United States Department of Agriculture

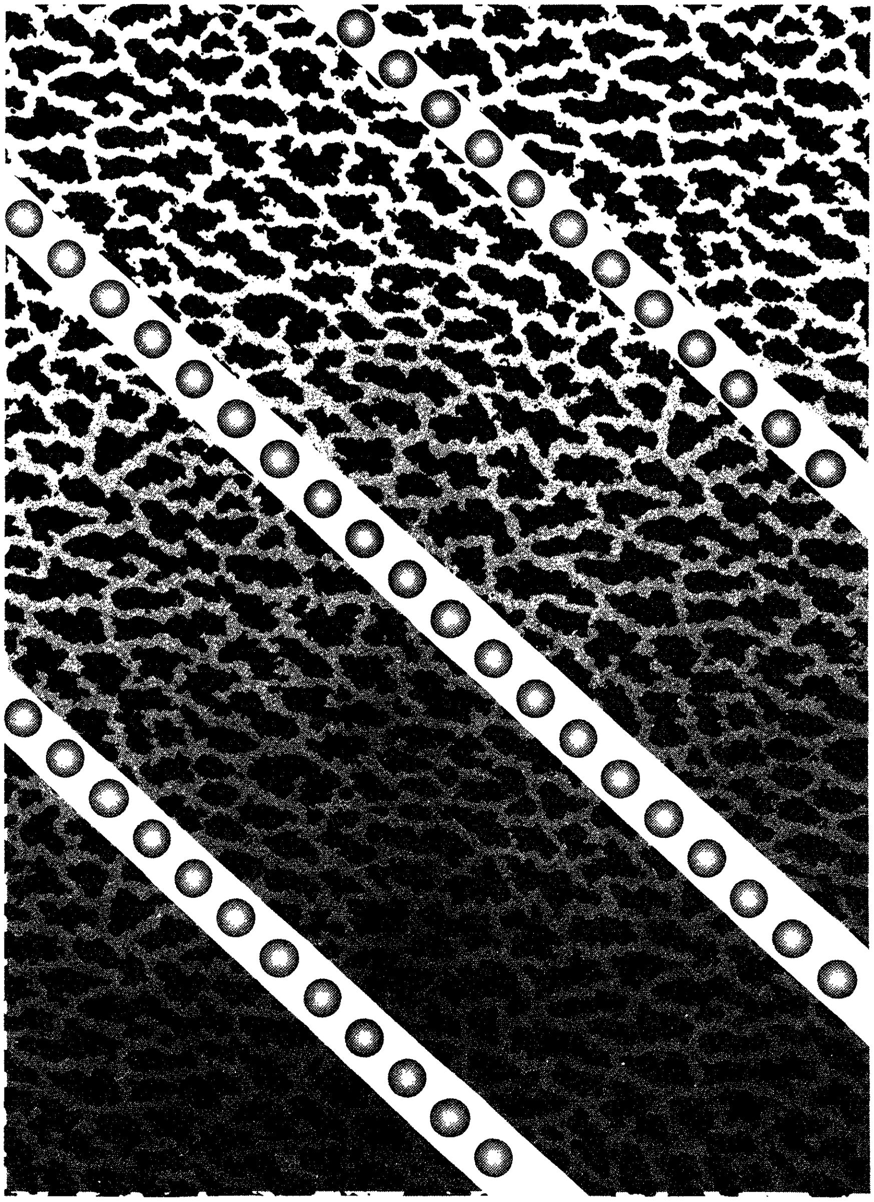
Forest Service

North Central Forest Experiment Station

Research Paper **NC-305**

Ion Movement In Acidified, Low Base Saturated Sand Soils

A. Ray Harris and Douglas M. Stone



North Central Forest Experiment Station
Forest Service—U.S. Department of Agriculture
1992 Folwell Avenue
St. Paul, Minnesota 55108
Manuscript approved for publication April 19, 1992
1992

Ion Movement In Acidified, Low Base Saturated Sand Soils

A. Ray Harris and Douglas M. Stone

Large areas of low base saturated sand soils occur in the upper Great Lakes Region. Displacement and leaching of ions by acid precipitation can have deleterious effects on the productivity of these soils and on the health and stability of vegetation types present. Concern is with forested watersheds of sandy soils and poorly buffered lakes.

