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Application of the Integrated Lake-Watershed Acidification Study model to watershed liming at Woods Lake, New York

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Abstract. Woods Lake, in the Adirondack Mountains of New York, was the site of the Experimental Watershed Liming Study (EWLS) in which base addition was investigated as a method for mitigation of lake acidity. In an effort to predict the duration of effects, the treatment was simulated using the Integrated Lake-Watershed Acidification Study (ILWAS) model. To simulate terrestrial liming, calcite was applied to treated subcatchments as a rapidly weathering mineral in the upper horizon. Soil solution and lake outlet chemistry showed a response to calcite addition within four months of the start of the simulation. Calcium concentrations, acid neutralizing capacities (ANC), and pH increased in the upper soil layer and aluminum concentrations decreased in the upper three soil layers (0–70 cm). The response of ANC was delayed in lower soil layers due to proton production associated with aluminum hydrolysis. Moreover, soil water pH in the third soil layer decreased in response to calcite treatment due to the displacement of hydrogen ions by calcium added to the exchange complex. Calcium concentrations, ANC and pH increased and aluminum concentrations decreased in the simulated lake outlet.

The modeled effects of calcite treatment on the soil and lake outlet chemistry were not as great as field observations. This was, in part, attributed to the model representation of the watershed, which did not include streams, ponds, or wetlands located in the treated subcatchments. Calcite applied to these saturated areas in the field readily dissolved, supplying ANC to lake water. Additionally, incorporation of calcite into a thick organic layer in the model diminished the possibility of dissolution by contact with overland flow. Observed concentrations of calcium, ANC, and pH in the outlet decreased after high values in the two years after treatment. Although the model failed to match observed short-term data, it may simulate the long-term response as calcium is transported through the soil. A long-term simulation of the model suggests that effects of base treatment will persist for at least 50 years.

Introduction

Many computer models have been developed in the past fifteen years to assess and predict both current and future impacts of acidic deposition on streams and lakes (Church et al. 1989). Model simulations can also be useful in the design of restoration projects to mitigate the effects of acid precipitation. The Experimental Watershed Liming Study (EWLS), in which pelletized limestone was applied to the watershed surrounding a lake, was initiated in 1989 at Woods Lake, New York, with the goal of restoration of a brook trout fishery. The Integrated Lake-Watershed Acidification Study (ILWAS) model (Gherini et al. 1985) was used to simulate the effects of calcite treatment on the watershed. In this paper we provide a brief description of the ILWAS model, its calibration and results of the simulated response of the lake to watershed liming. These simulations were compared to observed data collected in the three years following base addition.

Background

After the addition of calcite to the watershed in October, 1989, the chemistry of the tributary streams, as well as the lake, improved sufficiently to sustain fish populations and spawning did occur in one of the lake's tributaries (Driscoll et al. 1996; Cirmo & Driscoll 1996; Burns 1996; Schofield & Keleher 1996). However, if watershed base treatment is to be considered a viable alternative to direct lake liming for mitigation of acidity, some estimate must be made of the duration of beneficial effects of liming. This determination is difficult for watersheds because there are many possible interactions for calcium derived from limestone with the soil and vegetation in the terrestrial ecosystem (Blette & Newton 1996; Geary & Driscoll 1996). The ILWAS model, a dynamic biogeochemical computer model previously applied to the watershed, was used to attempt to determine the sinks of applied calcium, and to predict effects of the calcite manipulation. In turn, it was hoped that simulation of the experiment would be a rigorous test for the model itself. Finally, extending model simulations to the future can provide some estimate for the duration of the calcite treatment.

ILWAS model

The ILWAS model was developed as part of the Integrated Lake Watershed Acidification Study (ILWAS) which began in the fall of 1977 and continued through 1983 (Goldstein et al. 1985). The observations and data collected were used to develop the ILWAS model, a mechanistic mathematical model which simulates the physical and biogeochemical processes occurring in a watershed, and determines the resultant chemistry of surface waters within that watershed. Details of the model's conceptualization, development, and theory have been previously described in detail (Goldstein et al. 1984; Gherini et al. 1985). ILWAS has been applied to more than 100 streams and lakes throughout the United States.

In simulating water quality, the ILWAS model calculates the concentrations of chemical constituents in throughfall, surface runoff, soil solution, and surface waters. This is achieved using mass balance techniques, and kinetic and equilibrium formulations to represent the major processes which

Table 1. Chemical and physical processes simulated by the ILWAS model (Davis et al. 1987).

Canopy Processes
- Dry Deposition
- Foliar Exudation
- Nitrification
- Solution Phase Equilibration
- Washoff

Snowpack Processes
- Accumulation
- Sublimation
- Leaching
- Nitrification

Surface Water Processes
- Gas Transfer
- Mixing (Advection and Dispersion)
- Heat Exchange
- Ice Formation and Melting
- Algal Nutrient Uptake
- Nitrification
- Reductive Loss of Strong Acid Anions
- Solution Phase Equilibration

Soil Processes
- Heat Transfer
- Biomass Loop
  - Litter Accumulation
  - Litter Decay
  - Organic Acid Decay
  - Nitrification
  - Nutrient Uptake
  - Root Respiration
- Abiotic Processes
  - Mineral Weathering
  - Competitive Cation Exchange (Al, Ca, Mg, K, Na, NH_4, H)
  - Anion Adsorption (SO_4, PO_4, organic acid ligand)
  - CO_2 Exchange
  - $Al(OH_3)$ (am) Dissolution-Precipitation
  - Solid-Liquid-Gas Phase Equilibration

influence water quality (Table 1). In ILWAS hydrogen ion concentrations are calculated from ANC, total inorganic carbon, total monomeric aluminum, and total organic acid analog using chemical equilibrium relationships.

The model is applied by dividing a hydrologic basin into subcatchments, each of which discharges water directly to a stream or lake. Each subcatchment is divided vertically into compartments with homogeneous characteristics: forest canopy, vegetation, and separate soil layers. Streams are divided into longitudinal segments, and lakes are divided vertically into well-mixed layers.

Input to the model includes both time-invariant and time-variant parameters. Time-invariant parameters include those that characterize each compartment (e.g., for a lake layer – thickness, area, initial temperature, and initial solution concentrations). Time-variant input consists of meteorological data (e.g., daily air temperature and precipitation) and chemical data (e.g., monthly air quality and precipitation solute concentrations). As output, the model calculates the aqueous concentrations of the major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+), major anions (SO_4^{2-}, NO_3^-, Cl^-), ANC, silicic acid, organic acid analog, total monomeric aluminum, organically complexed monomeric aluminum, and pH in throughfall, soil water, and surface waters.

