) for integrated studies on Long Range Transport of Air Pollutants (LRTAP) on forests.

MATERIALS AND METHODS

Soil samples come from a pit (3 m x 1.5 m x 1 m) dug on the southernly exposed slope of lake Laflamme watershed (47°17' North and 71°14' west; altitude = 795 m). Mean annual temperature is 0.3° C and mean annual precipitation is 1 450 mm (33% as snow). The soil is classified as an orthic ferro-humic podzol of the Laurentide series developed on glacial till and it supports a 50-year-old Abies balsamea (L.) Mill. and Betula papyrifera Marsh. stand. The herbaceous plant Oxalis montana Raf. covers most of the forest floor. Texture of the B horizons is a sandy loam with 71% sand, 19% loam and 10% clay. Chemical characteristics are given in Table 1. Samples from the organic horizons LF and H, Ae and spodic horizons (Bhf, Bf_1, Bf_2 and Bf_3) were separated in the field and put in plastic bags. Within 24 hours, each horizon was sieved using a 6 mm screen and stored at 2°C.

Table 1. Chemical characteristics of the orthic ferro-humic podzol sample for the in vitro acidification experiment. Each value is the mean of three analytical determinations.

HORIZON*	pH (H_2O)	pH (0.01M $CaCl_2$)	C (W.B.) %	N (Kjeldahl) %	C/N	EXCHANGEABLE BASES cmoles (p+)Kg^{-1}			EFFECTIVE CEC	B.S. %
						Ca	Mg	K		
LF	4.14	3.74	53.1	2.06	25.8	26.0	3.02	1.93	39.6	78
H	3.77	3.22	47.3	2.03	23.3	19.9	2.09	0.97	37.7	61
Ae	4.27	3.47	1.37	0.07	19.6	0.31	0.06	0.06	1.84	23
Bhf	4.12	3.71	5.24	0.26	14.4	0.81	0.11	0.09	5.36	19
Bf_1	4.33	4.03	4.24	0.19	22.3	0.56	0.05	0.04	3.59	18
Bf_2	4.56	4.26	3.37	0.14	24.1	0.40	0.03	0.03	2.67	17
Bf_3	4.63	4.37	1.85	0.08	23.1	0.28	0.02	0.02	1.70	19

* see Figure 1 for horizons depth.

Because the design of this experiment included the analysis of soil percolates from three different depths, three types of soil columns where reconstituted (H, Bf_1 and Bf_3). A complete column (a Bf_3 column) is illustrated in Fig. 1 with the corresponding depth of each horizon. Preliminary essays were made to know how much soil (in g of moist soil) was needed to reconstitute a given horizon to a given depth (from the means of 17 profiles near the main pit) and density. Columns were made of acrylic tubes (4 inches (= 10 cm) I.D.) and closed at the bottom with a plate of the same material. Silicium powder (300 g) and glass wool (20 g) prewashed with 1 N HCl and deionized water were used as a filter. A vaccuum of 0.3 atmosphere was applied to each column by the outlet hole, to avoid saturation during the period of application (16-24 hours per week). Deionized water and four acid treatments (pH 4.3, 3.3, 2.9 and 2.6) were applied in triplicate on H and Bf_1 columns. Due to lack of space and materials, Bf_3 columns did not receive the pH 2.6 treatment. During 8 weeks, 500 mL wk^{-1} (62 mm wk^{-1}) of deionized water (pH 5.6) was applied drop by drop to each column. The control and acid treatments continued thereafter for 54 weeks. The acid treatments were made with deionized water acidified with a 2:1 equivalent ration of H_2SO_4 and HNO_3. In the treatments, H^+ concentrations were 50, 500, 1 250 and 2 500 μmoles (p^+) L^{-1} respectively which gave an approximate pH of 4.3, 3.3, 2.9 and 2.6. This corresponded to 3, 30, 70 and 140 years of H^+ deposition on the watershed based on the actual annual deposit.

After the 62 periods of application, all columns were dismantled and horizons separated for chemical analysis. Before chemical analysis, soils were dried at room temperature and sieved using a 2 mm screen.