Acid precipitation can mobilize heavy metals and toxic Al cations in the soil solution and groundwater (Liu *et al.* 1990). Soil processes that displace ions from these soils may affect surface water quality and aquatic life. High anion loading from acid precipitation can decrease the nutrient status of low base saturated soils by producing highly acidic percolate (Reuss 1983; Reuss and Johnson 1985, 1986; Seip and Rustad 1984). In these acidic soils as the ionic strength of the soil solution is increased Al and H are displaced from cation exchange sites lowering the pH of the solution (Richter *et al.* 1988). Forest soils usually are naturally acidic due to the production of humic and carbonic acids but acidification can be accelerated by acid deposition (White *et al.* 1988).

Negative acid neutralizing capacities (ANC) were produced in leachate from soil columns having less than 15 percent base saturation (Harris and Stone 1990). High concentrations of mobile anions can cause negative ANC in soil waters, and upon carbon dioxide degassing these solutions can retain a pH of 5.0 or less (Reuss and Johnson 1985).

The purpose of this study was to evaluate the response of low base saturated acidic soils to further acidification by determining: (1) how acidified precipitation produces acid leachate in these soils; (2) which cations are most likely to be displaced; and (3) which anions are most important in this process.

METHODS AND MATERIALS

Intact soil columns (15 x 150 cm) were collected in October, 1984, on national forests in northeast Minnesota, northern Wisconsin, and Upper Michigan, an area that has a precipitation pH gradient of 4.9 to 4.4 (Harris and Verry 1985; Nichols and Verry 1985; Glass and Loucks 1986). The sites selected were excessively drained sands formed in moderately weathered glacial outwash. Taxonomically, the soils included frigid Eutric Haplorthods, and Spodic and Typic Udipsamments (USDA Soil Conservation Service 1975). Vegetation on the sites reflected the low nutrient status of the soils (Harris and Stone 1990). A total of nine sites were sampled, comprised of three sites selected to represent base saturations in each of the ranges of 0-10, 10-20, and 20-40 percent.

Lysimeter construction, installation, and sampling procedures were described previously (Harris and Stone 1990). Briefly, the columns were transported to the Forestry Sciences Laboratory at Grand Rapids, Minnesota, and instrumented with 70-micron porous polyethylene filter candles at 10, 20, 40, 60, and 90 cm depths and

---

A. Ray Harris is a Research Soil Scientist and **Douglas M. Stone** is a Research Forester with the North Central Forest Experiment Station, Grand Rapids, Minnesota.

a 70-micron porous plate at the bottom. The porous plate was replaced later with a filter candle when caps were installed to prevent further leakage problems at the column bottoms. The columns were buried, around a subterranean sampling structure, to help obtain representative soil temperatures and CO_2 partial pressures. The columns were covered with fiberglass panels with side vents to allow light and air to enter, but not precipitation.

To evaluate the buffering effect of organic matter on the acidification process, the humus layer was removed from each column and replaced with one of three types of litter-humus caps prepared from 400 g of ground litter-humus of jack pine, or mixed hardwood, or an equal weight of quartz sand. Kentucky-31 Bluegrass was established on all columns to stabilize the cover and to provide an active root system and a source of carbon dioxide.