Application of the ILWAS model typically begins with calibration. Basin data are used to quantitatively characterize the system to be simulated. Initial conditions (e.g., lake stage, soil and surface water quality) are established for the simulation starting point. The model is then run using actual meteorological and air quality data as input. The model output – the quantity and chemistry of water at various locations in the system (throughfall, soil solution, surface water) – is made to coincide with observed values by adjustment of calibration parameters (e.g., evapotranspiration coefficients, cation exchange selectivity coefficients). The simulated results are typically compared to the observed data using graphical procedures. Because the ILWAS model simulates many processes, calibration of these processes should follow a logical order. The general rules for calibration are: 1) calibrate system hydrologic processes before calibrating chemical processes; 2) calibrate in the same order as water flows through the basin; and, 3) calibrate on an annual basis first, then seasonally, and finally calibrate to the instantaneous (daily) behavior.

Woods Lake Modeling

Woods Lake was used for the formulation and testing of the ILWAS model and, as such, underwent a rigorous calibration (Gherini et al. 1985). The model was also used by Davis (1988) and Davis & Goldstein (1988) to simulate an application of limestone to the watershed. However, observations from subsequent research suggested that some of the input parameters to the model needed to be changed prior to simulation of the EWLS. In the original calibration, the watershed was subdivided into 8 subcatchments. Subcatchment boundaries were redrawn to obtain 5 subcatchments to better reflect observed movements of overland and groundwater flow (Driscoll et al. 1995, this issue). Lake level was adjusted to account for destruction of a beaver dam at the outlet of the lake which had forced lake levels to decrease by about one meter. The soil component of the model was configured with 4–5 horizons, the fifth layer being a lower till present only in subcatchments II and III. Layer 1 (15 cm thick) represented the organic horizon, layer 2 the E horizon (5 cm thick), layer 3 the B horizon (50 cm thick), and layer 4 an upper till (50–200 cm thick). In the initial calibration of the model, lateral flow was routed primarily through layer 1 (Fig. 1). Later research suggested that more water flowed through deeper horizons en route to the lake. Hydraulic conductivities in deeper horizons were increased to allow greater lateral flow through the lower soil layers. A chemical recalibration of the soil solution was required due to these changes in soil layer flow.

The EWLS study did not monitor preciptation amounts, temperature or wet/dry deposition chemistry, all of which are required as input to the model. Because the ILWAS study provided a complete dataset between 1978 and 1981, the same meteorological and wet/dry chemistry deposition input files were used for the new simulations. While this allowed for easier comparisons with results of earlier modeling studies, the use of an old dataset could be a potential problem when comparing simulated output with the observed data collected after watershed calcite addition. Climatological conditions were different in the three years following treatment (1989–1992) than in 1978–1981. Additionally, studies have shown marked changes in atmospheric deposition in the Northeast during the last decade (Driscoll et. al. 1989; Driscoll & van Dreason 1993).

The ILWAS model was designed to predict the effect of changes in atmospheric deposition, not the application of soil amendments. Therefore, application of calcite to the soil required some modification to the model. In an earlier simulation of terrestrial liming at Woods Lake (Davis & Goldstein 1988), the addition of calcite was simulated by increasing the dry deposition of calcium, total inorganic carbon (TIC), and ANC. Davis and Goldstein modified the computer code so that application dosages, equivalent to 3 and 0.4 Mg ha^{-1} of $CaCO_3$ per hectare, could occur over the entire watershed during the spring or winter. In their simulations it was assumed that applied calcite would be fine enough to instantaneously dissolve immediately after application.

In the EWLS experiment, limestone crushed to the consistency of fine sand was pelletized to avoid windblown application to reference subcatchments. The binder used was designed to dissolve upon contact with water, but two years after treatment calcite was visible under leaf litter (Blette & Newton 1996). Because the applied calcite dissolved slowly, we decided it would be more realistic to represent it as a mineral in the organic horizon, albeit with a more rapid weathering rate than other native minerals. In model simulations, calcite was added to the upper layer of the soil, at amounts corresponding to a field application of 8.2 Mg ha^{-1}. This was the targeted deposition amount for the company applying the pelletized limestone (10 Mg ha^{-1} limestone with 82% calcite = 8.2 Mg ha^{-1}). A lower deposition amount, 6.9 Mg ha^{-1}, was recorded in the field (see Driscoll et al. 1996, this issue), however we chose to use the targeted application rate because amounts of calcite collected in the field after application were highly variable. Because an absolute weathering