The pH was determined in H_2O and in 0.01 M $CaCl_2$ with a soil solution ratio of 1:2 for the mineral horizons and 1:5 for the organic horizons. Exchangeable bases (Ca, Mg and K) were extracted with 1.0 N NH_4Cl and concentrations determined with atomic absorption spectrophotometry (Ca and Mg) and atomic emission spectrophoto-metry for K. Nitrous oxyde and acetylene flame was used for Ca and Mg. Effective exchangeable acidity was extracted with 1.0 N KCl and titrated with 0.1 N NaOH; after adding KF, back titration with 0.1 N HCl was performed to determine exchangeable Al (12). Effective CEC was then obtained by adding exchangeable bases to effective exchangeable acidity.

The Duncan Multiple Range Test was performed on the mean of each treatment for each horizon. All the horizons with the same treatment were used in the comparisons, so that n is of unequal size (for pH 5.6, 4.3, 3.3 and 2.9, n = 9 for LF and H; n = 6 for Ae, Bhf, and Bf_1; and n = 3 for Bf_2 and Bf_3; for pH 2.6, n = 6 for LF and H, and n = 3 for Ae, Bhf and Bf_1).

RESULTS AND DISCUSSION

In this report, the variable pH ($CaCl_2$) will not be discussed thoroughly because most of the conclusions are the same as in the case of pH (H_2O). However, pH ($CaCl_2$) is 0.46 ± 0.02 (S.E.M.) smaller than pH (H_2O). This difference is greater in the Ae horizon (0.68) while it is only 0.33 in the Bf_2 and Bf_3 horizons. When the columns had been dismantled the LF horizon was separated into two equal parts of 2.5 cm each: the top (LF1); the bottom (LF2). The Student T test (p = 0.05) between means of these two layers of LF, revealed that pH (H_2O) is lower in LF1 (Fig. 1) for the pH 2.6 (2.67 vs 2.79) and 2.9 (3.01 vs 3.12) treatments, pH ($CaCl_2$) does not show this significant difference. But in LF2, for treatments at pH 4.3 and 5.6, pH ($CaCl_2$) is significantly lower than in LF1 while the differences are not significant for pH (H_2O), even if the tendancy is toward a lower pH for LF2.

This tendancy is also reflected in the content of exchangeable bases and exchangeable effective acidity where pH is correlated positively with the former and negatively with the latter. Because the differences noted between LF1 and LF2 are small and mostly non-significant, results from LF1 only are used in Fig. 2 while the average of LF1 and LF2 is used in Fig. 3.
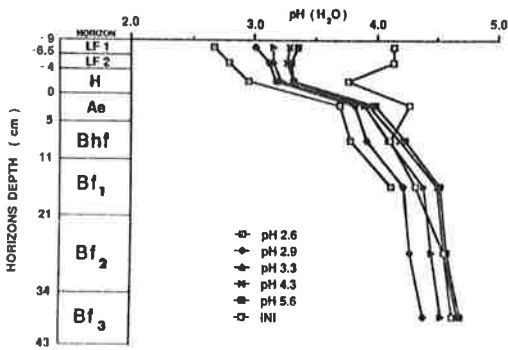
Figure 1. Mean pH (H_2O) of organic and mineral horizons of a podzol before (INI) and after percolation with deionized (pH 5.6) and acidified water (pH 4.3 to pH 2.6).

Coefficients of variation (CV)

Compared to the other variables measured in this experiment, pH was less variable with coefficients of variation of < 1 to 3% (from an average estimation in each horizon); greater variations were noted for the organic horizons. CV for the exchangeable bases, H and Al varied from 4 to 19% except for the low content of exchangeable Ca in Bf_2 horizon where CV was 44%. For all the measured exchangeable elements in the organic horizons CV was always greater in the top centimeters ($CV_{LF1} > CV_{LF2} > CV_H$). This observation is similar as that for pH. This pattern of variation is probably related to the nature of the organic material and to the prime effects of the treatments in the top of the soil columns.