Rainwater was collected on a greenhouse roof, stored at 3-5°C in a polyethylene tank, and adjusted to pH 5.4 or 4.2 with H_2SO_4+HNO_3 (1:1) or NaOH. Half of the 216 soil columns received precipitation with each of the two pH values. From 1985 through 1987, treatment rates were 126 cm per year, representative of mean precipitation in the northeastern United States. In 1988 and 1989, treatment rates were reduced to 88 cm per year, similar to that of northern Minnesota. The precipitation rate was reduced to see if treatment rate as well as treatment pH was controlling acidification of soil water. Treatments were applied weekly throughout the growing season, and the bottom effluent was collected weekly the first year but usually biweekly or monthly in following years. Both treatment water and effluent were analyzed for acid neutralizing capacity (ANC), pH, Ca, Mg, K, Na, NO_3, SO_4, and PO_4. Elemental concentrations were determined using a DC plasma emission spectrometer (McHard *et al.* 1979); total Kjeldahl nitrogen (TKN), total P, and NH_4 by automated colorimetric procedures (USEPA 1983); NO_3, SO_4, and PO_4 by ion chromatography (USEPA 1986); ANC by Gran titration (Kramer 1984, USEPA 1986); and pH by glass electrode.

In the spring of 1989, the bottom plates were replaced with self sealing caps because some of the base plate joints had failed, resulting in loss of leachate and potential sample contamination from outside water. Leakage due to failure of these bottom joints precluded calculation of ion budgets before 1989.

RESULTS AND DISCUSSION

Ion concentrations in rainwater were highly variable, both among storms and from year to year. A single storm in the spring of 1985 resulted in mean levels of Ca, Mg, K, NO_3, and SO_4 approximately double those of the following 4 years (table 1). In addition to NO_3 and NH_4, organic-N was a significant portion (30 to 50 percent) of the total N collected in precipitation.

Soil water at all depths acidified to a significantly lower pH and ANC by the second year under both pH treatments (table 2). Precipitation rate apparently was a major controlling factor in reduction

Table 1.—*Average concentration (ueq/l) of ions in rainfall collected on glass at Grand Rapids, Minnesota*

Year	Ca	Mg	K	Na	Org-N[1]	NH_4	NO_3	PO_4[2]	SO_4
1985	146	45	20	7	44	20	126	12	74
1986	32	15	3	10	30	61	25	8	44
1987	54	13	14	9	11	50	40	12	37
1988	86	32	10	40	31	46	53	11	46
1989	53	27	9	4	51	31	43	10	43

[1] Calculated as NH_4.

[2] Total P reported as PO_4.

Table 2.—*Average leachate acid neutralizing capacity (ANC) in ueq/l and pH by depth (cm) and pH treatment, fall 1985-1989*

Soil depth	Year	5.4 pH treatment ANC	5.4 pH treatment pH	4.2 pH treatment ANC	4.2 pH treatment pH
10	1985	9.4[1]	5.3	11.4	5.3
	1986	2.6	5.1	- 8.1	4.9
	1987	5.6	5.2	- 4.9	5.0
	1988	- 1.1	5.2	-11.0	5.0
	1989	20.6	5.4	5.6	5.3
20	1985	55.9	6.3	27.7	6.2
	1986	1.4	5.2	- 3.2	5.0
	1987	5.0	5.2	- 1.7	5.1
	1988	- 2.7	5.2	-10.4	5.0
	1989	- 7.4	5.2	-21.7	5.1
40	1985	—	—	—	—
	1986	5.1	5.3	- 0.1	5.2
	1987	5.7	5.3	1.1	5.2
	1988	- 6.1	5.3	- 3.2	5.3
	1989	- 0.5	5.3	-16.9	5.2
150	1985	64.2	6.5	66.8	6.5
	1986	11.1	5.6	14.9	5.6
	1987	15.6	5.7	14.3	5.6
	1988	17.7	5.6	17.6	5.7
	1989	39.9	6.1	31.0	6.0

[1] Means connected by the same vertical line do not differ significantly at the 0.05 percent level. Tukey's HSD test.

of both of these parameters. An apparent equilibrium level that existed during 1986 through 1988 shifted significantly in 1989 when pH and ANC of leachate increased at both the 10 and 150 cm depths. The precipitation rate was reduced by 30% starting in 1988. The lower rate decreased the amount of hydrogen entering the soil system (Binkley *et al.* 1989).