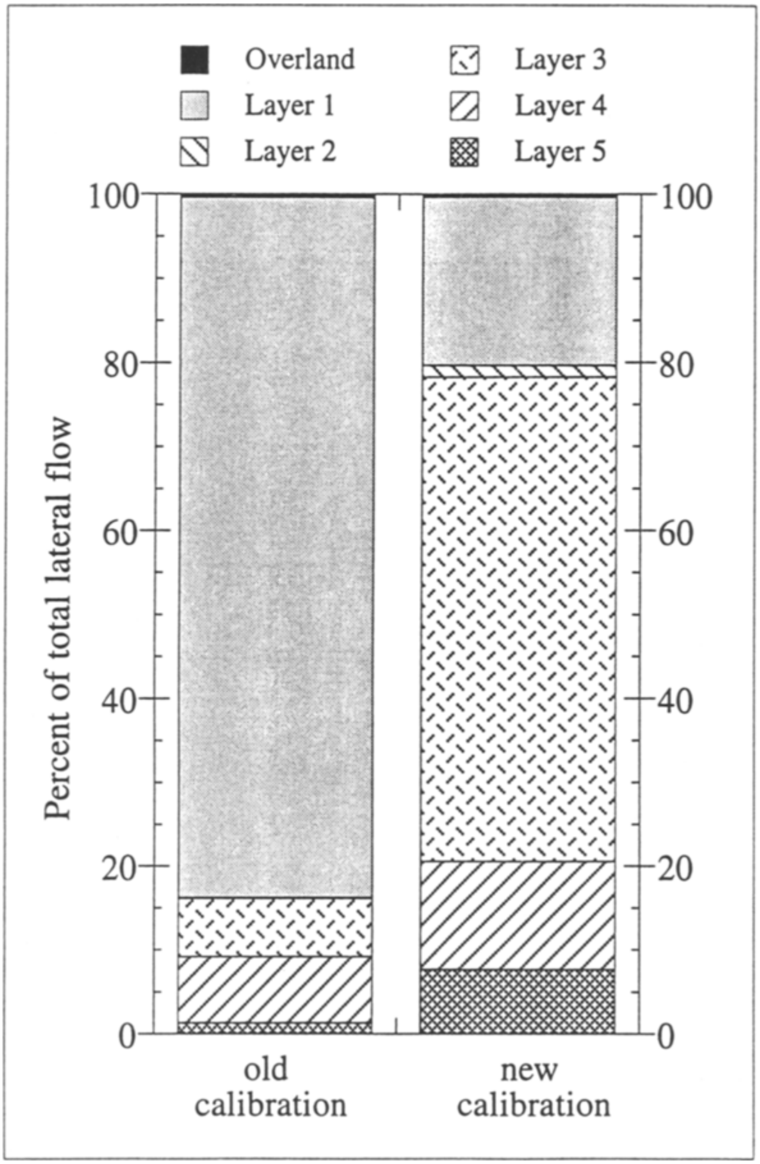

Fig. 1. Simulated percentage of annual lateral flow through soil layers for the original ILWAS calibration of Woods Lake and the revised calibration. Total cumulative flows were 4.35e06 m^3 in the original (Gherini et al. 1985), and 4.19e06m^3 in the revised calibration.

rate for the calcite in the soil was not determined, three rates were simulated, 10, 50 and 100 moles/year (Fig. 2). These rates are 4–5 orders of magnitude greater than the weathering rates of other minerals in the horizon. Observed

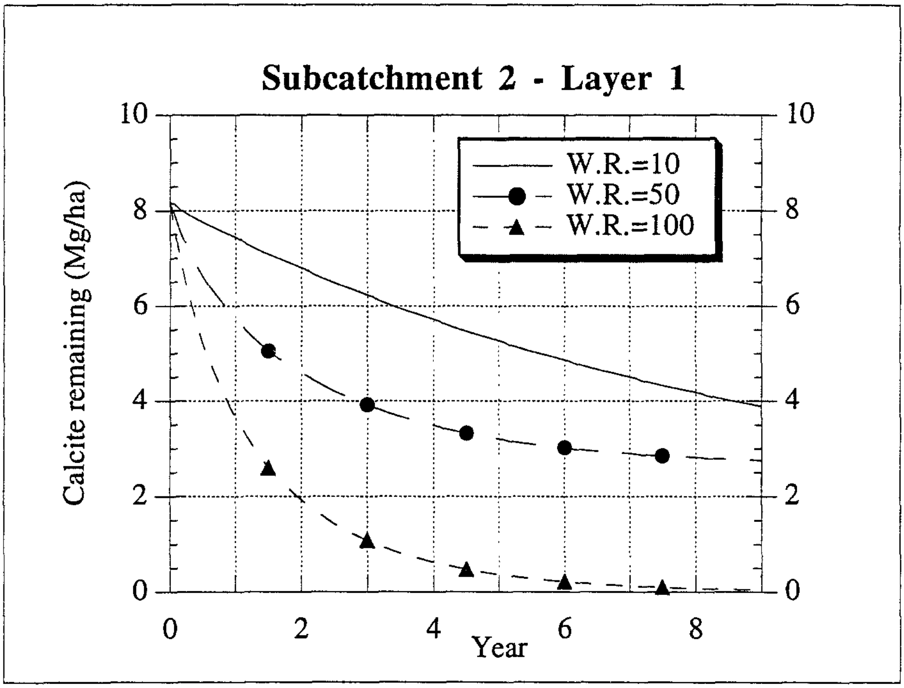

Fig. 2. Simulated amount of calcite remaining in the first layer of subcatchment II using different weathering rates. A weathering rate of 50 moles/year resulted in an amount which most closely matched field observations 2 years after calcite addition.

Table 2. Variations in critical values for simulation of watershed calcite treatment at Woods Lake.

Scenario	$CaCO_3$ wgt %	Weathering rate mol/year	CEC $cmol_c\ kg^{-1}$
Base case	0.00	0	50
Scenario 1	2.73	50	50
Scenario 2	2.73	50	20

data indicated that roughly half of the applied calcite remained two years after treatment (Blette & Newton 1996). Simulations of calcite loss most closely agreed with observed data when a weathering rate of 50 moles/year was used.

Results from the field experiment indicated that the cation exchange capacity (CEC) changed markedly in response to liming, roughly doubling in the organic horizon due to the pH-dependent CEC associated with soil organic matter (Blette & Newton 1996). The ILWAS model does not simulate pH-dependent changes in CEC. Because the increase in CEC in the upper horizon appeared to occur relatively rapidly, simulations were conducted using a CEC greater than pre-treatment values. An additional simulation was conducted using a lower CEC to judge the effect of increased CEC on soil solution and exchange chemistry. Base cation densities were the same for both the low and high CEC simulations.

Simulations were conducted for the basecase and with an application of 8.2 Mg ha^{-1} calcite to the upper horizon in subcatchments II and IV (approximately 50 percent of the watershed) (Table 2). Simulations were generally run for periods of nine to eighteen years, beginning on September 1. Trends in the results were defined by tracking the value on August 31 of each year. An additional fifty year run was conducted for the basecase and Scenario 1 to assess the long-term response of the Woods Lake watershed to calcite treatment.

Results and Discussion

Soil chemistry model results

Results from a nine-year model simulation showed immediate increases in pH, ANC, and calcium concentrations in the upper layer due to rapid dissolution of added calcite. After three years calcium concentrations were 100 μeq/l, versus 20 μeq/l in the basecase, on August 31 of the ninth year of the simulation. Acid-neutralizing capacities approached positive values, increasing 54 μeq/l above basecase concentrations. An increase in calcium concentration was also noted in layers 2 and 3 within 2–3 months of the simulation's start. After 3 years, calcium concentrations had increased 24 μeq/l and 5 μeq/l above basecase concentrations in layers 2 and 3, respectively (Table 3). The ANC in layers 2 and 3 did not show the marked increase observed in layer 1. In the second layer, ANC was lower than basecase levels for nearly 3 years. Levels only increased 25 μeq/l in layer 2 nine years after treatment, versus 108 μeq/l in layer 1 (Table 3). In the third layer ANC was consistently less than basecase levels for the entire simulation period. This decrease coincided with declines in soil solution concentrations of aluminum in each of the horizons. While the increase in calcium concentration in layer 1 more than offset the loss of ANC associated with aluminum hydrolysis, this pattern did not hold true in deeper horizons. In the third layer calcium increased by only 11 μeq/l after nine years while aluminum decreased by 24 μeq/l, resulting in a net loss of ANC of 10 μeq/l relative to basecase values. Likewise, while the soil water pH in the first layer increased above basecase levels immediately

Table 3. Summary of soil solution chemistry from ILWAS simulations of calcite application to the Woods Lake watershed. Values are from August 31 of simulation years 3, 6 and 9. All units in μeq/l.

