

## Forest soil solutions: Acid/base chemistry and response to calcite treatment

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**Abstract.** Soil solution chemistry was investigated at a forested watershed draining into Woods Lake, N.Y. as part of the Experimental Watershed Liming Study (EWLS). The objective of this study was to assess the response of soil water to watershed treatment of calcite ( $\text{CaCO}_3$ ). This material was applied in an effort to mitigate the effects of acidic atmospheric deposition. Soil solutions draining Oa and Bs horizons in reference subcatchments were characterized by low pH and acid neutralizing capacity (ANC) due to elevated concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and organic anions relative to the sum of base cation ( $C_B$ :  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) concentrations. Seasonal and spatial variation of pH and ANC in soil solutions appeared to be largely controlled by variations in the concentrations of dissolved organic acids which, in turn, were regulated by reactions of Al with soil organic matter. Nitrate was positively correlated and  $\text{SO}_4^{2-}$  was negatively correlated with  $\text{Ca}^{2+}$  and Al concentrations in reference soil solutions, indicating that changes in  $\text{NO}_3^-$  influences spatial and seasonal variations in  $\text{Ca}^{2+}$  and Al concentrations. On this basis,  $\text{NO}_3^-$  appears to be important in soil acidification and the dynamics of drainage water acidity. Comparison of our results with historical data for the site showed declines in concentrations of  $\text{SO}_4^{2-}$ , which are consistent with decreases in emissions of  $\text{SO}_2$  in the eastern U.S. and atmospheric deposition of  $\text{SO}_4^{2-}$  to the Adirondack region. Mineral soil solutions have shown large increases in concentrations of  $\text{NO}_3^-$ . Declines in concentrations of  $C_B$  and increases in concentrations of Al have occurred over the last ten years, suggesting depletion of soil pools of exchangeable basic cations and increased sensitivity to acidic deposition. Calcite ( $\text{CaCO}_3$ ) treatment of 6.89 Mg/ha resulted in a significant increase of  $\text{Ca}^{2+}$ , ANC and pH in both Oa and Bs horizon soil solutions. Soil water response to  $\text{CaCO}_3$  addition was most evident during the first year after treatment, apparently due to macropore transport of particulate and dissolved  $\text{CaCO}_3$ . However, increases in ANC and pH in the mineral soil waters were not sustained and appeared insufficient to result in substantial improvement in surface water quality over the 43 month study period.

### Introduction

Atmospheric deposition of strong acids may result in the acidification of surface waters draining acid-sensitive watersheds. These watersheds are generally characterized by shallow surficial deposits and acidic soils that have limited ability to neutralize strong acid inputs by the supply of base cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{K}^+$ ) from mineral weathering and/or cation

exchange reactions and/or retention of strong acid anions (e.g.,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) by biogeochemical processes. As a result, strong acid inputs are not completely neutralized resulting in elevated concentrations of  $\text{H}^+$  and Al in soil waters which are ultimately transported to surface waters. High concentrations of  $\text{H}^+$  and Al may have deleterious effects on aquatic biota and water quality (Cronan & Schofield 1979; Baker & Schofield 1982; Baker et al. 1990; Driscoll & Postek 1995).

The addition of alkaline materials such as calcite ( $\text{CaCO}_3$ ; liming) has been a common practice historically for counteracting surface water acidity (Fraser et al. 1982). In most applications, the alkaline material has been applied directly to acidic lakes to increase acid neutralizing capacity (ANC) and pH (Olem 1990). However, continued inputs of acidic drainage waters result in the reacidification of base-treated lakes, so the duration of treatment is largely a function of lake hydraulic retention time (Wright 1985). Direct lake treatment also has limited ability to neutralize the near shore region of lakes during episodic run-off (Booth et al. 1986; Gubala et al. 1991; Porcella et al. 1991; Rosseland & Hindar 1991) and therefore may be unable to protect fish spawning areas. Alternatively, by adding alkaline material to watershed soils it is possible to neutralize acidic drainage waters prior to emergence as surface water (Hindar & Rosseland 1991; Dalziel et al. 1991; Stoner & Donald 1991) and increase pools of exchangeable base cations in soil (Warfvinge 1988).

Previous studies in the northeastern U.S. have shown that variations in hydrologic flow path is an important factor regulating the acid-base chemistry of surface waters (Chen et al. 1984; Driscoll et al. 1991). Acidic lakes are generally located in watersheds characterized by thin deposits of surficial materials and the resulting hydrology exhibits shallow flow paths. In these lake/watershed systems, the upper soil horizons play an important role in regulating the release of acidity or ANC to other compartments within the ecosystem (i.e., lower mineral soil, stream, lake). Calcite application may be effective in these watersheds since treatment is typically confined to the upper soil horizons (Lathwell & Reid 1984).

The objective of this study was to identify the solutes which most strongly influence the acid/base chemistry of soil waters and to assess the effects of  $\text{CaCO}_3$  addition on soil solution chemistry in soil horizons. Soil solution chemistry in both untreated and treated forest plots was studied over a period of 43 months to evaluate the effects of  $\text{CaCO}_3$  treatment. A detailed description of the experimental treatment is provided in Driscoll et al. (1996, this volume).

## Methods

### *Site Description*

Soils in the Woods Lake Watershed consist of well drained to poorly drained Spodosols (Becket Series Haplorthods, Fragiorthods and Haplaquods; Cronan 1985). Vegetation is predominantly deciduous (88% watershed cover) with some coniferous stands (5% watershed cover) located along the perimeter of the lake (Cronan 1985). The watershed has been divided into five subcatchments based on topography and surface drainage (Driscoll et al. 1996, this volume). Subcatchments II and IV were selected for  $\text{CaCO}_3$  treatment because of their large hydrologic contribution to the lake. Subcatchments I and V were used for reference areas. Calcite was applied by helicopter in October, 1989, with an average dose of 6.89 Mg (million grams) /ha measured at the treated subcatchments during the manipulation (Driscoll et al. 1996, this volume).

Soil conditions on the southeast and northwest sides of the lake basin differ markedly. The northwest subcatchments (I, II and III) are drier because of the thicker surficial materials and southerly exposure. The soil has a prominent Spodosol character with a thick (10 to 20 cm), highly acidic organic horizon, and distinct E (3 to 6 cm) and B horizons. Subcatchment IV often exhibits saturated soil conditions due to shallow depth to bedrock (approximately 1 meter) and northerly exposure. Soils in this subcatchment often have indistinct horization (E horizon generally absent) and groundwater is frequently located at or near ground surface. Subcatchment V has intermediate dryness and soil horization. As a result of shallow soil depth, the southeast side of the basin also has numerous wind thrown trees.

### *Soil Solution Sampling*

Soil solutions were collected in zero-tension lysimeters that were constructed and installed according to methods described by Driscoll et al. (1989). Lysimeter trays were positioned at variable depths depending on horizon thickness below the Oa and within the upper Bs horizon. At each lysimeter site, three to four replicate lysimeters were used to sample Oa and Bs soil solutions. A total of 15 lysimeter collection sites were established for the study (Fig. 1).

Soil solutions were extracted from each lysimeter using a vacuum hand pump. Samples collected from individual lysimeters were composited for each horizon. Five hundred mL and 60 mL composite samples were then collected for chemical analysis. Soil solution was sampled at three-week intervals from April, 1989 through May, 1990. The sampling frequency was relaxed to six-week intervals during the remainder of 1990 since composition

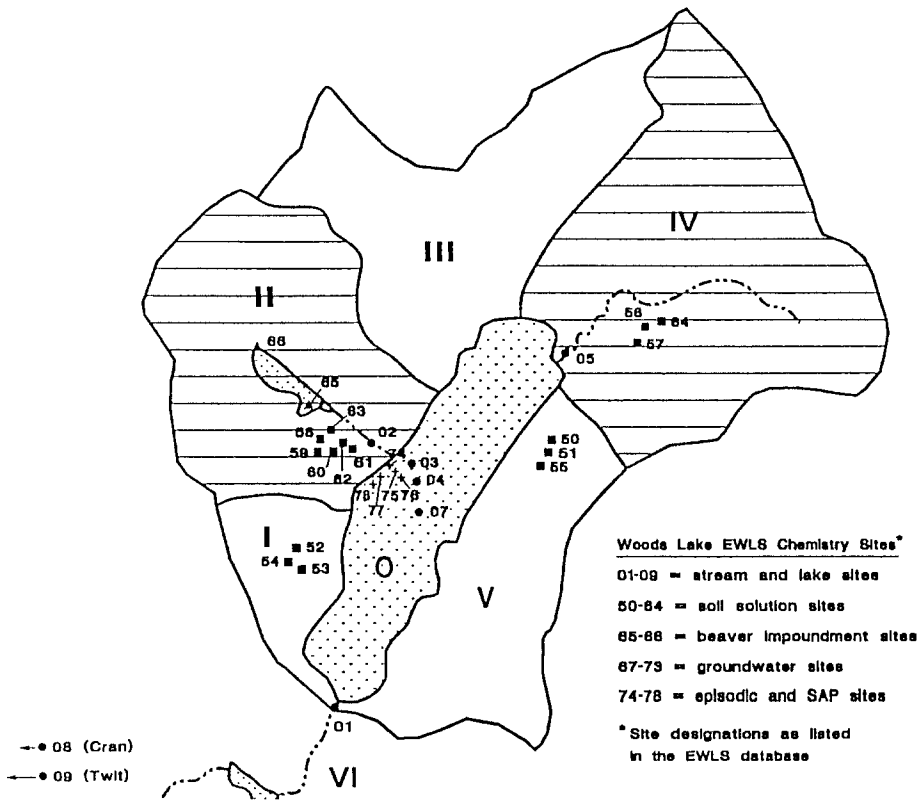


Fig. 1. The subcatchments of Woods Lake watershed. Subcatchments I and V are reference sites. Subcatchments II and IV were treated with calcite in October 1989.

did not change rapidly with time. Soil solutions were sampled once during winter, 1991 and quarterly thereafter until the conclusion of sampling in fall, 1992.