Despite the increase in ANC and pH at the 10 and 150 cm depths, ANC decreased and pH remained the same at the 20 and 40 cm levels. Average base saturation was <15 percent in the soil between 10 and 40 cm and >15 percent in the surface and lower levels. The lower base saturations in this portion of the profile apparently caused the ANC to remain negative.

Concentrations of ions in leachate collected during midsummer at the 150 cm depth varied substantially over the 5-year period (fig. 1). Ion concentrations in spring and fall collections were lower due to less evaporative loss, but midsummer values were more representative of overall concentration levels during the treatment season. Nitrate exhibited the greatest yearly differences, ranging from 100-200 ueq/L in 1987 and 1988 to 600-700 ueq/L in 1986 and 1989. However, treatment differences in NO_3 associated with pH of applied rainwater were statistically significant only in 1985 and 1989. In general, cation concentrations paralleled those of NO_3 (K concentration in 1986 was an exception). Treatment differences in cation concentrations attributable to precipitation pH were small and rarely significant. Sulfate mobility was inversely related to NO_3; *i.e.*- much of the SO_4 was adsorbed in 1986 and 1989 when NO_3 concentrations were high, but moved readily in the leachate during the remaining years when NO_3 concentrations were

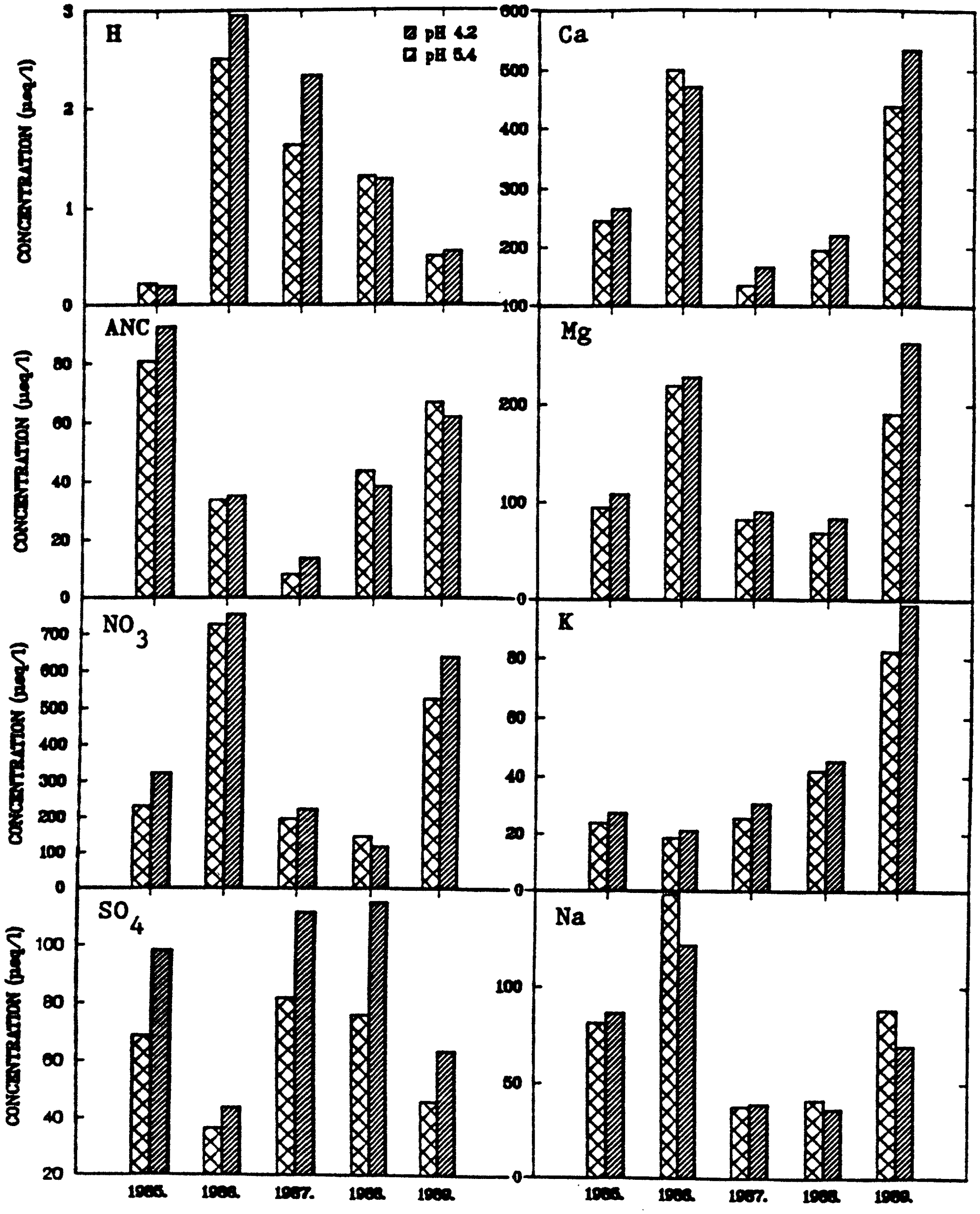


Figure 1.—*Average midsummer ANC and ion concentrations in leachate at 150 cm.*

Table 3.—*Contribution of nitrogen components to total nitrogen in precipitation and leachate, 1989*

Source	NH_4	Org-N[1]	NO_3	Total