Effects on pH

Percolation of deionized water and endogenous production of H^+ associated with nitrification, multiplied the proton activity (antilog ($-pH$)) of LF, H and Ae by 6.5 (pH 4.14 to 3.30), 2.8 (pH 3.77 to 3.32) and 2 (pH 4.27 to 3.99) times respectively (Fig. 1). Spodic horizons (Bhf to Bf_3) reacted differently with a final proton activity exceeding the initial values only when the lowest treatments pH 2.9 and 3.3 were applied respectively for the two first (Bhf, Bf_1) and the two last (Bf_2, Bf_3) horizons. Exogenous sources of acidification from the acidified treatments caused a significant decrease of pH which is gradual from pH 5.6 to pH 2.6 (or to pH 2.9 for Bf_2 and Bf_3 horizons). As expected, the effects of treatments are more pronounced in the top organic horizons. Compare to the pH 5.6 control, their is 4.8 (pH 3.35 to 2.67), 3.2 (pH 3.30 to 2.79) and 2.3 (pH 3.32 to 2.95) times more H^+ activity in the pH 2.6 treatment, respectively for LF1, LF2 and H horizons. It is interesting to note that the first mineral horizon Ae (the grayish eluviated and poor in exchangeable bases horizon) maintained a final pH of 3.70 even after being treated which much more acid water, coming from the upper organic horizons leached with the pH 2.6 acidified treatment. In the spodic horizons, pH 2.9 treatment caused a 0.3 unit pH decrease which is equivalent to the double of H^+ activity in the control. The pH 2.6 treatment gave a final pH of 3.79 and 4.13 for Bhf and Bf_1; this is equivalent to 2.8 and 2.5 times the H^+ activity of the control.