### Analytical Methods

After collection, samples were transported to Syracuse University for analyses. Each soil lysimeter sample was analyzed for all major solutes. A detailed description of the analytical methods used in this study is provided in Driscoll et al. (1996, this volume). Concentrations of naturally occurring organic anions were estimated by the discrepancy in charge balance of solutes measured in individual soil solutions (Driscoll et al. 1989; 1994).

### *Data Analysis*

Statistical analyses were performed using Statistical Analysis Systems (SAS Institute, Inc.) software. Simple statistics (i.e. number of observations, mean, standard deviation, maximum and minimum) were computed for each subcatchment using data from all lysimeter locations in that particular subcatchment. The calculations were grouped into discrete time intervals corresponding to the time following  $\text{CaCO}_3$  treatment. Frequency distributions of soil water solutes were initially tested for normality. Reference and treated subcatchments were tested individually using frequency plots and the Shapiro-Wilk test. Only dissolved  $\text{H}_4\text{SiO}_4$  concentrations in reference soil solution were distributed normally. Scatter plots were also developed for selected pairs of soil solution solutes to determine the linearity of relationship. In most instances, a non-linear relationship was observed. Non-parametric methods were used for comparison and correlation analysis because of the absence of normal frequency distributions and linear interrelationships. Spatial and temporal variability including the effects of  $\text{CaCO}_3$  treatment were assessed using the Wilcoxon Rank Sum test for independent group comparison (i.e., Oa vs. Bs solutions, or comparison of different sites) and the Wilcoxon Signed Rank test for paired group comparison (i.e., same site horizon before and after treatment). The response of soil solutions to the calcite treatment was assessed by performing comparison testing of soil water in both reference and treated subcatchments before and after treatment. Treatment effects were concluded to be significant only when differences in solute trends were exhibited between soil solutions collected in reference and treated subcatchments. Comparison testing was performed at a 0.05 level of significance. Correlation between solutes in soil water was performed by calculating Spearman Rank correlation coefficients ( $r_s$ ).

## **Results and discussion**

### *Reference Soil Solution Chemistry*

#### *Horizontal Patterns*

Reference Oa and Bs horizon soil solutions in the Woods Lake watershed (Table 1; Fig. 2) generally exhibited patterns characteristic of Spodosols impacted by atmospheric deposition in the northeastern U.S. (David and Driscoll 1984; Driscoll et al. 1985; Cronan 1985). Soil solutions draining the Oa horizon had low pH and ANC due to elevated concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and naturally occurring organic anions relative to concentrations of base cations. Sulfate and  $\text{NO}_3^-$  were the dominant anionic species comprising

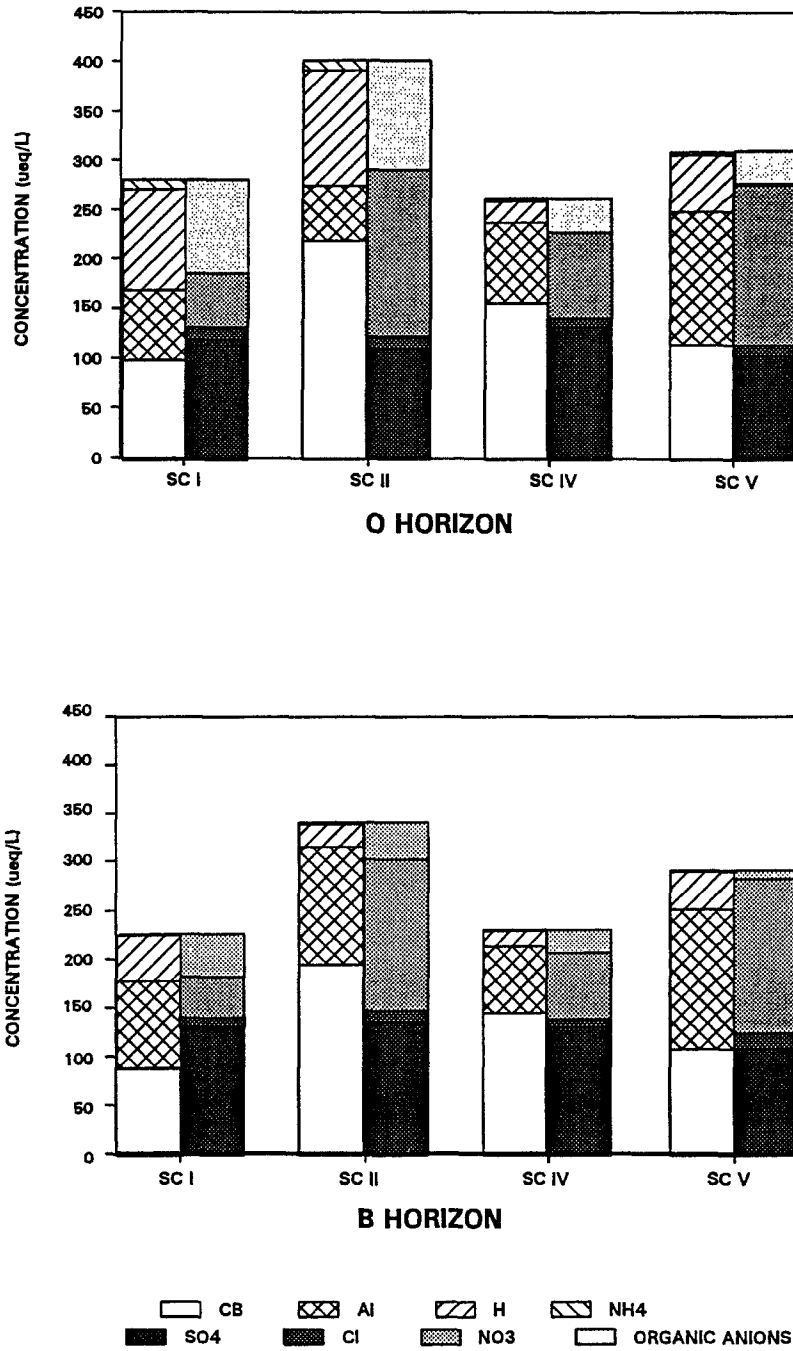


Fig. 2. Charge balances of Oa and Bs horizon soil solutions for each of the subcatchments monitored prior to calcite treatment.

on average 39% and 37% of the total anionic charge, while organic anions comprised 21%. The sum of base cations ( $C_B$ ) accounted for 47% of the total cationic charge, and Al and  $H^+$  comprised 28% and 23% respectively. Oa horizon leachate also had high concentrations of dissolved  $H_4SiO_4$  suggesting that this horizon is an important zone of weathering and this process may be important in supplying dissolved  $H_4SiO_4$  and associated base cations to the ecosystem.

pH and ANC increased as solutions were transported from the forest floor into mineral soil (Bs), primarily as a result of DOC removal (from a mean value of  $940 \mu\text{mol C/L}$  to  $480 \mu\text{mol C/L}$ ). This process resulted in a decrease in the total anionic charge in soil solution from 296 to  $260 \mu\text{eq/L}$  and altered the anionic charge distribution to 48%, 37% and 11% for  $SO_4^{2-}$ ,  $NO_3^-$  and organic anions, respectively. The  $C_B$  concentrations were approximately the same in Oa and Bs horizon soil solutions, and comprised about the same proportion of cationic charge (47%). Concentrations of Al increased (38% of cationic charge) and  $H^+$  ion concentration decreased (12% of cationic charge) in soil waters from the Oa to Bs horizons. The release of Al from the mineral soil to soil water was also partially responsible for the increase in pH and ANC in Bs horizon soil solutions.