	Basecase			Scenario 1			Difference between basecase and scenario 1		
Layer 1									
Year	3	6	9	3	6	9	3	6	9
pH	4.0	4.0	4.0	4.3	4.4	4.4	0.3	0.4	0.4
Ca	21	23	26	104	134	159	84	111	133
ANC	−63	−61	−59	−9	21	49	54	82	108
Altm	43	39	36	21	17	15	−21	−22	−21
Oac	198	191	186	128	126	121	−70	−65	−64
Layer 2									
Year	3	6	9	3	6	9	3	6	9
pH	4.1	4.0	4.0	4.1	4.1	4.2	0.0	0.1	0.2
Ca	24	23	24	47	65	78	24	42	54
ANC	−51	−52	−52	−47	−36	−27	4	16	26
Altm	43	41	39	25	20	17	−17	−20	−22
Oac	169	170	171	163	154	145	−6	−17	−26
Layer 3									
Year	3	6	9	3	6	9	3	6	9
pH	4.3	4.3	4.2	4.2	4.2	4.2	0.0	0.0	0.0
Ca	17	17	17	22	25	28	5	8	11
ANC	−10	−12	−14	−22	−23	−24	−12	−11	−10
Altm	92	90	89	71	68	65	−21	−22	−24
Oac	105	106	107	109	110	110	4	4	3

Ca = calcium, ANC = acid-neutralizing capacity, Altm = total monomeric aluminium, Oac = Organic acid analog

following treatment, the pH in the second layer was lower than the basecase for more than three years. While pH eventually exceeded basecase values, the pH still occasionally dropped below the basecase during spring snowmelt. Soil solution pH in the third layer remained consistently below the basecase throughout the nine year period. The analog triprotic organic acid in the model dissociates as a function of pH. As pH increases, more of the organic acid is adsorbed to the soil. After three years, organic acid concentrations decreased by 70 μeq/l in the first layer, reflecting adsorption due to an increase in pH.

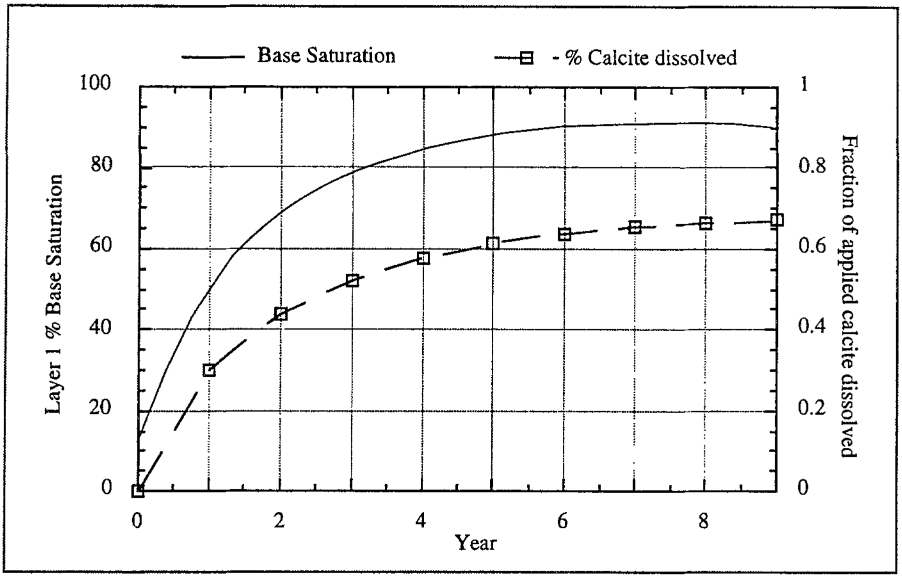

Fig. 3. Simulated base saturation of layer 1 and fraction of calcite dissolved from layer 1. Base saturation peaked at 91% in the seventh year of the simulation. As the base saturation increases, the rate of dissolution decreases.

Table 4. Comparison of changes in soil solution chemistry in the field (after Geary & Driscoll 1994) with results from model simulations. Field lysimeters were placed beneath the O horizon, model values are for the 15 cm thick Layer 1 (O horizon).

	Field-Subcatchment IV		Model simulation (year 3)	
	Pre-treat	*9/91 to 10/92*	*Basecase*	*Treated*
Ca (μeq/l)	46	108	18	107
pH	3.9	4.7	4.0	4.3
ANC (μeq/l)	−26	0.4	−41	−2
Altm (μeq/l)	108	54	82	37

Altm = total monomeric aluminum

Effects in deeper horizons were not as significant, with an increase of 6 μeq/l and decrease of 4 μeq/l in the second and third layers, respectively.

Soil solution concentrations in the third year of the model simulation compared somewhat favorably with observations from soil lysimeters placed beneath the O horizon (Geary & Driscoll 1996) (Table 4). Although soil water concentrations were highly variable between individual lysimeter sites, mean values collected after treatment (9/91–10/92) indicated elevated levels