Effects on exchangeable bases, H and Al

Organic horizons

Acidification was more effective in changing the balance between the base cations (Ca, Mg and K) and the acid cations (H and Al) in LF and H horizons than in the other mineral horizons (Fig. 2a-f). This change is mainly due to an exchange reaction between H^+ and exchangeable Ca, effective CEC remaining constant. Respectively for LF and H, percentage of base saturation (B.S.) was 79 and 61% before spraying, which decreased to 58 and 49% with the effect of endogenous acidification estimated by the pH 5.6 control. Additional acid load from the treatments enhanced the loss of bases and B.S. decreased to 15 and 17% after application of the pH 2.6 treatment.
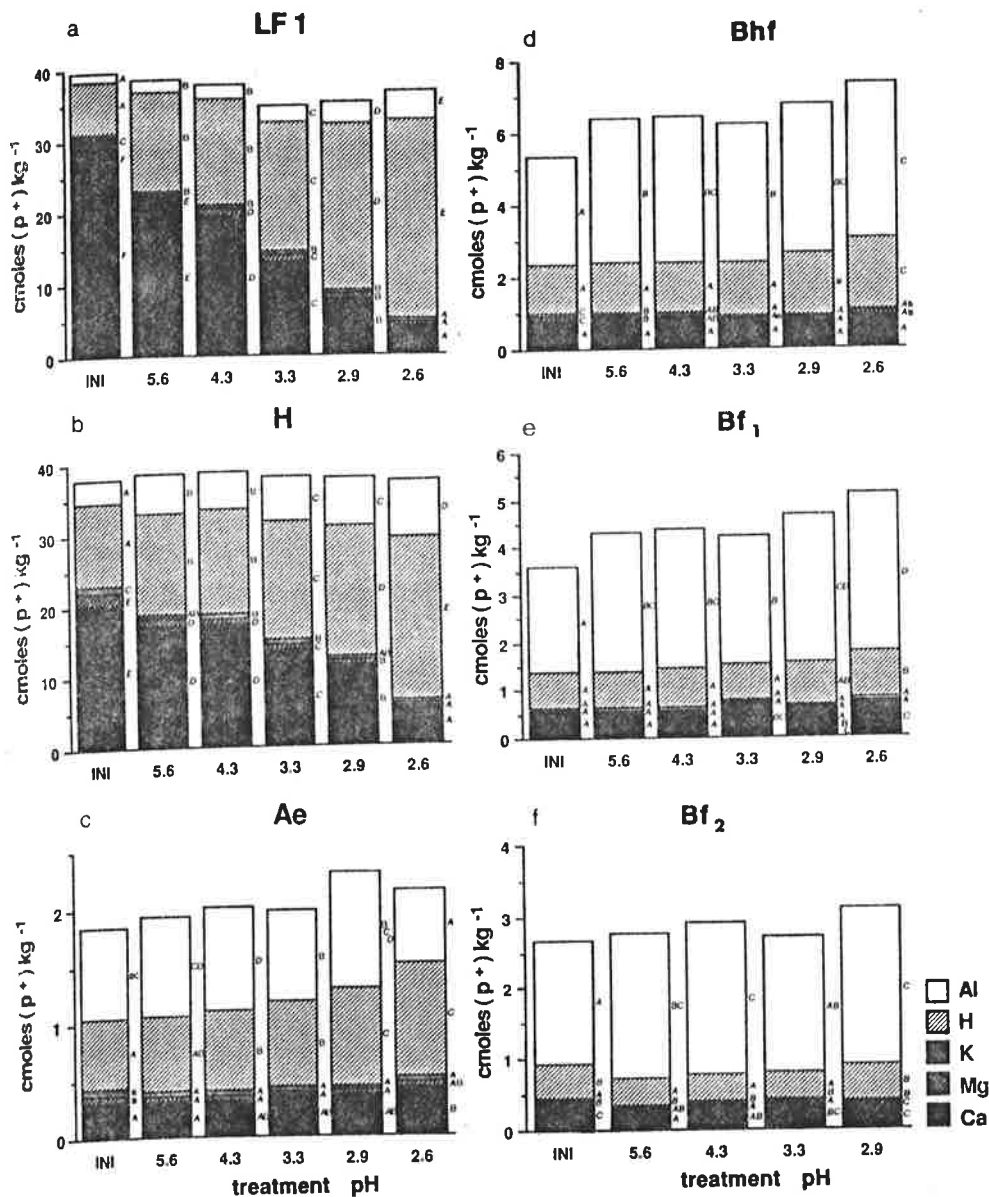
Figure 2a-f. Mean exchangeable* Ca, Mg, K, H and Al in the organic (LF1, H) and mineral horizons (Ae, Bhf, Bf$_1$, Bf$_2$) of a podzol before (INI) and after percolation with deionized (pH 5.6) and acidified water (pH 4.3 to pH 2.6).

* Means of a given element followed by different letters are significantly different at p = 0.05.
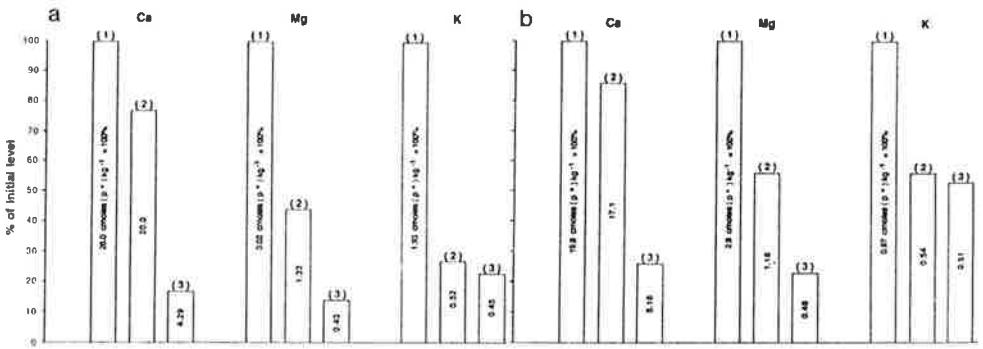
Figure 3a-b. Exchangeable Ca, Mg and K in the LF (a) and H(b) horizons of a podzol expressed as percentage of initial level (1) after percolation of deionized water at pH 5.6 (2) and acidified water at pH 2.6 (3).