While soil water concentrations of Al increased in the mineral horizon, values were not markedly greater than concentrations in the organic horizon. The source of Al in the forest floor is not known with any certainty (Driscoll et al. 1985). Possible sources that have been cited include throughfall, root and leaf litter, and mixing with mineral soil through physical disturbance (Driscoll et al. 1989). Measurements of total monomeric aluminum (Alm) in throughfall at Woods Lake were characterized by very low concentrations ( $1.2 \pm 0.46 \mu\text{mol/L}$ , mean  $\pm$  SD), largely occurring as organic monomeric aluminum (Alo) ( $1.0 \pm 0.4 \mu\text{mol/L}$ ; C.T. Driscoll unpublished data). As mentioned previously, high concentrations of dissolved  $H_4SiO_4$  exist in forest floor soil solutions. These are also suggestive of mineral supply in the forest floor. Another potentially important source of Al and possibly dissolved  $H_4SiO_4$  to the forest floor, especially in hydrologic source areas, is transport from the lower mineral horizon by groundwater (Fig. 3). This transport mechanism may also play an important role in drier areas that become temporarily saturated during snowmelt. Support for this process is evident by comparison of soil solution chemistry in the more well-drained subcatchments (I and II) with the wetter subcatchments (IV and V) at Woods Lake watersheds. Our results generally show higher concentrations of Al in Oa horizon solutions in soils of subcatchments IV and V, which are often saturated (Table 1).

Table 1. Mean solute concentrations in soil water (in  $\mu\text{mol/L}$ , except pH and ANC ( $\mu\text{eq/L}$ )) during four intervals in the Experimental Watershed Liming Study (EWLS). Data are shown for reference (I and V) and calcite treated (II and IV) subcatchments. The intervals were selected to correspond to the periods before treatment (4/89–9/89), immediately after treatment (1/89–3/90), an intermediate time after treatment (6/90–12/90) and a longer time after treatment (9/91–10/92). Standard deviations appear in parentheses. The number of observations (n) is given at the top of each column.

O Horizon Reference

Parameter	Subcatchment I (Reference)					Subcatchment V (Reference)				
	Calcite Applied to Subcatchments II & IV during 10/89					Calcite Applied to Subcatchments II & IV during 10/89				
	4/89 to 9/89 n=7-10	11/89 to 3/90 n=9-10	6/90 to 12/90 n=4-15	9/91 to 10/92 n=12-18	4/89 to 9/89 n=8-12	11/89 to 3/90 n=7-9	6/90 to 12/90 n=4-11	9/91 to 10/92 n=6-10		
ANC	-123.6 (43.8)	-114.6 (27.8)	-124.3 (40.9)	-118.1 (30.7)	-102.5 (85.7)	-43.5 (46.5)	-67.0 (30.8)	-63.4 (28.3)		
pH	3.96 (0.16)	3.99 (0.11)	3.96 (0.14)	3.99 (0.11)	4.11 (0.29)	4.31 (0.21)	4.31 (0.21)	4.19 (0.26)		
DOC	1706.7 (824.9)	1402.4 (755.1)	1292.7 (564.2)	1436.5 (545.1)	430.7 (137.6)	513.6 (376.5)	502.5 (228.0)	875.8 (394.2)		
SO <sub>4</sub> <sup>2-</sup>	71.8 (15.0)	61.2 (9.8)	61.3 (19.7)	60.9 (7.3)	60.1 (12.5)	51.6 (5.6)	45.0 (4.7)	56.6 (7.2)		
Cl <sup>-</sup>	26.3 (18.1)	17.2 (10.2)	6.2 (2.8)	11.2 (4.9)	8.8 (4.2)	11.9 (2.6)	12.1 (20.8)	11.0 (2.1)		
NO <sub>3</sub> <sup>-</sup>	67.2 (31.0)	53.1 (37.8)	52.8 (32.2)	17.7 (8.0)	200.4 (79.4)	194.4 (96.9)	154.4 (72.2)	70.5 (46.8)		
NH <sub>4</sub> <sup>+</sup>	17.6 (17.1)	14.5 (20.7)	14.2 (13.1)	7.0 (8.0)	3.8 (4.2)	3.7 (4.8)	1.7 (2.6)	7.9 (7.6)		
Na <sup>+</sup>	17.5 (6.7)	23.6 (7.5)	15.6 (7.0)	15.9 (6.0)	19.0 (5.8)	19.5 (6.8)	17.8 (12.9)	16.0 (5.6)		
K <sup>+</sup>	22.2 (17.3)	6.8 (2.5)	14.7 (16.7)	8.2 (9.2)	21.2 (12.1)	13.3 (9.7)	20.9 (11.5)	15.8 (13.3)		
Ca <sup>2+</sup>	34.4 (14.2)	26.6 (10.9)	29.6 (11.6)	22.1 (7.2)	33.5 (13.2)	41.4 (14.7)	34.6 (10.3)	26.3 (3.4)		
Mg <sup>2+</sup>	7.6 (2.0)	6.6 (1.6)	7.1 (2.8)	4.9 (1.3)	7.1 (3.2)	7.4 (1.6)	7.7 (1.8)	13.3 (1.4)		
Al <sub>im</sub>	27.1 (12.2)	31.7 (6.9)	27.0 (9.2)	25.5 (5.4)	57.6 (16.4)	60.6 (22.1)	55.3 (18.2)	30.4 (10.6)		
Al <sub>o</sub>	15.9 (5.2)	16.3 (5.0)	13.7 (4.6)	13.7 (4.4)	12.0 (8.7)	10.7 (8.7)	8.0 (2.8)	9.5 (4.2)		
H <sub>4</sub> SiO <sub>4</sub>	70.1 (20.6)	89.8 (14.5)	65.3 (22.4)	81.3 (22.7)	66.7 (27.7)	94.8 (14.9)	70.0 (17.1)	76.9 (14.3)		



Table 1 (continued)  
O Horizon Treatment

Parameter	Subcatchment II (Treated)				Subcatchment IV (Treated)			
	4/89 to 9/89 n=2-5	11/89 to 3/90 n=15-16	6/90 to 12/90 n=7-20	9/91 to 10/92 n=12-17	4/89 to 9/89 n=9-18	11/89 to 3/90 n=12	6/90 to 12/90 n=5-15	9/91 to 10/92 n=12-18
ANC	-207.0 (107.9)	-85.8 (108.4)	-218.7 (44.0)	-138.2 (49.2)	-26.1 (19.7)	4.7 (33.4)	-18.6 (9.6)	0.4 (9.7)
pH	3.79 (0.25)	4.32 (0.91)	3.68 (0.07)	3.94 (0.20)	4.45 (0.14)	4.85 (0.64)	4.53 (0.10)	4.67 (0.07)
DOC	2317.8 (929.6)	2077.6 (1293.1)	2449.0 (1035.7)	2225.3 (500.9)	315.5 (181.8)	282.8 (102.1)	319.7 (152.4)	360.4 (131.0)
SO <sub>4</sub> <sup>2-</sup>	83.2 (23.6)	80.3 (25.1)	53.3 (17.4)	56.7 (11.7)	72.8 (9.0)	70.3 (16.3)	61.4 (6.3)	72.8 (8.5)
Cl <sup>-</sup>	22.2 (16.8)	24.5 (20.4)	4.8 (2.8)	12.4 (5.7)	8.6 (6.3)	14.0 (9.9)	5.4 (2.2)	10.0 (3.1)
NO <sub>3</sub> <sup>-</sup>	318.0 (132.4)	284.6 (145.5)	161.5 (114.6)	4.7 (29.4)	74.4 (39.1)	115.8 (34.7)	103.6 (78.0)	29.2 (17.7)
NH <sub>4</sub> <sup>+</sup>	27.3 (13.2)	7.8 (5.6)	1.3 (10.5)	14.3 (14.8)	4.7 (10.2)	2.8 (4.4)	7.0 (10.0)	3.8 (5.6)
Na <sup>+</sup>	57.4 (52.2)	37.4 (44.8)	20.9 (19.5)	17.5 (13.3)	26.4 (13.0)	25.0 (4.1)	17.9 (5.2)	13.5 (4.8)
K <sup>+</sup>	36.8 (26.5)	2.0 (15.0)	36.8 (13.3)	22.2 (13.0)	11.6 (11.3)	8.4 (2.9)	8.1 (4.4)	3.7 (1.7)
Ca <sup>2+</sup>	37.1 (15.1)	135.1 (99.3)	67.7 (45.3)	42.9 (24.2)	23.4 (6.0)	51.2 (26.0)	73.2 (50.0)	54.1 (20.1)
Mg <sup>2+</sup>	11.9 (4.3)	20.1 (8.6)	15.1 (4.6)	11.8 (5.0)	5.8 (1.6)	7.3 (1.9)	8.9 (3.1)	6.1 (0.7)
Alm	52.6 (17.4)	27.3 (2.7)	18.7 (14.9)	13.1 (5.9)	34.6 (7.5)	37.5 (22.1)	30.0 (10.7)	18.4 (6.0)
Alo	28.9 (8.5)	14.0 (7.3)	11.6 (5.1)	10.3 (4.0)	6.4 (2.0)	4.3 (1.6)	5.4 (1.8)	3.5 (1.7)
H <sub>4</sub> SiO <sub>4</sub>	108.5 (32.1)	151.5 (45.3)	203.8 (24.5)	172.1 (38.5)	62.9 (10.8)	95.8 (13.7)	99.9 (17.1)	89.8 (20.6)

