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Effects of watershed liming on the soil chemistry of Woods Lake, New York

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Abstract. The effects of watershed liming on the exchange complex of a forest soil were investigated at Woods Lake, in the west-central Adirondack Park, New York. Attempts to neutralize lake acidity via direct application of calcite during the 1980's were short-lived due to a short hydraulic retention time. The Experimental Watershed Liming Study (EWLS) was initiated to investigate watershed base addition as a potentially more long-term strategy for mitigation of lake acidity. In this paper we discuss the changes in the exchangeable soil complex which occurred in response to the calcite addition and attempt a mass balance for calcite applied to the watershed.

An extensive sampling program was initiated for the watershed study. Soil samples were collected from pits prior to and in the two years following treatment to evaluate changes in soil chemistry. Calcite addition significantly altered the exchange complex in the organic horizon. Increases in pH caused deprotonation of soil organic matter and increases in cation exchange capacity, providing additional exchange sites for the retention of added calcium. Exchangeable acidity decreased to very low values, allowing the base saturation of upper organic horizons to increase to nearly 100 percent.

Post-treatment sampling found that approximately 48 percent of the calcite remained undissolved in the soil's Oe horizon two years later. Dissolution of the calcite was affected by field moisture conditions, with greater dissolution in wetter areas of the watershed. Mass balances calculated for calcium applied to the watershed suggest that only 4 percent of the calcium was removed through the lake outlet. Approximately 96 percent of the calcium applied remained within the watershed; as undissolved calcite, on soil exchange sites or stored in the vegetation, groundwater or surface waters of the watershed.

Introduction

During the 1970's and 1980's 'acid rain' research largely focused on the causes and effects of acidification by anthropogenic sources, and reducing acidification through emission controls. However, additional research focused on alleviating the problems caused by acidic precipitation. The addition of 'lime', generally crushed limestone, to lakes to increase their pH and acid neutralizing capacity (ANC) became a management tool in Norway and Sweden (Lessmark & Thornelof 1986). Many lakes in the U.S. have also been treated to improve waters for fish populations (Porcella 1989). However, the lasting effects of lake liming may be tempered by the short hydraulic retention time of a treated lake, which would require frequent re-liming to maintain desirable water quality.

Terrestrial application of lime has long been an agricultural practice to counteract cationic losses occurring as the result of vegetation uptake and crop removal. Dissolution of lime in acid soils supplies calcium and magnesium to plants, and increases both base saturation and soil pH. An increase in soil pH can also increase the availability of other nutrients (e.g. Mo, P), promote nitrogen fixation, and reduce the release of inorganic aluminum which can be toxic to plants (McLean & Brown 1984; Nohrstedt 1988). Field liming experiments have been conducted on both agricultural and forest soils. The major difference between the two approaches is that forest applications are primarily conducted on the surface of the soil, while agricultural applications incorporate lime into the soil. It is difficult to extrapolate the results of agricultural studies to forest liming due to this difference in application techniques. Also, many agricultural studies are conducted on fields where active cropping is occurring and are monitored for only a short period of time (1–2 years). Most forest liming studies have focused on the effects of liming on soil chemistry and tree growth (Foster et al. 1988; Tveite et al. 1990; Derome 1990; Persson et al. 1990). However, a few forest studies have been initiated to evaluate the effects of liming on the quality of waters draining treated areas (Adams & Evans 1989; Westling & Hultberg 1990; Howells & Brown 1986; Brown et al. 1988; Grieve 1990).

The Experimental Watershed Liming Study (EWLS) was initiated to determine whether application of limestone to the soils of a watershed could increase the duration of acid neutralization in a lake with a short hydraulic retention time. The primary hypothesis of the study was that calcium ions supplied from added calcite would adsorb on soil exchange sites, increasing the base saturation. Water subsequently routed through soil layers would be more effectively neutralized (via cation exchange) before draining to the lake, allowing for neutralization of lake water, with a corresponding increase in pH and decrease in the concentration of toxic inorganic monomeric aluminum. In this paper we evaluate the transport and fate of calcite and calcium following application to the watershed. The response of the soil exchange complex and a mass balance for calcium applied to the watershed are also discussed.