	- - - - -	*meq*	- - - - -	
Precipitation				
pH 5.4	0.43	0.64	0.57	1.64
pH 4.2	0.50	0.57	0.86	1.93
Leachate				
pH 5.4	0.00	0.29	4.63	4.92
pH 4.2	0.00	0.36	5.56	5.92

[1] Calculated as NH^4.

low. Part of the pH treatment differences was due to the SO_4 added to adjust the rainwater pH. ANC values decreased from 1985 through 1987 (fig. 1). Beginning in 1988, they increased in response to the reduced precipitation rate, and by 1989 were about 66 percent of initial values.

The 1989 contributions of the different nitrogen components indicate active mineralization and nitrification (table 3). Total-N in leachate exceeded that added in precipitation by three times for both pH treatments. Nitrate output, however, exceeded inputs by more than six times in the pH 4.2 treatment and by eight times at pH 5.4.

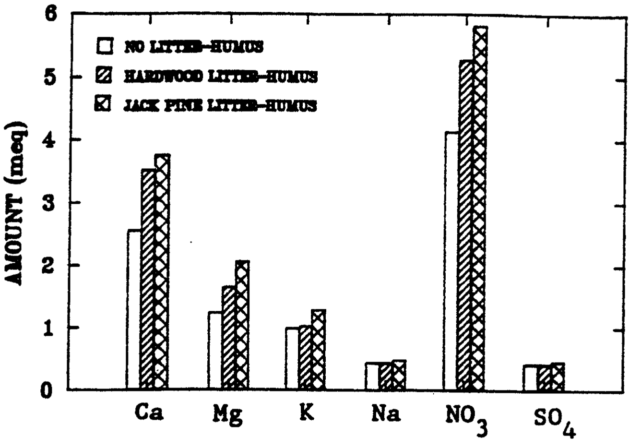


Figure 2.—*Average ion amount in leachate per column at the 150 cm depth by litter-humus treatment, 1989.*

Although the data do not indicate the cause of the high mineralization and nitrification episodes, temperature, seasonal inputs and storage, and soil column conditions certainly all had impacts. Because 85 to 88 percent of the NO_3 in the leachate came from soil N stores, a high nitrification cycle probably would not recur for several years. Both NH_4 and organic-N are important inputs into the total N-budget and must be considered when evaluating NO_3 impacts on the soil system. As Li *et al.* (1988) found in their study on the potential buffering of a forested Entisol, H produced from mineralization and nitrification processes replaced cations and was retained by the soil system.