One of the major observations from this experiment is illustrated in Fig. 3. Relative to the initial level (100%), loss of exchangeable K in the control (73 and 44% for LF and H) was much more pronounced than loss in exchangeable Mg (56 and 44%) and exchangeable Ca (23 and 14%). These losses could be related directly to the cation mobility ($K_m > Mg_m > Ca_m$) and inversely to the respective saturation of each cation ($K_s < Mg_s < Ca_s$). The added acidification from the acid treatments had the opposite effect. Compare to the pH 5.6 control, loss of exchangeable K (13 and 6%) in the pH 2.6 treated LF and H horizons was lower than the loss in exchangeable Mg (67 and 59%) and exchangeable Ca (79 and 70%). It seems that percolation of the internally generated H^+ and possibly NH_4^+ could exchange efficiently with exchangeable K so that a minimum level was attained without any exogenous source of H^+.

Mineral horizons

Effects of acidification are not immediately obvious in the mineral horizons. This could be explained by the buffering effect of the upper organic horizons, the relative high bulk density and the low base saturation which is 22% in Ae and 14-16% in B horizons. In general, their was an increase in effective exchangeable acidity not followed by an equivalent decrease in exchangeable bases so that CEC_E increased. Maximum increase of CEC_E was observed in Bhf and Bf_1 horizons under pH 2.6 treatment with 40% more than the initial level. Increase of exchangeable Al in pH 5.6 control was noted for all the mineral horizons and corresponded to 93 and 100% of the increase in CEC_E respectively for Bhf and Bf_1. This increase in exchangeable Al was related to the high concentration of total Al and NO_3^- in soil solution. Compared to the initial level, there was in the control a small but significant decrease of exchangeable Mg and K in Ae (Fig. 2c) and Bhf horizons (Fig. 2d). Also a significant decrease of exchangeable Ca in Bf_2 (Fig. 2f) and Bf_1 horizons (not represented) was observed. Part of the total calcium leached from the most acid treated horizons, accumulated gradually in the mineral horizons except in Bhf. However, the total accumulation of exchangeable Ca in the pH 2.6 treated Ae, Bhf and Bf_1 horizons (200 mmoles (p^+) m^{-2}), accounted only for 12% of the total loss in the organic horizons (1690 mmoles (p^+) m^{-2}).

Analysis of percolates from a preliminary experiment where H_2SO_4 only was used as exogenous acidifier (data not published), show very high concentrations of NO_3^- and NH_4^+ in the organic percolates and of NO_3^- and total Al in the spodic percolates. This was related to humus desintegration and discoupling of the nitrogen cycle enhanced by the in vitro conditions: disturbance of the soil integrity; absence of living roots; near optimum humidity, temperature, and O_2 pressure for ammonification and nitrification; intense circulation of soil water which may have impeded accumulation of toxic products and leached out inhibitors of nitrification.

First results from percolate analysis in the present experiment indicate that evolution of nitrification in Bf_1 columns, was identical to the former experiment with a NO_3^- peak (= 3 mmoles (e^-) L^{-1}) occurence, after 16 weeks of percolation. Aluminum concentration varied from 17 to 20 mg L^{-1}. Without accounting for H^+ consumption by the process of ammonification, endogenous production of H^+ by nitrication during 24 weeks of spray in the preliminary experiment, was equivalent to a treatment at pH 2.82 and 2.45 respectively for the H and Bf_1 columns. Inhibition of nitrification by the acid treatments was significant only in the organic horizons but nitrification remained active with an internal H^+ production equivalent to a pH 3.07 treatment when the exogenous source was at pH 2.9. Similar results were observed by Hern et al. (13) on a podzol sample on the same site and on an another podzol from Turkey Lake, Ontario.