Study Area

Woods Lake is a headwater lake located in the west-central Adirondack Park of New York State. The watershed covers an area of 208 hectares, with

122 meters of relief. Surficial sediments consist mostly of thin till, although seismic refraction surveys have found depths to bedrock as great as 10 meters on the northwest shore of the lake. There are numerous small bedrock outcrops of hornblende granitic gneiss in the watershed, primarily on the southeastern side of the lake. The soils of the watershed are young (<12,000 years), and exhibit the Spodosol profile typical of the region. Dominant contributors to mineral weathering in the soils are plagioclase and potassium feldspars and Ca-rich hornblendes (April & Newton 1985). Calcium is the dominant exchangeable base cation in all horizons.

The watershed was investigated during the Integrated Lake Watershed Acidification Study (ILWAS) in the 1980's. April & Newton (1985) attributed the low pH and ANC of Woods Lake to the inability of the watershed's surficial sediments to neutralize acidic deposition. With a shallow depth to bedrock, most water entering the lake moves as overland flow or shallow interflow through organic soil horizons. Because little acid neutralization occurs in these horizons, waters entering the lake are lower in pH than they would be in a watershed with thicker surficial sediments.

Methods

An extensive field sampling program accompanied the project. Six sampling transects, ranging from 450 to 765 meters in length, were established in the treated subcatchments II and IV. Study plots (20 × 20 meters) were established at 30 meter intervals along each line. These 33 plots were the sites of vegetation, forest floor and soil bag studies (Driscoll et al. 1996; this issue, Figure 2). The limestone used for the watershed experiment was obtained from a Watertown, NY quarry. Rocks were crushed to a consistency of fine sand with approximately 70% less than 0.149 mm. This crushed stone was pelletized using a water soluble calcium lignosulfonate binder to a size of 1.41–4 mm. The binder was designed to allow pellets to disintegrate to their original grain size with a minimum of moisture. However, pellets generally took longer to dissolve in the field than in the laboratory. Details of the application of the pelletized limestone to the watershed can be found in Driscoll et al. (1996, this issue).

Post-treatment undissolved calcite

Forest floor samples were collected one and two years following treatment to determine the amount of undissolved calcite remaining on the ground. Sample locations were located adjacent to vegetation plots, within soil sampling plots and at additional random locations within the treated subcatchments. To ensure a consistent sample area, a 25 cm^2 template was constructed to collect the samples. The small area of the template allowed for analysis of a whole sample without further splitting which could result in loss of calcite, due to differences in the physical characteristics between the treatment material and the soil. Nine samples, alternately spaced within a 5 × 5 template grid, were collected from each sample location. The amount of calcite in samples was determined by reaction with 2N HCl in a closed system, a variation of a method described by Gross (1971). Reagent grade calcite was used for the standardization so that the total amount of actual calcite in samples was determined. The amount of calcite present in the bulk pelletized limestone was also determined using this method.

Soil Chemistry

Soil sampling plots were established at random locations in three subcatchments. Two plots were located in both subcatchments II and IV and one in the reference subcatchment I (Driscoll et al. 1996, this issue). Soil pits in the plots were excavated prior to treatment, and one and two years after treatment, to characterize changes in exchangeable soil chemistry. Triplicate samples from each horizon were collected from pre-treatment pits which were excavated to the C horizon. The sampling protocol was changed following treatment to more intensively sample the O horizon, which is made of 3 fairly distinct subhorizons, the Oi, Oe and Oa. A sheet metal template, measuring 20 × 20 × 17 centimeters, was driven into the ground until the top was flush with the forest floor surface. Each pit was generally completed to a depth of at least 40 cm, within the Bs1 or Bs2 horizon. Two pits in each plot were sampled in 1990, and one pit per plot was sampled in 1991. Samples from each horizon were removed from within the template and analyzed for exchangeable ion chemistry.

The response of the soil to calcite addition was also monitored by the placement of ‘soil bags’ at the Oa-E interface in plots along the vegetation transects, using the method of David et al. (1990). Each bag contained 200 grams of B horizon soil collected from a pit on the perimeter of the watershed. The soil was packed into disks bound by Nytex-mesh bags (250μm mesh size). Bags were removed 6 months, one year and two years following treatment and analyzed for exchangeable ion chemistry.