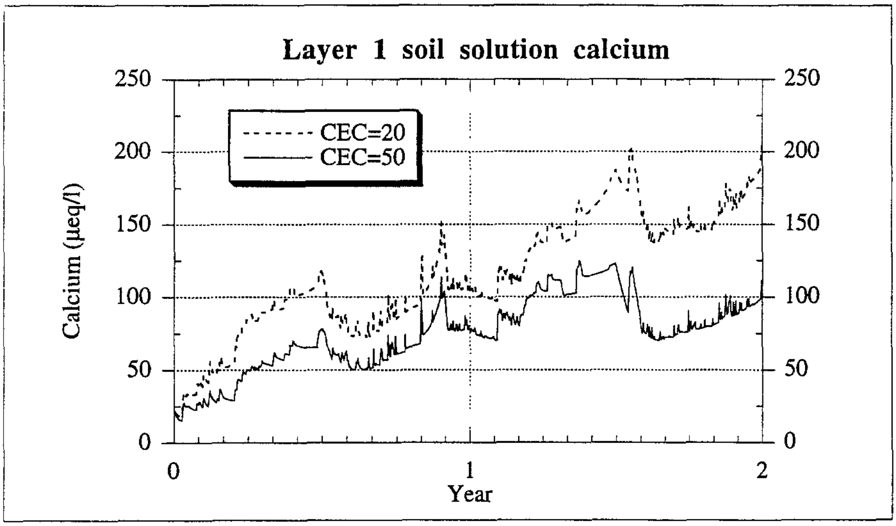

Fig. 4. Simulated concentration of calcium in the first layer when the model is run with a CEC of 50 $\mathrm{cmol_c\ kg^{-1}}$ and 20 $\mathrm{cmol_c\ kg^{-1}}$. A higher exchange capacity results in a reduced flux of calcium from the soil horizon into the lake.

of calcium, ANC and pH, and a decrease in aluminum in soil solutions from subcatchment IV. While pre-treatment concentrations in the field were generally greater than model values, the trends after treatment were comparable.

As was observed in the field, the addition of calcite to the soil resulted in a large increase in the base saturation of the first horizon as calcium was retained on the soil exchange complex. The pH decrease in waters draining layers 2 and 3 in the early years of the simulation could also be due to the displacement of hydrogen ion by calcium in the upper layer and downward transport with drainage water. While percent base saturation in the basecase remained less than 20 percent, values in the limed simulation increased to a maximum value of 91 percent in the 7th year of the simulation (Fig. 3). Values of percent base saturation then decreased slowly, to 86 percent after 18 years. This decline reflects the reacidification of the organic horizon, due to continued deposition of hydrogen ion and displacement of calcium from exchange sites into solution. The rate of reacidification ultimately regulates the duration of calcite treatment and effects on soils and surface waters. There was modest change in the base saturation of deeper horizons; layer 2 increased from 4.5 to 15.5 percent and layer 3 increased from 3 to 3.5 percent over a nine year period. This pattern reflects the ability of the organic horizon to sequester calcium ions.

An additional simulation was conducted to evaluate the effect of an increase in pH-dependent CEC observed following base addition (Blette &

Newton 1996). An increase in CEC from 20 to 50 $\text{cmol}_c\ \text{kg}^{-1}$ diminished changes in soil solution chemistry by facilitating retention of Ca^{2+} and diminishing drainage water losses. While 7 years were needed for base saturations to reach 90 percent in the high-CEC simulation, the low-CEC simulation required only 2 years to achieve a similar value. Soil solution concentrations of calcium in the low-CEC soil were 100 μeq/l above that of the high-CEC soil two years after calcite addition (Fig. 4). Similarly, ANC and pH were higher in the low-CEC soil, and aluminum concentrations were lower. This simulation demonstrates the importance of CEC in moderating cation release. The observed increase in the CEC of organic horizons in the field after treatment likely diminished the transport of calcium to surface waters and deeper soil horizons as calcium ions were retained on exchange sites in the organic horizon.

Lake outlet chemistry model results

Because calcite was added to the watershed, and not the water column of the lake, treatment effects in the lake outlet were not immediate. Calcium concentrations began to increase within four months of the start of the simulation, although the magnitude of the increase was much less than that which was observed in soil solution concentrations from layers 1 and 2. Most of the water entering the lake was routed through the third layer where soil solution concentrations increased only 5 μeq/l after 3 years. Both pH and ANC failed to show a substantial difference from basecase levels until 8–11 months after treatment. After three years, the ANC approached positive values and after eight years was consistently positive, with values as high as 28 μeq/l. In the 9th year of the simulation pH increased to as high as 6.5, although it still declined to 4.8 during spring snowmelt (compared to 4.3 in the basecase).

After three years, aluminum concentrations measured on August 31 had decreased by 10 μeq/l and concentrations were nearly zero during the fall (Table 5). In the 9th year of simulation the maximum concentration of aluminum during spring snowmelt had decreased from a value of 60 μeq/l to 38 μeq/l. Total inorganic carbon also showed a response to base treatment, with concentrations increasing 6, 45 and 163 μeq/l above base case levels after 3, 6, and 9 years. The simulated increase in the organic soil horizon CEC from 20 to 50 $\text{cmol}_c\ \text{kg}^{-1}$ also altered lake chemistry. Calcium concentrations, pH and ANC were all lower, and aluminum concentrations greater, in the high-CEC simulation.

Although trends from the model simulations generally agreed with observations from the field, the absolute comparison of simulated and observed lake concentrations was not so favorable. Observed mid-October concentrations of calcium and other chemical parameters for the lake and stream WO4, and

Table 5. Summary of water chemistry at the lake outlet from ILWAS simulations of calcite application to the Woods Lake watershed. Values are from August 31 of simulation years 3, 6 and 9. All units in μeq/l.

	Basecase			Scenario 1			Difference between basecase and Scenario 1		
Lake									
Year	3	6	9	3	6	9	3	6	9
pH	4.8	4.8	4.8	5.4	6.0	6.5	0.6	1.2	1.7
Ca	89	89	89	106	114	125	18	25	35
ANC	−10	−10	−10	0	7	19	10	17	29
Altm	12	12	11	1	0	0	−11	−11	−11
Alom	2	2	2	0	0	0	−1	−2	−2
Oac	7	7	7	6	6	6	−1	−1	−1
TIC	183	183	183	189	228	346	6	45	164
NO_3	12	12	11	10	10	8	−2	−2	−3

Ca = calcium, ANC = acid-neutralizing capacity, Altm = total monomeric aluminium, Alom = organic monomeric aluminium, Oac = organic acid analog, TIC = total inorganic carbon, NO_3 = nitrate

Table 6. Comparison of mid-October values for selected chemistry paramaters with model output data.