In an acidification experiment with lysimeters containing undisturbed brown podzol, Freisleben and Rasmussen (14) noted NO_3^- leaching due to experimental conditions. The endogenous acid input was estimated at 408 mmoles (p^+) m^{-2} yr^{-1}. Skeffington and Brown (15) concluded that after five years of acid treatment on a humo-ferric podzol, nitrification was responsible for an annual average H^+ input of 740 mmoles (p^+) m^{-2}. This was equivalent to a pH 3.3 acid treatment which reduced the difference between acid and control monolyths. Brown (16) in an another paper based on the same experiment, had observed that exchangeable K and Mg in litter from both the control and acid treated lysimeters was appreciably less than in litter taken from the source site. Bergkvist (17) in a lysimeter study with a ferric podzol did not find any appreciable difference in K^+ leaching when he compared the acid treatments (pH 3.40 and 3.11) to the control However, net leaching of K^+ (input-output) at 35 cm depth in the control was equivalent to 14% of the initial extractable pool while no net leaching of Ca^{2+} was noted.

CONCLUSION

In the present experiment, homogeneity resulting from soil columns reconstitution gave the opportunity to compare each horizon at its initial state with a control (pH 5.6) and acidified treatments. However, experimental conditions enhanced soil organic matter decomposition and endogenous production of H^+ which narrowed the differences between the control and the treated horizons. This was particularly true for the monovalent mobile K^+ cation who was leached so easily in the control that differences with the extreme acidified treatments were mostly not significant. This stresses the importance to evaluate the initial state of the soil before comparing non-acidified vs acidified treatments in lysimeter studies.

REFERENCES

1. D.W. Johnson and D.W. Cole, Environment International 3, 79-90 (1980).
2. G. Abrahamsen, in Ecological Impact of Acid precipitation, D. Droblos and A. Tollan, eds. NIRPAP, Oslo, Norway, p.58-63 (1980).
3. Van Breemen, N. and Jordens, E.R., in Effects of Accumulation of Air pollutants in Forest Ecosystems, Ulrich and Pankrath, eds, 171-182 (1983).
4. A.J. Friedland, G.J. Hawley and R.A. Gregory in Air Pollutants Effects on Forest Ecosystems, St. Paul, Minnesota, p. 95-106 (1985).
5. B. Ulrich, in Effects of Acid Precipitation on Territrial Ecosystems, T.C. Hutchinson and M. Havas eds. New York pp.255-282 (1980).
6. J.O. Reuss, in USDA Forest Service General Technical Report NE-23 Upper Darby, Pennsylvania, L.S. Dochinger and T.A. Seliga eds. (1976).
7. R.A. Skeffington, in Effects of Accumulation of Air Pollutants in Forest Ecosystems, New York, B. Ulrich and J. Pankrath eds. pp.219-231 (1983).

8. B. Bernier, M. Brazeau, A. Brousseau and C. Camiré, Recherches sur le dépérisse-
    ment et le statut nutritif de l'érablière des Appalaches du Québec. Université
    Laval, Québec (1985).
9. A. Lafond, Contribution 1.   Fonds de Recherches Forestières de l'Université
    Laval, Qué. (1958).
10. T.D. Phu, Canadian Journal of Forest Research 5, 73-79 (1975).
11. Tyler, G., Berggren, D., Bergkvist, B., Falkengren-Grerup, V., Folkeron, L. and
    Rüchling, A., in NATO workshop on effects of Air Pollutants, especially Acid
    Deposition, on Forest, Agriculture and Wetlands, Toronto, May 12-17 (1985).
12. G.W. Thomas, in Methods of Soil Analysis - Part 2. A.L. Page, R.H. Miller and
    D.R. Keeny eds. Agronomy 9, pp.159-165 (1982).
13. J.A. Hern, G.K. Rutherford, G.W. van Loon. Canadian Journal of Forest Research
    15, 839-847 (1985).
14. N.E.V. Freiesleben and L. Rasmussen, in Acid Precipitation Part 2, ed. by H.A.
    Martin, Water, Air and Soil Pollution, Vol. 31, pp.965-969 (1986).
15. R.A. Skeffington and A. Brown, in Acid Precipitation Part 2, by H.C. Martin ed.
    Water, Air and Soil Pollution, Vol. 31 p. 891-897 (1986).
16. K.A. Brown, Soil Biology and Biochemistry Vol. 17 No 1 pp. 31-38 (1985).
17. Bo Bergkvist, in Acid Precipitation Part 2, H.C. Martin ed. Water, Air and Soil
    Pollution, Vol. 31, 901-916 (1986).