Table 1 (continued)  
B Horizon Reference

Parameter	Subcatchment I (Reference)					Subcatchment V (Reference)						
	Calcite Applied to Subcatchments II & IV during 10/89					Calcite Applied to Subcatchments II & IV during 10/89						
	4/89 to 9/89 n=5-9	11/89 to 3/90 n=9-10	6/90 to 12/90 n=4-14	9/91 to 10/92 n=12-18	4/89 to 9/89 n=10-12	11/89 to 3/90 n=8-9	6/90 to 12/90 n=5-11	9/91 to 10/92 n=6-10	4/89 to 9/89 n=10-12	11/89 to 3/90 n=8-9	6/90 to 12/90 n=5-11	9/91 to 10/92 n=6-10
ANC	-32.5 (30.4)	-43.1 (30.0)	-51.9 (36.6)	-36.5 (24.0)	-36.0 (19.8)	-15.9 (6.0)	-32.9 (18.6)	-11.65 (11.8)	4.33 (0.11)	4.45 (0.07)	4.37 (0.11)	4.57 (0.08)
pH	4.40 (0.06)	4.32 (0.16)	4.30 (0.19)	4.38 (0.14)	4.33 (0.11)	4.45 (0.07)	4.37 (0.11)	4.57 (0.08)	381.6 (211.8)	329.3 (94.5)	393.5 (137.0)	352.0 (124.5)
DOC	651.4 (117.6)	609.8 (121.5)	629.3 (171.4)	652.1 (139.2)	381.6 (211.8)	329.3 (94.5)	393.5 (137.0)	352.0 (124.5)	59.9 (12.0)	55.9 (9.3)	45.7 (4.6)	63.2 (4.0)
SO <sub>4</sub> <sup>2-</sup>	80.3 (12.5)	68.4 (10.2)	59.4 (9.2)	66.7 (5.6)	59.9 (12.0)	55.9 (9.3)	45.7 (4.6)	63.2 (4.0)	10.9 (7.0)	11.2 (2.5)	10.2 (16.3)	11.1 (2.5)
Cl <sup>-</sup>	14.8 (10.7)	9.8 (3.0)	5.5 (2.2)	10.2 (3.7)	10.9 (7.0)	11.2 (2.5)	10.2 (16.3)	11.1 (2.5)	238.5 (127.9)	213.6 (145.0)	148.4 (47.1)	70.9 (40.9)
NO <sub>3</sub> <sup>-</sup>	37.6 (26.5)	43.2 (35.9)	41.3 (29.0)	15.2 (20.0)	238.5 (127.9)	213.6 (145.0)	148.4 (47.1)	70.9 (40.9)	3.0 (0.7)	1.7 (1.2)	1.9 (2.7)	2.4 (1.2)
NH <sub>4</sub> <sup>+</sup>	4.4 (4.7)	0.9 (0.6)	0.4 (0.7)	3.0 (2.0)	1.7 (1.2)	3.9 (4.6)	2.7 (2.7)	2.4 (1.2)	21.0 (3.7)	21.4 (2.0)	21.2 (13.8)	20.0 (4.3)
Na <sup>+</sup>	24.5 (5.4)	24.6 (4.7)	24.4 (5.2)	21.3 (4.2)	21.0 (3.7)	21.4 (2.0)	21.2 (13.8)	20.0 (4.3)	14.0 (5.3)	10.2 (7.4)	16.5 (7.2)	11.8 (3.7)
K <sup>+</sup>	11.8 (15.0)	4.2 (2.6)	7.9 (5.2)	2.9 (1.9)	14.0 (5.3)	10.2 (7.4)	16.5 (7.2)	11.8 (3.7)	31.0 (10.3)	33.1 (7.1)	30.5 (5.0)	24.3 (2.1)
Ca <sup>2+</sup>	25.2 (6.7)	22.6 (6.2)	25.4 (8.7)	19.6 (4.2)	31.0 (10.3)	33.1 (7.1)	30.5 (5.0)	24.3 (2.1)	6.6 (3.1)	6.7 (1.7)	7.2 (1.4)	14.9 (2.1)
Mg <sup>2+</sup>	7.4 (2.9)	6.0 (1.7)	6.8 (1.8)	5.0 (0.9)	6.6 (3.1)	6.7 (1.7)	7.2 (1.4)	14.9 (2.1)	54.1 (16.8)	57.4 (21.3)	54.6 (14.9)	31.2 (9.7)
Al <sub>im</sub>	35.8 (13.0)	35.6 (9.0)	36.3 (8.8)	29.5 (5.7)	54.1 (16.8)	57.4 (21.3)	54.6 (14.9)	31.2 (9.7)	7.0 (2.8)	5.6 (2.1)	7.0 (3.3)	4.0 (2.2)
Al <sub>o</sub>	12.8 (2.4)	10.3 (2.7)	10.4 (1.9)	8.3 (2.9)	7.0 (2.8)	5.6 (2.1)	7.0 (3.3)	4.0 (2.2)	69.4 (19.9)	90.2 (15.0)	75.5 (20.5)	88.2 (19.6)
H <sub>2</sub> SiO <sub>4</sub>	69.9 (17.8)	86.8 (10.5)	65.8 (2.8)	80.0 (29.8)	69.4 (19.9)	90.2 (15.0)	75.5 (20.5)	88.2 (19.6)				

Table I (continued)  
B Horizon Treatment

Parameter	Subcatchment II (Treated)						Subcatchment IV (Treated)					
	Calcite Applied to Subcatchments II & IV during 10/89			Calcite Applied to Subcatchments II & IV during 10/89			Calcite Applied to Subcatchments II & IV during 10/89			Calcite Applied to Subcatchments II & IV during 10/89		
	4/89 to 9/89 n=3-5	11/89 to 3/90 n=12	6/90 to 12/90 n=4-17	9/91 to 10/92 n=12-17	4/89 to 9/89 n=7-12	11/89 to 3/90 n=10-12	6/90 to 12/90 n=5-15	9/91 to 10/92 n=12-18	4/89 to 9/89 n=7-12	11/89 to 3/90 n=10-12	6/90 to 12/90 n=5-15	9/91 to 10/92 n=12-18
ANC	-48.7 (20.9)	20.3 (71.9)	-31.6 (46.2)	-23.4 (30.0)	-25.9 (13.1)	7.7 (18.1)	-5.3 (12.5)	1.2 (8.5)				
pH	4.18 (0.16)	5.22 (1.00)	4.50 (0.59)	4.47 (0.18)	4.45 (0.10)	5.10 (0.73)	4.79 (0.46)	4.72 (0.07)				
DOC	1082.8 (345.0)	664.6 (253.8)	612.8 (387.3)	1092.4 (799.4)	235.8 (49.2)	185.7 (55.2)	247.1 (137.6)	250.6 (23.7)				
SO <sub>4</sub> <sup>2-</sup>	77.3 (15.8)	86.4 (23.7)	64.5 (10.6)	68.3 (10.7)	74.8 (8.5)	65.7 (5.4)	59.5 (6.0)	75.3 (7.2)				
Cl <sup>-</sup>	15.8 (11.7)	1.6 (6.0)	6.0 (3.5)	11.5 (4.2)	12.0 (7.3)	10.2 (2.0)	4.6 (1.2)	9.4 (1.1)				
NO <sub>3</sub> <sup>-</sup>	225.7 (66.9)	125.8 (63.9)	206.0 (135.5)	62.0 (122.6)	57.4 (18.1)	81.1 (33.3)	75.1 (45.3)	29.2 (21.9)				
NH <sub>4</sub> <sup>+</sup>	7.9 (7.7)	2.6 (2.2)	3.0 (3.3)	4.3 (2.7)	3.4 (5.2)	2.9 (5.7)	0.6 (0.9)	2.2 (1.9)				
Na <sup>+</sup>	32.7 (10.6)	30.0 (9.5)	24.9 (9.2)	21.1 (14.5)	24.8 (7.2)	23.5 (5.3)	20.1 (4.2)	15.7 (1.9)				
K <sup>+</sup>	19.6 (5.0)	17.0 (3.1)	26.2 (21.8)	15.2 (11.7)	6.6 (2.2)	6.6 (2.8)	6.9 (2.7)	3.9 (1.6)				
Ca <sup>++</sup>	49.5 (25.0)	90.9 (46.2)	67.4 (52.2)	29.0 (10.8)	22.7 (5.1)	60.4 (32.5)	58.3 (38.9)	48.8 (13.5)				
Mg <sup>++</sup>	17.1 (7.8)	17.1 (3.1)	17.1 (6.7)	9.5 (2.8)	5.2 (0.7)	7.1 (1.7)	8.6 (3.5)	6.4 (0.6)				
Alm	67.5 (3.8)	36.5 (31.9)	55.3 (31.8)	39.0 (19.9)	35.6 (0.6)	27.5 (24.3)	28.8 (12.5)	20.2 (7.6)				
Alo	2.0 (7.7)	11.1 (6.7)	12.3 (5.8)	12.3 (5.2)	6.0 (1.4)	3.2 (1.6)	4.2 (1.5)	2.4 (1.1)				
H <sub>2</sub> SiO <sub>4</sub>	125.9 (53.5)	183.1 (37.4)	182.9 (6.7)	177.6 (29.4)	68.3 (8.1)	84.3 (9.5)	95.8 (9.7)	96.5 (13.1)				