	Date	pH	H (μeq/l)	Ca (μeq/l)	ANC (μeq/l)	Altm (μeq/l)	SO_4 (μeq/l)
Lake outlet	10/10/1988*	6.7	0.2	157	94	3	129
	10/16/89	6.6	0.3	129	87	12	129
	10/15/90	7.0	0.1	279	197	8	94
	10/18/91	6.9	0.1	197	97	4	na
WO4 outlet	10/10/1988*	4.6	25.1	55	−25	75	141
	10/16/89	6.4	0.4	349	235	22	157
	10/15/90	6.1	0.8	202	40	28	113
	10/7/91	4.9	12.6	126	−5	35	na
Model	10/15/89	4.9	12.6	94	−7	9	130
3 year dataset	10/15/90	5.0	10.0	100	−2	8	139
	10/15/91	6.0	1.0	108	7	1	139
	10/15/92	5.4	4.0	108	3	4	139
	10/15/93	5.7	2.0	112	7	3	143
	10/15/94	6.3	0.5	117	16	1	141

* pre-treatment values

modeled lake outlet are shown in Table 6. The observed calcium concentration in the outlet in October, 1991 was approximately 40 μeq/l higher than 1988 (pre-treatment) concentrations. In model simulations, calcium concentrations increased only 14 μeq/l after 2–3 years. Differences between observed and simulated concentrations could be due, in part, to differences between the observed lake chemistry prior to watershed base treatment and values during the 1978–1981 ILWAS study. The discrepancy can be attributed to the residual effects of direct lake treatment experiments which occurred prior to EWLS (Driscoll et al. 1996, this issue). Measured calcium concentrations in October, 1988 were approximately 160 μeq/l while concentrations in October, 1984, prior to the inception of lake liming studies in the watershed, were about 80 μeq/l. Lake pH and ANC in 1988 were 6.7 and 100 μeq/l, respectively, versus the 1984 values of 5.1 and 3 μeq/l. In the first year of the model simulation, the calcium, pH and ANC were 90 μeq/l, 4.7 and -7 μeq/l, respectively. These values are much more similar to values from October, 1984, before lake liming. The model could not legitimately have been calibrated to the pre-watershed treatment conditions of 1988 because the chemistry of the lake at that time was not due to terrestrial influences so much as to the effects of direct lake liming. Differences between the observed and simulated values may also have been due to the amount and chemistry of precipitation used in the model input compared to values observed in the three years following the field experiment.

Modeled and Observed Fluxes

After nine years of simulating the base addition the model showed a cumulative calcium flux of 1295 keq from the lake outlet. Although the methods of simulating the calcite treatment were different, the calcium flux from the outlet compared favorably with the flux of 1505 keq modeled by Davis & Goldstein (1988). However, the outlet calcium flux simulated by the model was much lower than that which was observed in the watershed. After accounting for background fluxes, a total flux of 605 keq of calcium was observed from the outlet for water years 1990 and 1991 (Burns 1996). In model simulations, the additional calcium flux due to calcite treatment (Scenario 1 flux less the basecase flux) was only 30 keq after two years and 65 keq after three years. Even after nine years of model simulation, the added flux was only 370 keq, about 235 keq less than the cumulative amount observed in the field two years following treatment.

Much of the calcium flux at the lake outlet is provided from subcatchment II, which released 247 keq of calcium during 1990–91. This catchment contains a beaver pond which was partially treated with calcite (Cirmo & Driscoll 1996). The modeled subcatchment does not include this pond, so perhaps it is more realistic to compare the flux in the model with that from the stream draining subcatchment IV. The flux measured from the WO4 outlet during the two year period was 48 keq, or 2.82 keq/ha, based on a contributing area of 17 hectares. The nine-year modeled calcium flux from the outlet was equivalent to 1.77 keq/ha. Thus, even if subcatchment IV is used for comparison, simulations of calcium loss were much lower than observed values.

To investigate why the model failed to match observed data, the internal fluxes of the model were evaluated. The model provides a yearly summary of the ion fluxes in soil solution due to the processes of weathering, cation exchange, litter decay, and uptake. Yearly fluxes were summed over the nine year simulation period to obtain the cumulative flux associated with each process (Fig. 5). The flux of calcium from a layer to the lake is essentially equivalent to the flux out of the layer less the input to the soil layer below it. Over the nine year period, 91 percent of the calcium weathered from calcite was retained on exchange sites in the upper horizon. The second and third layers also showed a net gain of calcium on exchange sites over the nine year period; unlike the basecase, which lost calcium from exchange sites in both horizons. An increase, over the basecase, in calcium draining from a layer was noted in the top three layers. Changes in calcium fluxes in the bottom two layers were minimal. After three years of simulation the transport of calcium to surface waters from layer 3 was only 4 keq greater than the basecase, while layer 1 transport was 52 keq greater than basecase levels. Sixty percent of the lateral flow of water in the watershed simulation is routed through layer 3, with only 20% passing through layer 1. Even though soil water concentrations of calcium in the upper layer (111 μeq/l) were much greater than the basecase (22 μeq/l), the volume of water flowing laterally through the horizon is low (Fig. 1). Most of the lateral drainage was instead routed through layer 3 where soil water concentrations of calcium were only 5 μeq/l higher than the basecase in the third year. Model simulations may have significantly underestimated export from soils to drainage waters if more lateral flow actually occured through the upper soil horizons in the field.

The calcite was applied to the watershed as a mineral in the first layer. While this may be a reasonable representation of the treatment, it resulted in some difficulties. The application method used in the model ignored initial transport of calcium dissolved from calcite via overland flow. During rain events, ephemeral channels which may contact the calcite on the forest floor carry water into streams. Overland flow in the model occurs only when the water table intercepts the surface. Because calcite is incorporated as a mineral in the upper layer, it isn't necessarily solubilized or transported by overland flow. The model also neglects macropore flow which could rapidly tranport water from the surface through the soil to drainage waters.