Soil samples were refrigerated at 4 °C until they were processed. Samples were oven dried at temperatures less than 21 °C and passed through a riffle splitter and 2mm sieve prior to analysis for exchangeable bases and acidity. Normally a solution of 1N ammonium acetate, which buffers the solution to a pH of 7, is used for the extraction of exchangeable bases (Thomas 1982). The NH_4^+ ion is accepted as an adequate index ion for most exchange reactions involving the base cations, Ca^{2+}, Mg^{2+}, $Na^{+}$and K^{+}. The Thomas method was modified to use 1N ammonium chloride (pH 5.3) as an extractant. This provides an unbuffered extractant, allowing the solution pH to approximate field conditions, so that the 'effective' concentration of exchangeable bases is determined. It is generally agreed that there is no good method for determination of exchangeable bases in soils containing free calcite (Thomas 1982). Strong acids produced as a by-product of the extraction can enhance the dissolution of calcite and overestimate values of exchangeable calcium. An extraction for exchangeable bases conducted on a sample of the pelletized limestone showed that the release of calcium associated with dissolution of calcite during the extraction was far less than the increase in exchangeable calcium noted in treated organic horizons. A dissolution experiment substituting NH_4Cl for HCl also suggested that NH_4Cl was not effective in the dissolution of calcite. Therefore, NH_4Cl was deemed an appropriate extracting agent for determination of exchangeable base cations with the assumption that any error associated with calcite dissolution during the extraction was minimal. The ion concentrations in extracted solutions were analyzed using a Perkin-Elmer Model 3030 atomic absorption spectrophotometer. Calcium and magnesium were analyzed by atomic absorption while sodium and potassium were determined by atomic emission. Lanthanum chloride was added to samples analyzed for calcium and magnesium to inhibit potential interferences from aluminum, silica, phosphate and sulfate.

Exchangeable acidity was determined by extraction with 1N potassium chloride (Thomas 1982). This method allows for the determination of total acidity and its components hydrogen ion and aluminum available at the field soil pH. The effective cation exchange capacity was calculated as the sum of exchangeable bases and total exchangeable acidity. Base saturation was computed as the sum of exchangeable bases divided by the effective cation exchange capacity. Note that our use of the term base saturation differs from that of traditional soil science which determines base saturation in buffered solutions. We felt that determination of unbuffered CEC and base saturation would be more useful in assessing the impacts of base treatment on Woods Lake soils.

Results

Applied and undissolved calcite

Dissolution experiments revealed that only 82 percent of the limestone applied to the watershed was calcite. Therefore, the target application rate of 10 Mg ha^{-1} limestone was actually equivalent to an application rate of 8.2 Mg ha^{-1}

Table 1. Post-treatment amounts of calcite (Mg ha^{-1}) on the forest floor. Values are for samples collected in 1990–1991, by transect and subcatchment. Values for the two years were combined because values for 1990 were not significantly different from those of 1991.

Transect	Mean	sd	se	cv	n
2100	4.47	3.71	0.32	83.06	135
2200	7.76	4.82	0.93	62.1	27
4100	0.69	0.71	0.14	102.87	27
4200	2.15	2.24	0.27	104.26	69
4300	1.13	0.75	0.18	65.77	18
4400	3.27	3.13	0.30	95.85	109
Add'l Subcatchment II*	6.55	4.94	0.69	75.4	51
Add'l Subcatchment IV*	6.00	3.9	0.65	65.05	36
Subcatchment II	5.39	4.35	0.30	80.72	213
Subcatchment IV	2.93	4.14	0.20	107.08	259
II and IV	4.04	3.92	0.18	97.15	472

* Additional forest floor samples were collected areas within catchment.

sd = standard deviation, se=standard error, cv=coefficient of variation, n = number of samples).

of calcite, 824 Mg over 103 ha of the 208 ha watershed. An average of 7.85 and 5.91 Mg ha^{-1} was recovered from the areas contributing to streams in subcatchments II and IV, respectively (see Driscoll et al. 1996, this issue).