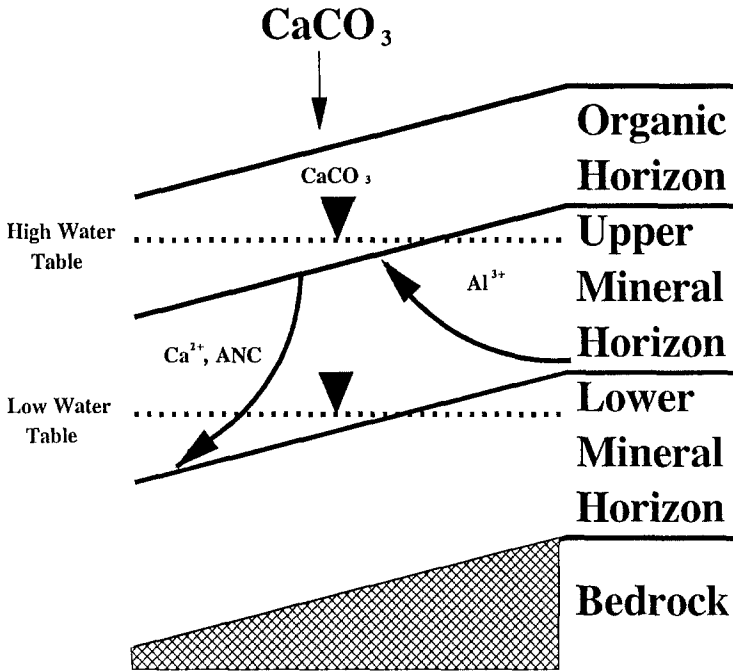


Fig. 3. Conceptual diagram illustrating the movement of water from the mineral soil upward to the organic horizon with increasing water table. This transport process may supply Al from the mineral soil to the forest floor. Wetting of the forest floor also facilitates the dissolution of  $\text{CaCO}_3$ .

#### *Spatial and Seasonal Patterns in Soil Solution Acidity*

While on the basis of charge balance,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  make greater contributions to ambient soil solution acidity in the Oa and Bs horizons, correlation testing patterns indicate that variations in concentrations of organic solutes (i.e., DOC) are most responsible for the spatial and temporal patterns in pH and ANC observed at the Woods Lake watershed. Analysis of data from all lysimeter sites in both soil horizons demonstrated a strong negative correlation of DOC with pH (Oa,  $r_s = -0.87$ ; Bs,  $r_s = -0.57$ ) and ANC (Oa,  $r_s = -0.86$ ; Bs,  $r_s = -0.54$ ). Correlation was greater in the Oa horizon due to the greater variation in DOC concentrations in this horizon. Correlation between these parameters was generally lower at individual lysimeter sites, suggesting spatial factors exert greater control over soil solution DOC concentration than temporal factors. Cronan & Aiken (1985) noted the importance of DOC in influencing the acidity of soil solutions in forested watersheds in the Adirondack Park, New York. Organic acids have also been implicated in the acidification of low ionic strength surface waters (Driscoll et al. 1989; 1994), although their mobility is thought to be limited in the Woods Lake

watershed (Cronan 1985) and organic anion concentrations were lower than  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  in Woods Lake (Driscoll et al. 1996, this volume).

Spatial variability of soil solution DOC concentrations appeared to be most strongly influenced by soil moisture. Since soil moisture was relatively uniform within each subcatchment, variation in soil solution acidity occurred mainly between subcatchments. Subcatchments I and II, which have southerly exposure and thicker surficial soils, are drier and have thicker organic horizons. Consequently, DOC concentrations were greater in both Oa and Bs horizon soil solutions resulting in elevated acidity. Soils in subcatchments IV and V were significantly wetter due to northerly exposure and shallow soil depth. The DOC concentrations of soil solutions in these subcatchments appeared to decrease primarily by dilution. James & Riha (1987) noted that the mass of DOC leached from the forest floor was largely independent of the soil solution/soil ratio, which was attributed to the relative kinetic inertness of soil organic matter.

Seasonal patterns of DOC concentrations in Oa and Bs horizon soil solutions also appear to result from variations in soil moisture, although elevated concentrations in the fall may be the result of decomposition of fresh leaf litter. Soil solution DOC concentrations were highest during summer and fall, when soil moisture is lowest, and lowest during winter, snowmelt and spring, when soil moisture is highest (Figs. 4 and 5). Correspondingly,  $\text{H}^+$  concentrations in soil solutions were greatest during summer and fall, and decreased during winter, snowmelt and spring. This pattern was not as apparent in subcatchment II, because high soil moisture persisted throughout the year and diminished temporal variation.

It has been suggested that organic acids are important in the transport of Al to the mineral soil due to the high affinity of organic solutes for Al (David & Driscoll 1984; Cronan & Aiken 1985). However, this process can also be viewed from a different perspective whereby Al retards the release of organic acids from organic horizons. Schnitzer & Skinner (1963) demonstrated that Al-organic matter complexes become increasingly insoluble as Al content increases. In our study it was observed that higher Al concentrations generally occurred in soil waters having lower DOC concentrations. These solutes were negatively correlated in both soil horizons (Oa,  $r_s = -0.61$ ; Bs,  $r_s = -0.19$ ). Soil solution concentrations of Al were generally lower in subcatchments I and II, which were characterized by elevated DOC concentrations (Table 1). Conversely, in subcatchments IV and V soil water concentrations of Al were elevated with lower DOC concentrations. Therefore, by constraining the DOC content of forest soil water, Al may also exert some influence over its acidity other than through hydrolysis reactions.

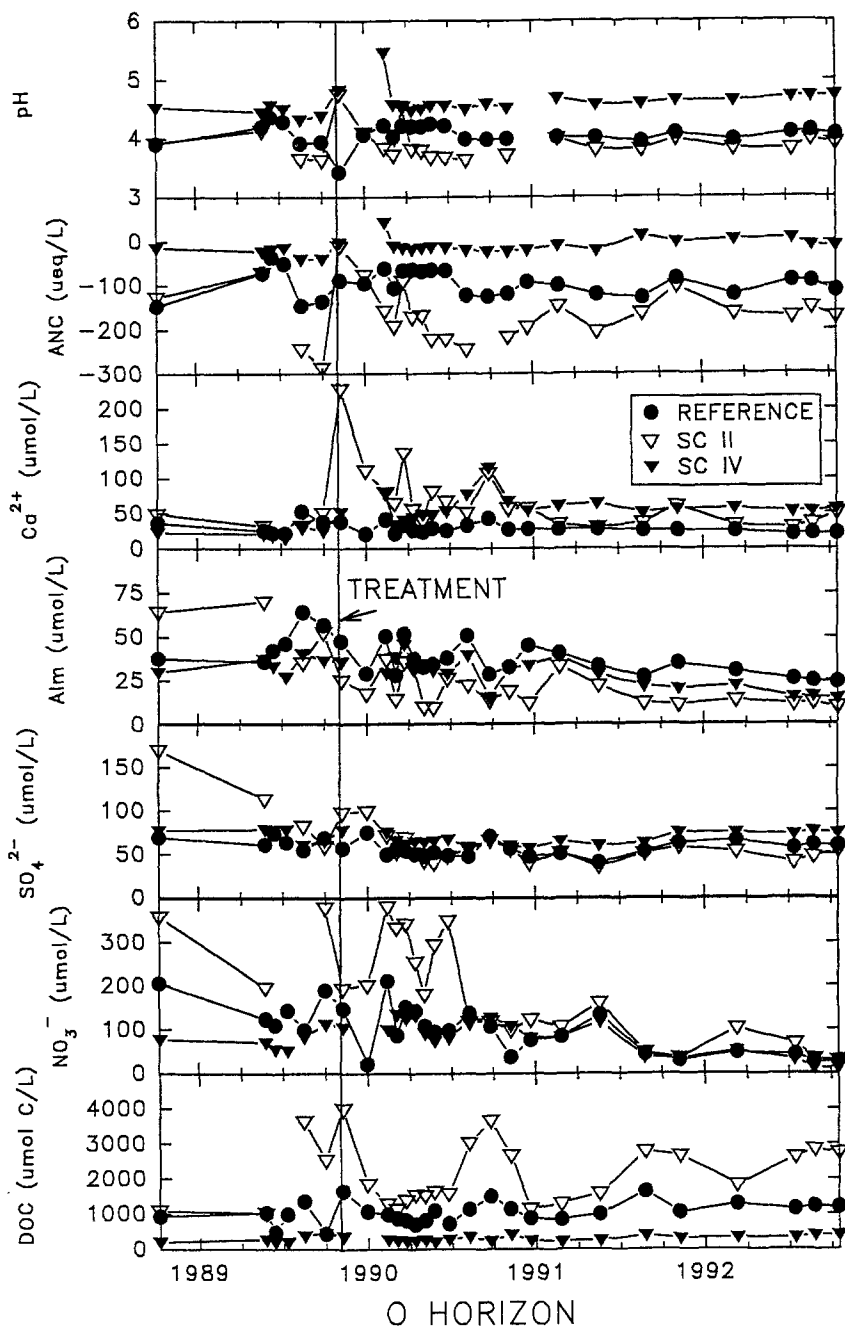


Fig. 4. Time-series of solute concentrations in Oa horizon soil waters for reference (I, V) and  $\text{CaCO}_3$ -treated (II, IV) subcatchments. Calcite treatment occurred during October 1989.