Decaying litter-humus on the column surfaces significantly increased leaching of Ca, Mg, and NO_3 at the 150-cm depth (fig. 2). Cation losses under the pine litter-humus treatment were not significantly higher than from the hardwood. Litter-humus treatments were not different for K, Na, and SO_4.

Much greater quantities of cations and NO_3 leached from the soil columns than were added in treatment solutions (table 4). In contrast, PO_4 and SO_4 were retained. The NO_3:SO_4 ratio indicates that more than 90 percent of the cations moved with NO_3, if DOC and bicarbonate are discounted. Thus, nitification was the predominant process governing cation leaching in these soils. Sulfate became important in cation movement during years when nitrification was lower (fig. 1). Overall, the trend for cation leaching was higher under the pH 4.2 than the pH 5.4 treatment.

SUMMARY AND CONCLUSIONS

Application of precipitation at rates similiar to those in the eastern United States acidified water in soil columns after 1 year of treatment and significantly reduced ANC and pH of leachate at all soil depths. At this high precipitation rate, few pH treatment differences in ion concentrations were significant except for SO_4. The acidification trend was reversed in 1989 at the deeper soil depths after rainfall application rates were reduced from 126 to 88 cm per year. At the lower treatment rate, both ANC and pH of leachate collected at 150 cm increased after 1

Table 4.—*Total ion amounts added and leached per column treated with precipitation adjusted to pH 5.4 and pH 4.2, 1989*

Source	Ca	Mg	K	Na	NO_3	SO_4	PO_4[1]
				meq			
Precipitation							
pH 5.4	0.56	0.33	0.10	0.09	0.57	0.75	0.19
pH 4.2	0.56	0.33	0.10	0.09	0.86	1.27	0.19
Leachate							
pH 5.4	3.00	1.56	1.05	0.55	4.63	0.37	0.00
pH 4.2	3.70	1.80	1.05	0.74	5.56	0.48	0.00

[1] Total P reported as PO_4.

year. However, ANC continued to decrease at the 10 to 40 cm soil depth where base saturation was less than 15 percent. These results suggest that precipitation rate may be as critical as anion loading in these low base saturated soils.

Calcium, Mg, and NO_3 leaching were higher in columns that had a litter-humus layer on the surface. Jack pine and hardwood litter-humus both accelerated cation leaching. High cation depletion rates occurred when mineralization and nitrification were high. Sulfate adsorption increased when NO_3 leaching was high.

We found that when base saturation was less than 15 percent, soil water ANC became negative and remained so upon degassing. This process was reversed when leachate percolated through a lower soil horizon with base saturation above 15 percent. Cation losses from the columns were much greater than inputs from precipitation. Movement of ions was greatest during years when nitrification increased NO_3 concentrations in the soil water and caused leaching of nutrient cations far above replenishment rates.

LITERATURE CITED

Binkley, D.; Driscoll, C.T.; Allen, H.L.; Schoeneberger, P.S.; McAvoy, E. 1989. **Acidic deposition and forest soils: context and case studies of the southeastern United States**. Ecological Studies 72. New York: Springer-Verlag. 152 p.

Glass, G.E.; Loucks, O.L. 1986. **Implications of a gradient in acid and ion deposition across the northern Great Lake States**. Environmental Science and Technology. 20: 35-43.

Harris, A.R.; Verry, E.S. 1985. **Wet deposition of sulfate and nitrate acids and salts in the United States**. In: Johansson, I., ed. Hydrological and hydrogeochemical mechanisms and model approaches to acidification of ecological systems: proceedings of International Hydrological program workshop; 1984 15-16 September. Uppsala, Sweden. Nat. Hydrol. Prog. Rep. 10. Stockholm, Sweden: Swedish National Committee for the International Hydrological Program: 57-65.