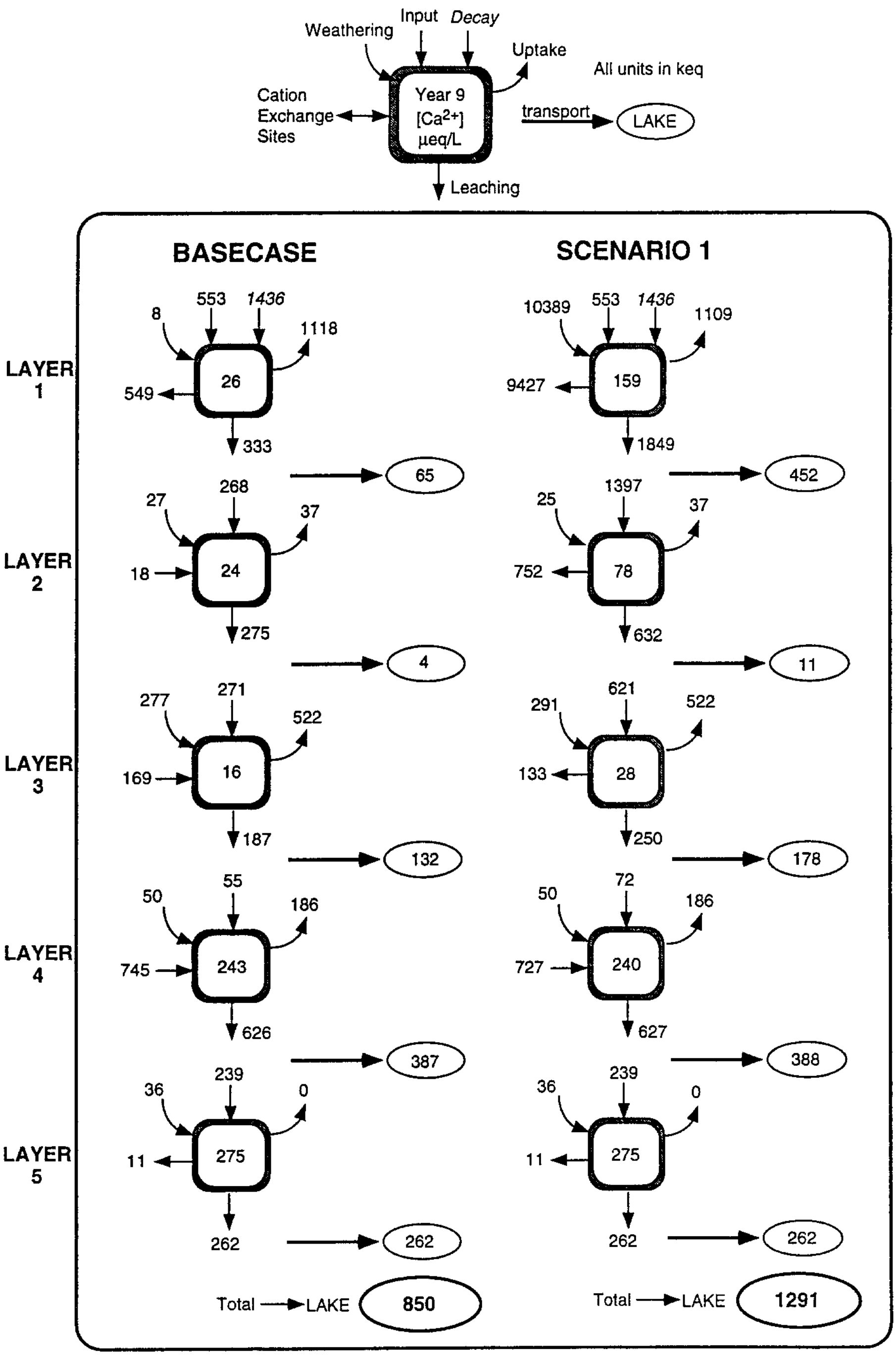

Fig. 5. Simulated calcium fluxes from each soil layer in the watershed (208 ha), summed over a nine year period, for the basecase and Scenario 1. Effects are restricted to the upper 3 horizons. Note that the soil exchanger provides calcium to the soil solution in layers 2 and 3 of the basecase, and receives calcium from solution in Scenario 1. To convert to kilograms over the entire watershed, multiply by 4.16832.

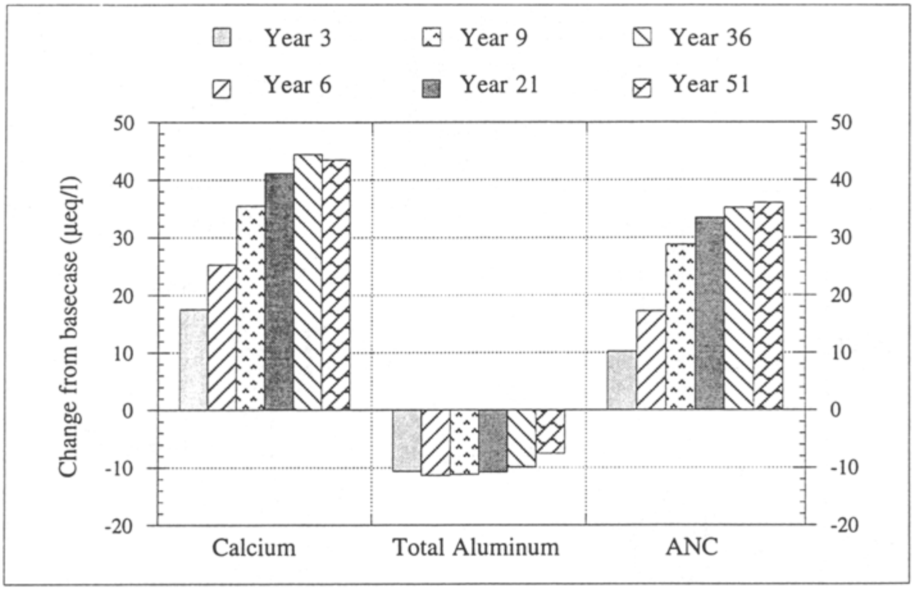

Fig. 6. Simulated change in calcium, aluminum and ANC concentrations from the basecase values for selected years of a 51year simulation. Values are those recorded on August 31 of the year. After the 36th year values begin to reapproach basecase values.

Results of a 50 year simulation

Observed results from the field appear to indicate that the length of elevated ANC conditions following watershed calcite addition exceeded that of direct base application to Woods Lake. Although results from simulations were not as great as was observed in the field, model calculations did show an immediate improvement in the water chemistry of the lake outlet. An important consideration for EWLS was to estimate the duration of effects for the terrestrial application of calcite. Despite problems with the model application discussed above, the application of ILWAS can allow for a determination of the rate of reacidification and the duration of terrestrial base treatment. A fifty year simulation was conducted using the basecase and parameters in Scenario 1. Results indicate that the effects of calcite treatment should persist for at least 50 years (Figs 6, 7). Model calculations suggest the effects of calcite addition begin to diminish after 36 years, as aluminum concentrations begin to increase towards basecase concentrations. By the 51st year calcium concentrations also begin to decrease towards the basecase concentration. This decline in calcium concentrations is partly due to the slowing rate of calcite dissolution. After two years of simulation 45% of the calcite applied to the