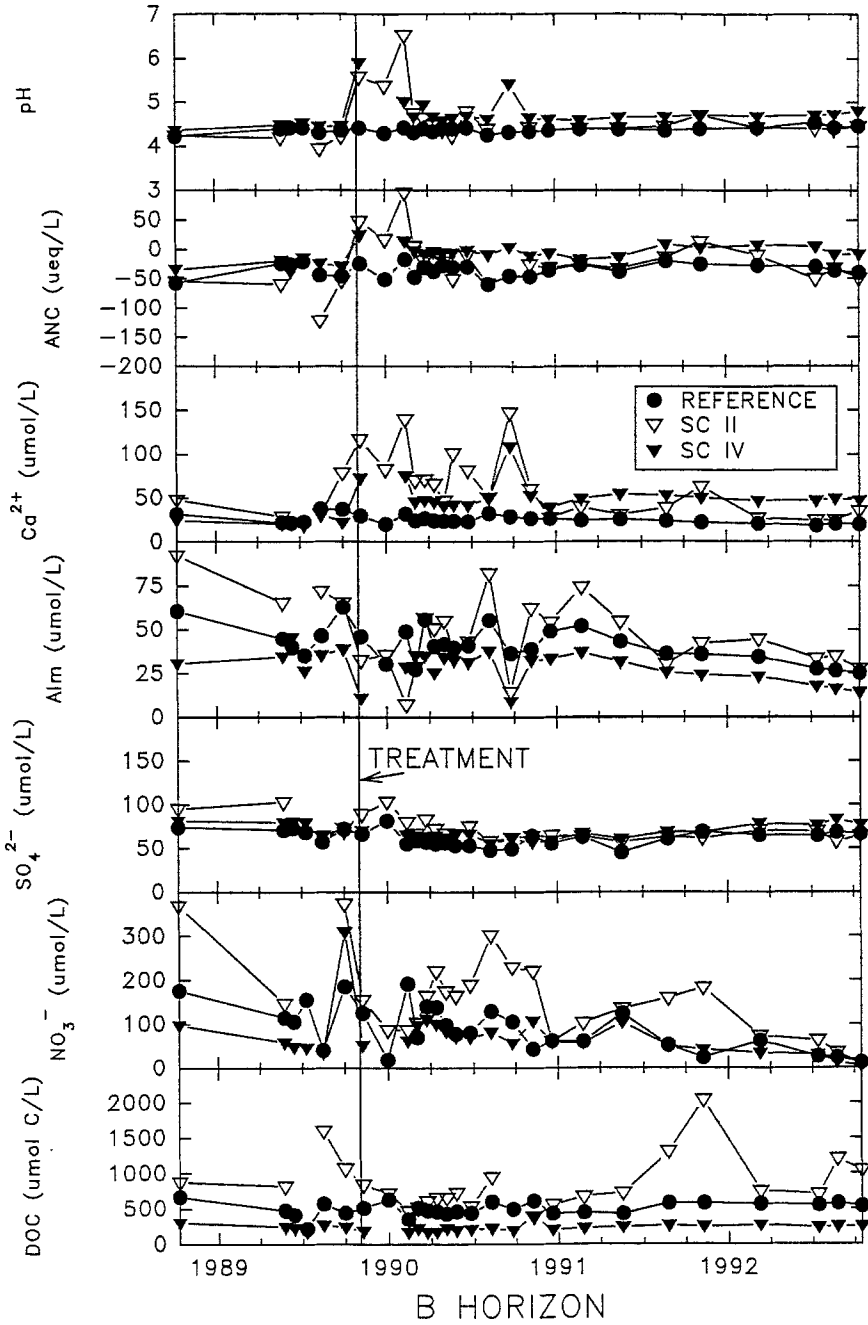


Fig. 5. Time-series of solute concentrations in Bs horizon soil waters for reference (I, V) and CaCO<sub>3</sub>-treated (II, IV) subcatchments. Calcite treatment occurred during October 1989.

Correlation testing indicated that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  had much less influence on the variability of soil solution  $\text{H}^+$  than DOC. Sulfate concentrations were uniform both spatially and temporally and would, therefore, exhibit little correlation with soil solution acidity. Conversely,  $\text{NO}_3^-$  exhibited significant spatial and temporal variability, but still was not highly correlated with soil solution  $\text{H}^+$ . However,  $\text{NO}_3^-$  was positively correlated with Al and  $\text{Ca}^{2+}$  in both Oa and Bs horizon soil solutions (Oa:  $\text{NO}_3^-/\text{Ca}^{2+}$ ,  $r_s = 0.47$ ;  $\text{NO}_3^-/\text{Al}$ ,  $r_s = 0.59$ ; Bs:  $\text{NO}_3^-/\text{Ca}^{2+}$ ,  $r_s = 0.58$ ;  $\text{NO}_3^-/\text{Al}$ ,  $r_s = 0.68$ ). Sulfate generally exhibited low negative correlation with these solutes (Oa:  $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ,  $r_s = -0.24$ ;  $\text{SO}_4^{2-}/\text{Al}$ ,  $r_s = -0.17$ , Bs:  $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ,  $r_s = -0.22$ ;  $\text{SO}_4^{2-}/\text{Al}$ ,  $r_s = -0.35$ ). This pattern may be influenced by  $\text{NO}_3^-$ , since  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were also negatively correlated (Oa,  $r_s = -0.38$ ); Bs  $r_s = -0.41$ ). Nodvin et al. (1988) reported that variations in  $\text{NO}_3^-$  influenced  $\text{SO}_4^{2-}$  concentrations in drainage waters. Inputs of nitric acid protonate oxide surfaces, enhancing the adsorption of  $\text{SO}_4^{2-}$  with decreases in pH.

Mulder et al. (1987) observed similar trends in woodland soil solutions of the Netherlands. Similarly, James & Riha (1989) observed that  $\text{NO}_3^-$  was more effective in mobilizing Al than  $\text{SO}_4^{2-}$  in forest floor-spodic Bs horizon sequences in laboratory soil columns. These findings indicate that processes regulating the concentration of  $\text{NO}_3^-$  are important in controlling temporal variations in the acid-base chemistry of soil and surface waters. These observations also have implications for N cycling in forested ecosystems especially under conditions of elevated  $\text{NO}_3^-$  leaching (Cronan 1985; van Breemen et al. 1987). High concentrations of  $\text{NO}_3^-$  in soil solutions may be symptomatic of inefficient N utilization that occurs in older growth forests such as the Adirondacks and other northeastern U.S.A. forests (Virtousek & Reiners 1975), coupled with elevated inputs of N from atmospheric deposition (Aber et al. 1989).

#### *Long Term Soil Solution Trends*

Some insight into long-term trends in soil solution chemistry at Woods Lake can be gained by comparing current data to that obtained by Cronan (1985) at the same site 10 years before (Fig. 6). Note, however, there were some key differences in the sampling programs of the two studies. First, we utilized zero-tension lysimeters while Cronan (1985) used tension lysimeters. Tension lysimeters sample matrix soil water plus gravity flow while zero-tension lysimeters sample gravity flow only. Different lysimeter type could affect chemical data. However, Postek (1992) found little difference in soil solution chemistry between these lysimeter types at a hardwood forest site in Maine. Lysimeters used by Cronan (1985) were located only in subcatchments I and II while ours were located throughout the watershed. Also, our lysimeters