Harris, Alfred Ray; Stone, Douglas M. 1990. **Using column lysimetry to evaluate acid precipitation effects**. Res. Pap. NC-291. St. Paul, MN: U.S. Department of Agriculture, Forest Service, North Central Forest Experiment Station. 38 p.

Kramer, J.R. 1984. **Modified Gran Analysis for acid and base titrations**. Environ. Geochem. Rep. 1984-2. Hamilton, Ontario, Canada: McMasters University. 32 p.

Li, C.S.; Bockheim, J.G.; Leide, J.E.; Wentz, D.A. 1988. **Potential for buffering of acidic precipitation by mineral weathering in a forested Entisol**. Soil Science Society of America Proceedings. 52: 1148-1154.

Liu, K.H.; Mansell, R.S.; Rhue, R.D. 1990. **Cation removal during application of acid solutions into air-dried soil columns**. Soil Science Society of America Proceedings. 54: 1747-1753.

McHard, J.A.; Foulk, S.J.; Nikdel, S.; Ullman, A.H.; Pollard, B.D.; Winefordnes, J.D. 1979. **Comparison study of four atomic spectrometric methods for the determination of metallic constituents in orange juice**. Analytical Chemistry. 51(11): 1613-1616.

Nichols, D.S.; Verry, E.S. 1985. **Evidence for the cultural acidification of lakes in the northern Lake States**. In: Air pollutants effects on forest ecosystems: symposium proceedings; 1985; St. Paul, MN. St. Paul, MN: Acid Rain Foundation: 253-265.

Reuss, J.O. 1983. **Implication of the calcium-aluminum exchange system for the effect of acid precipitation on soils**. Journal of Environmental Quality. 12: 591-595.

Reuss, J.O.; Johnson, D.W. 1985. **Effect of soil processes on the acidification of water by acid deposition**. Journal of Environmental Quality. 14: 26-31.

Reuss, J.O.; Johnson, D.W. 1986. **Acid deposition and the acidification of soils and waters**. New York: Springer-Verlag. 119 p.

Richter, D.D.; Comer, P.J.; King, K.S.; Sawin, H.S.; Wright, D.S. 1988. **Effects of low strength solutions on pH of acid forested soils**. Soil Science Society of America Journal. 52: 261-264.

Seip, H.M.; Rustad, S. 1984. **Variations in surface water pH with changes in sulfur deposition**. Water Air and Soil Pollution. 21: 217-223.

U.S. Department of Agriculture, Soil Conservation Service. 1975. **Soil taxonomy a basic system of soil classification for making and interpreting soil surveys**. Agric. Handb. 436. Washinton, DC: U.S. Department of Agriculture, Soil Conservation Service. 754 p.

U.S. Environmental Protection Agency. 1983 (revised). **Methods of chemical anaysis of water and wastes**. EPA-600, 4-79-0.20. Cincinnati, OH. 625 p.

U.S. Environmental Protection Agency. 1986. **National surface water survey, eastern lake survey (phase 1 - synoptic chemistry), Analytical Methods Manual**. EPA-600, 4-86-009. U.S. EPA, Las Vegas, NV: U.S. EPA. 180 p.

White, G.N.; Feldman, S.B.; Zelazny, L.W. 1988. **Rates of nutrient release by mineral weathering**. Tech. Bull. 542. New York, NY: National Council of Paper Industries, Air Stream Improvement. 66 p.

Harris, A. Ray; Stone, Douglas M.
1992. **Ion movement in acidified, low base saturated sand soils**.
Res. Pap. NC-305. St. Paul, MN: U.S. Department of Agriculture,
Forest Service, North Central Forest Experiment Station. 7 p.

Describes factors causing cation export in leachate in low base saturated forested sand soils. Reports the effects of varying acid precipitation and litter-humus treatments on ion movement and interaction.

KEY WORDS: ANC, acid precipitation, nitrification, cation movement.