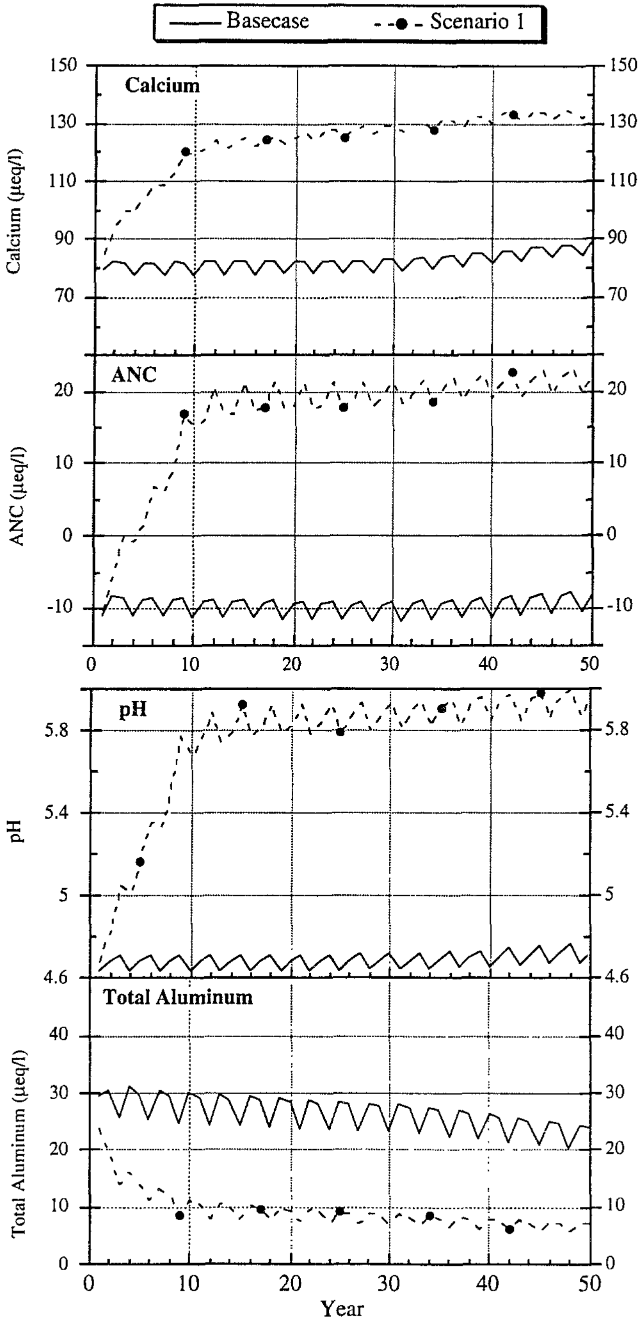

Fig. 7. Annually averaged values for calcium, ANC, pH and total aluminum over a 51 year simulation period.

watershed dissolved, similar to field observations (Blette & Newton 1996). However, the rate of calcite weathering diminished as the base saturation increased and soil solution chemistry of the first layer changed (Fig. 3). After nine years of simulation only 67% of the calcite had dissolved, indicating a diminishing rate of calcite dissolution. When the rate of calcium supplied by calcite dissolution declined below the rate of strong acid input from atmospheric deposition, reacidification of the soil and drainage water occurred. While dissolution in the field is not necessarily controlled by the base saturation of the layer, it will also likely diminish with time due to organic coatings, diminished surface area, and higher calcium, pH and total inorganic carbon in soil.

Conclusions

The ILWAS model was used to simulate the response of Woods Lake, NY to terrestrial application of calcite in an effort to predict the duration of base treatment. Comparison of the model results with the observed manipulation data also provided a test of the model's ability to simulate terrestrial biogeochemical processes. For model simulations, calcite was applied as a rapidly weathering mineral in the upper soil layer. There was an immediate effect of calcite dissolution on the soil solution and lake chemistry. Calcium concentrations, pH, and ANC increased in the upper soil layer within the first year of the simulation. The effects in lower soil layers were more complex. Calcium concentrations increased in layers 2 and 3 within three years, while ANC slowly increased due to proton production from calcium exchange in the upper layer and hydrolysis of aluminum. The soil water pH in layer 2 was below basecase levels for 3 years, and in layer 3 remained below basecase levels for 9 years. In the lake, calcium concentrations increased within four months of the simulation's beginning. ANC and pH did not change significantly until eight months after calcite treatment. Aluminum concentrations decreased significantly in lake water.

While the model did predict a response to calcite addition which agreed with the trends observed in the field experiment, the export of calcium through the outlet was lower than observed values. This discrepancy is probably due to a few factors. The application technique used in the model incorporated calcite into a 15 cm thick horizon. Calcite in the field was applied to the surface where it may have had more contact with incoming throughfall. The CEC of soils at Woods Lake increased markedly following base addition. However, the model fails to simulate pH-dependent CEC, using a fixed CEC. This problem was accounted for by setting the CEC in the model higher than initial field values. The immediate increase in CEC likely diminished the flux of calcium from soil layers in the model simulations.

The model simulations did not include physical features of the watershed which facilitated the dissolution of calcite and supply of calcium to surface waters. In the field, calcite was applied to streams, and wetlands in treated subcatchments which serve as variable source areas. Additionally, the beaver pond in subcatchment II was partially treated. The calcium released from the beaver impoundment had a large impact on the stream water draining the subcatchment (Cirmo & Driscoll 1996) and on the lake outlet (Burns 1996), but was not included in the representation of the model. The model could be altered to account for these areas by greater segmentation of the watershed. However, calcite dissolution is enhanced in these variable source areas. Once the readily dissolved calcite is depleted we would predict that the surface water concentrations of calcium and ANC will decrease to values more in line with model predictions, as soil exchange processes become the more important source of calcium. Certainly this seems to be the case for both the outlet and the stream draining subcatchment IV, where the ANC was decreasing to pre-liming levels by 1991 (Cirmo & Driscoll 1996). The model may not have provided accurate predictions of the immediate effects of direct calcite application to channels and variable source areas, but may, in fact, effectively simulate the long-term effects of base treatment.

The model predicts that the ANC in the lake outlet will be approximately 25 μeq/l higher than pre-treatment concentrations by 1999. The pH will be greater than 5.5 and aluminum concentrations should be about 10 μeq/l less than before treatment. Although the model predicts that calcite in the first horizon will have completely dissolved after 45 years, the positive effects of calcite addition are predicted to last longer than fifty years. This could be an overestimate if calcite in the field dissolves more rapidly. However, even if this is the case, the effects have surpassed those attained by direct application of calcite to the lake.

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