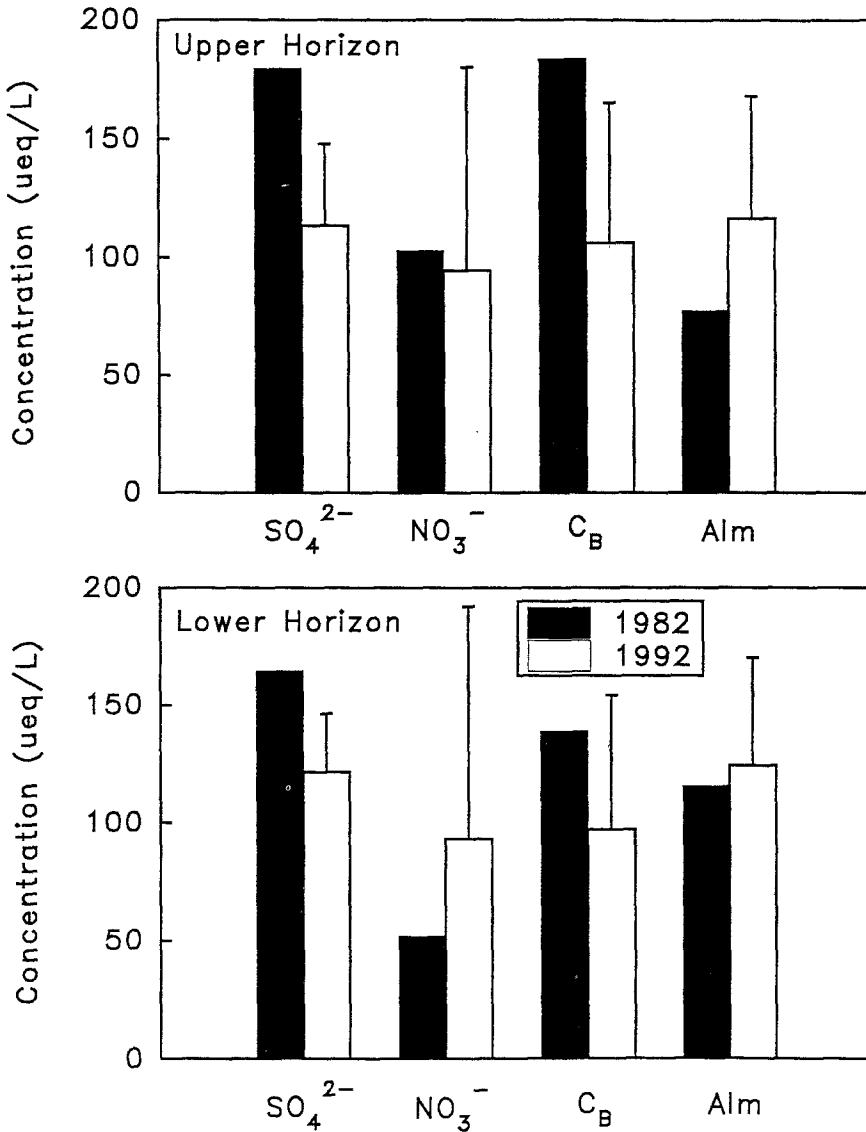


Fig. 6. Comparison of current annual mean concentrations of selected solutes in soil solutions from upper and lower soil horizons in Woods Lake watershed with Cronan (1985). Standard deviations were not available for Cronan (1985) data and are shown for current data only.

were installed at variable depths corresponding to Oa and Bs horizons, while Cronan's (1985) were installed at constant depths of 20 cm and 50 cm. Finally, Cronan's sample collections were more intensive during the summer season than the winter season. Our sampling was more evenly distributed

throughout the year. Despite these limitations, there is considerable interest in the recovery of drainage waters in response to declining atmospheric depositions of solutes, so a comparison of our results with those of Cronan (1985) may be instructive. Note, however, that this comparison is not intended to be statistically rigorous, which is impossible without raw data from the Cronan (1985) study.

Total anion charge (excluding organic anions) has declined approximately 25% (78  $\mu\text{eq/L}$ ) and 7% (17  $\mu\text{eq/L}$ ) in Oa and Bs horizons, respectively, over the last ten years at Woods Lake watershed. This decrease is largely attributed to decreases in  $\text{SO}_4^{2-}$ , which has declined approximately 40% (60  $\mu\text{eq/L}$ ) in each horizon (Fig. 6). Driscoll & van Dreason (1993) reported a decline in precipitation and surface water concentrations of  $\text{SO}_4^{2-}$  for the Adirondack region, from 1982 to 1991, which is consistent with declines in emissions of  $\text{SO}_2$  in the eastern U.S. The rate of  $\text{SO}_4^{2-}$  decline in surface waters ranged from 2.0 to 6.4  $\mu\text{eq/L-yr}$ , similar to the rate we observed for soil waters at Woods Lake (6  $\mu\text{eq/L-yr}$ ). Conversely,  $\text{NO}_3^-$  concentrations have remained approximately constant in the Oa horizon while an increase of approximately 100% (50  $\mu\text{eq/L}$ ) was evident in the Bs horizon. The rate of increase in mineral soil water  $\text{NO}_3^-$  (5  $\mu\text{eq/L-yr}$ ) was somewhat greater than increases in surface water  $\text{NO}_3^-$  reported by Driscoll & van Dreason (1993; 0.5 to 2  $\mu\text{eq/L-yr}$ ) for approximately the same period in the Adirondack region. Note that these increases in  $\text{NO}_3^-$  concentrations have occurred despite constant patterns of  $\text{NO}_X$  ( $\text{NO}_2 + \text{NO}$ ) emissions for the eastern U.S. (Butler & Likens 1991) and precipitation inputs of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for the Adirondacks (Driscoll & van Dreason 1993). The reason for this increase in  $\text{NO}_3^-$  leaching is unclear but it may be attributed to continued deposition of elevated inputs of  $\text{NO}_3^-$  coupled with declining retention by the forest ecosystem (Aber et al. 1989) or mobilization of pools of N by forest vegetation.

Declines in soil water  $\text{SO}_4^{2-}$  have been coincident with decreases in the  $C_B$ , approximately 40% (65  $\mu\text{eq/L}$ ) and 30% (40  $\mu\text{eq/L}$ ) in Oa and Bs horizon soil solutions, respectively. Over the same period, Al concentrations in soil solutions have increased by 60% (45  $\mu\text{mol/L}$ ) and 15% (17  $\mu\text{mol/L}$ ) in Oa and Bs horizons, respectively. Soil solution pH increased from 3.88 to 4.10 in the Oa horizon and decreased from 4.52 to 4.38 in the mineral horizon over the last ten years. The decline in soil water  $C_B$  is consistent with decreases in concentrations of anions and may suggest reduced leaching of  $C_B$  from cation exchange sites (Reuss & Johnson 1986). The observed increase in concentrations of Al is problematic. This pattern may suggest depletion of available pools of base cations in Woods Lake soil, which may indicate a shift in soil pH buffering from exchange of base cations to Al release. Note that Driscoll & van Dreason (1993) reported that several Adirondack

lakes exhibited declines in ANC from 1982–1991 while no lakes showed increases in ANC. The long-term changes in soil waters at Woods Lake watershed would appear to be consistent with the long-term trends in the water chemistry of Adirondack lakes. The apparent acidification of soil water and possible depletion of base cations in soil provides additional justification to investigate the application of calcite to the watershed at Woods Lake.

### *Soil Water Response to Calcite Application*

Most watershed applications of calcite are made to hydrologic source areas such as wetlands and streams because of slow dissolution rates in upland soils, and high cost associated with the treatment of whole watersheds (Brocksen et al. 1990; Hindar & Rosseland 1991). Since the EWLS was a comprehensive ecosystem investigation designed to evaluate the response of an entire forested watershed to  $\text{CaCO}_3$  addition, it offered an excellent opportunity to evaluate the relative contribution of the various watershed compartments to supplying  $\text{CaCO}_3$  to an acidic drainage lake.

In our study, calcite treatment resulted in an increase of  $\text{Ca}^{2+}$ , ANC and pH in soil solutions of treated subcatchments (Table 1; Figs. 4 and 5). Similar effects were observed in soils (Blette & Newton 1996a, this volume), streams (Cirmo & Driscoll 1996, this volume) and the lake (Driscoll et al. 1996, this volume). Other work has also documented increases in  $\text{Ca}^{2+}$  and pH in watershed drainage waters following land application of calcite (Hinder & Rosseland 1991; Stoner & Donald 1991; Dalziel et al. 1991).

Increases in solute concentrations were most evident for six months following treatment. We speculate that this rapid initial response was due to macropore transport of dissolved and particulate  $\text{CaCO}_3$  through soil under non-equilibrium conditions. Marshner et al. (1992) noted increases in pH at soil depths of 20 cm within one week of treatment which was also attributed to macropore transport. Similar rapid transport processes occurred as a result of direct dissolution in wetlands or streams and overland flow, which likely contributed to the immediate response of streams (Cirmo & Driscoll 1996, this volume) and the lake (Driscoll et al. 1996, this volume) to the calcite application, and marked changes in stream chemistry during storm events (Newton et al. 1996, this volume) during the EWLS study. Short-term watershed responses have also been noted by Stoner & Donald (1991) in the application of calcite to whole catchments and hydrologic source areas in Wales, and by Dalziel et al. (1991) in catchment liming studies at Loch Fleet, Scotland.

Chemical models that have been used to assess watershed application of calcite do not include rapid hydrologic transport of unreacted or partially reacted calcite to surface water and typically invoke ion exchange equilibria

of solutions with soil prior to discharge to surface water (Davis & Goldstein 1988; Blette & Newton 1996b, this volume). On the basis of the EWLS and other watershed liming studies, these processes clearly need to be incorporated into modeling efforts to accurately predict short term drainage water response.

The initial response of soil water to calcite treatment was greater in subcatchment II than subcatchment IV (Table 1; Figs. 4 and 5). This pattern may be due to the drier conditions in this subcatchment which may favor macropore transport. Marshner et al. (1992) suggested that dry conditions would enhance macropore transport because of the hydrophobic nature of forest floor organic material. While wetter conditions reduced initial solute concentrations in subcatchment IV, these same conditions have also enhanced  $\text{CaCO}_3$  dissolution over the longer term, resulting in a more sustained response. Comparison testing showed that increases in ANC/pH, and  $\text{Ca}^{2+}$  in this subcatchment have remained significant through the final sampling in fall 1992, demonstrating the potential for application of calcite to wetter soils to provide longer term improvement to watershed drainage waters.

It was difficult to assess the effects of  $\text{CaCO}_3$  treatment on Al concentrations in soil water since concentrations declined in both reference and treated subcatchments throughout the study. Nevertheless, the decrease in Al was greater in treated subcatchments than reference subcatchments (Table 1). Cirno & Driscoll (1996, this volume) observed a marked reduction of Al concentrations in streamwater following treatment. Similar decreases in Al concentrations were observed in peat pore water (Yavitt & Fahey 1996, this volume) and in the water column of Woods Lake (Driscoll et al. 1996, this volume). This suggests that treatment effects on Al concentrations in watershed drainage waters observed thus far are not necessarily due to changes in upland soil solutions. Indeed calcite inputs to wetlands, near stream zones or directly to surface water could contribute to decreases in surface water Al. Other watershed liming studies have noted decreases of Al in drainage waters after treatment. Stoner & Donald (1991) observed general decreases in Al concentrations following whole catchment liming. In contrast, a more variable response occurred in the liming of moorland hydrologic source areas, due to intermittent release of Al from untreated areas under different hydrologic conditions. Unlike surface waters (Cirno & Driscoll 1996, this volume), calcite treatment appeared to have no effect on the fraction of monomeric Al occurring as organic monomeric Al in soil waters.

The response of soil water to the calcite application declined in both subcatchments by the fall following treatment (Figs. 4 and 5). This pattern may have been due to leaf litter shielding calcite from throughfall decreasing calcite dissolution and macropore transport. Decreases in  $\text{Ca}^{2+}$  concentrations

in the soil solution of subcatchment II were more rapid than subcatchment IV, approaching reference concentrations within one year after treatment. Again this response was most likely due to the drier conditions in this subcatchment and provides additional support to the approach of restricting watershed calcite application to hydrologic source areas.

Many of the secondary changes (not directly related to the application of  $\text{CaCO}_3$ ) in soil solution chemistry paralleled observations for other watershed compartments during EWLS. Dissolved  $\text{H}_4\text{SiO}_4$  increased in Oa and Bs horizon soil solutions in both subcatchments following treatment. Cirno and Driscoll (1996, this volume) also observed significant increases in dissolved  $\text{H}_4\text{SiO}_4$  in streamwater following treatment which was attributed to accelerated dissolution of amorphous Si at higher pH. Sodium concentrations decreased in Oa and Bs horizon soil solutions following treatment, which agrees with the findings of Blette & Newton (1996a, this volume) who documented a decrease in exchangeable Na in most upper soil horizons following treatment. This decrease may be due to the preferential displacement of  $\text{Na}^+$  by  $\text{Ca}^{2+}$  as a result of  $\text{Na}^+$  relatively low affinity for soil.

Concentrations of DOC in Oa horizon soil solution in subcatchment II increased immediately following treatment (Fig. 4), but rapidly returned to pre-application concentrations. The apparent increase in DOC in this subcatchment may also have been due to the general pattern of increase in DOC concentration that occurs in the fall due to lower soil moisture and decomposition of fresh leaf litter. Changes in DOC were not observed in subcatchment IV possibly due to saturated conditions in this area that have resulted in much more dilute DOC concentrations. Any increases, therefore, may not be easily detected. Cirno & Driscoll (1996, this volume) also observed short-term increases in DOC concentrations in stream water following the calcite treatment to Woods Lake watershed. Cronan et al. (1992) did not observe any response of DOC to calcite treatment.

Marshner et al. (1992) observed elevated  $\text{NO}_3^-$  concentrations in response to calcite treatment which was attributed to increased nitrification. In our study,  $\text{NO}_3^-$  concentrations also appeared to increase in response to treatment in subcatchment II (Figs. 4 and 5). The response was immediate in Oa horizon soil solutions and persisted for about six months following treatment. This increase in  $\text{NO}_3^-$  was evident in studies of the forest floor (Simmons et al. 1996, this volume), stream chemistry (Cirno & Driscoll 1996, this volume) and lake chemistry (Driscoll et al. 1996, this volume). Simmons et al. (1996, this volume) reported that mineralization of soil organic N was inhibited and nitrification was enhanced following  $\text{CaCO}_3$  treatment. Our results are generally consistent with these observations, although it was difficult to assess changes in  $\text{NH}_4^+$  due to low background concentrations. Since increases in

$\text{NH}_4^+$  were not evident in soil water following base application, it seems likely that increased concentrations of  $\text{NO}_3^-$  were attributed to enhanced nitrification, rather than increased mineralization of soil organic nitrogen. This response suggests that nitrification in Woods Lake soil may be inhibited by conditions of low pH. Similar increases were not observed in subcatchment IV which may be due to the suppression of nitrification by high soil moisture.

Nitrate appears to have then been transported into the mineral soil since elevated  $\text{NO}_3^-$  concentrations were observed about six months after base application and remained elevated for about six months. Nitrate concentrations in soil water, streamwater (Cirno & Driscoll, 1996, this volume) and lake water (Driscoll et al. 1996, this volume) suggest that increases in  $\text{NO}_3^-$  evident immediately after calcite treatment returned to near pre-treatment concentrations in 1991.

For soil drainage to increase the pH of surface water appreciably, positive ANC values (Driscoll et al. 1996, this volume) must be attained (Reuss & Johnson 1986). Although soil solution chemistry has generally responded as expected to the treatment (i.e., increase in  $\text{Ca}^{2+}$ , ANC and pH), the magnitude of response observed to date has been insufficient to mitigate surface water acidity. It appears that changes in surface water chemistry observed within three years after calcite treatment were probably not directly linked to changes in the soil solution chemistry of upland soil. Driscoll et al. (1996, this volume) noted that the increased supply of ANC after treatment has largely occurred through the dissolution of calcite applied to stream and wetland areas, which supports the methodology of liming hydrologic source areas as is currently practiced in most watershed liming applications.

Despite the relatively small perturbation observed thus far, the potential of calcite to mitigate watershed soil acidification is evident. Three years following treatment Oa and Bs horizon soil solution increases of ANC/pH and  $\text{Ca}^{2+}$  remained significant in subcatchment IV and elevated in subcatchment II, despite low soil moisture conditions in this subcatchment. The reduction in Al concentrations was greater in treated subcatchments than reference subcatchments. We expect these trends to continue over the next few years since only about 50% of the added calcite has dissolved (Blette & Newton 1996a, this volume) and calcite is known to penetrate untilled soil very slowly. Brown & Munsell (1939) estimated the downward movement of calcite in untilled soil at 1 to 3 cm/yr. At this rate we would not expect the full impact of lime to reach the lower Oa horizon for at least 5 years (i.e., 1994) after application.

## Conclusions

The major conclusions of our soil solution study are as follows:

1. Reference Oa and Bs horizon soil solutions were characterized by low pH and ANC due to the elevated concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and organic anions relative to concentrations of base cations. While elevated concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  contributed to ambient soil solution acidity, spatial and temporal variability was largely attributed to variations in concentrations of organic acids. Aluminum was the most abundant cation in soil solutions and appears to influence DOC concentrations in both soil horizons.
2. Nitrate concentrations were positively correlated with  $\text{Ca}^{2+}$  and Al in organic and mineral soil horizons in reference subcatchments, while  $\text{SO}_4^{2-}$  exhibited a low negative correlation with these solutes. This pattern suggests that  $\text{NO}_3^-$  could play an important role in surface water acidification especially during episodic events.
3. Comparison of current soil water chemistry with historical observations for Woods Lake watershed show declines in  $\text{SO}_4^{2-}$  in Oa and Bs horizons and increases in  $\text{NO}_3^-$  in the Bs horizon. Declines in  $C_B$  have occurred coincident with increases in Al. These patterns are consistent with recent trends in the chemistry of Adirondack surface waters.
4. Calcite application of 6.89 Mg/ha has produced statistically significant increases of  $\text{Ca}^{2+}$ , pH and ANC (Oa and Bs horizons) in subcatchment IV over a three-year study period. Calcite impacts were greatest during the first year following application especially in subcatchment II, which is attributed to macropore transport of particulate and dissolved  $\text{CaCO}_3$ . Longer term treatment impacts were less in subcatchment II apparently due to lower soil moisture demonstrating the importance of liming hydrologic source areas that have higher soil moisture. With the exception of the first year, the magnitude of ANC increase in upland soil was insufficient to improve surface water quality. Increases in ANC noted thus far have been attributed to  $\text{CaCO}_3$  dissolution in streams, wetlands and other hydrologic source areas that discharge to Woods Lake (Driscoll et al. 1995, this volume).

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