Forest floor samples collected and analyzed in 1990 and 1991 showed that calcite remained largely undissolved in the soil. Although samples were not analyzed, the applied material was still visible within the Oe horizon in June 1994. The pellets of limestone were not visible, having broken upon impact or contact with water. Instead, the material persisted as a coating on leaf litter, or as a cemented cake, a 'lime sandwich', between leaf layers. This reduction of total surface area possibly slowed dissolution. Because the surface of the forest floor is fairly dry most of the year, contact of the calcite with water is restricted to storm and snowmelt events. Calcite was not as visible in wetlands and areas adjacent to the lake and streams where there is an increased possibility of contact with water. The spatial variability in calcite recovered at forest floor sites was surprising considering the small area over which the samples were collected, 9 samples within 625 cm^2. Standard deviations were as great as 100 percent of the mean (Table 1). The average amounts of calcite remaining for the years 1990 and 1991 were 5.78 and 4.84 Mg ha^{-1} in subcatchment II and 3.08 and 2.65 Mg ha^{-1} in subcatchment IV. However, because differences between the amount of calcite remaining in 1990 and 1991 were not significant, values for the two years were pooled in order to compare application and post-application calcite amounts. Although comparison with the values of applied calcite are tenuous, due to differences in analytical techniques, there was a significant difference between the amount of calcite applied (1989) and remaining (1990–91).

Soil Chemistry

Soil samples were collected from pits at six sites located in the two treated subcatchments and a reference subcatchment during the 3 year study. Because horizon depths and thicknesses varied greatly, even within a sampling plot, chemical characteristics were grouped by horizon rather than depth. Samples collected from untreated reference sites showed no significant changes over the three year period and were grouped with pre-treatment samples to increase the population size for statistical analyses. The pre- and post-treatment values by horizon for exchangeable cations, exchangeable acidity, cation exchange capacity and base saturation are shown in Table 2.

Cation exchange capacities in pre-treatment soil samples ranged from a high of 26 $cmol_c\ kg^{-1}$ in the Oi horizon to 2 $cmol_c\ kg^{-1}$ in the E horizon. The Bh horizon, below the E, had an elevated CEC of 7.5 $cmol_c\ kg^{-1}$, reflecting the presence of organic matter translocated from the Oa horizon. Calcium was the predominant exchangeable base cation in unlimed soils, comprising approximately 80 percent of exchangeable base cations in organic horizons and approximately 50 percent in mineral horizons. Values of calcium ranged from 17 $cmol_c\ kg^{-1}$ in the Oi horizon to less than 0.1 $cmol_c\ kg^{-1}$ in the Bs horizon. Total exchangeable acidity in the organic horizons was high, with most of the acidity contributed by exchangeable hydrogen (73–83%), the norm in soils with a large organic matter contribution to CEC (Thomas & Hargrove 1984). Most of the exchangeable acidity in mineral horizons was due to exchangeable aluminum (70 ± 17%). Base saturations steadily decreased with depth from 80 percent in the Oi horizon to less than 8 percent in B horizons (Table 2).

The soil chemistry of the organic horizons changed dramatically after treatment. The CEC increased in all horizons; sites in the organic horizons were filled by exchangeable calcium, and in mineral horizons by exchangeable acidity. Exchangeable calcium, the only base cation which showed a significant response to calcite addition, increased from 17 to 37 $cmol_c\ kg^{-1}$ in the Oi, from 8.5 to 35 $cmol_c\ kg^{-1}$ in the Oe, and from 6 to 10 $cmol_c\ kg^{-1}$ in the Oa horizons. Total exchangeable acidity decreased from 5 to 1 $cmol_c$

kg^{-1} in the Oi, 8 to 2 $cmol_c$ kg^{-1} in the Oe, and 8 to 6 $cmol_c$ kg^{-1} in the Oa horizon. Exchangeable aluminum decreased to nearly 0 in the Oi and Oe horizons. Exchangeable hydrogen ion also decreased by approximately half in the organic horizons. Exchangeable acidity increased in mineral horizons, although differences between pre- and post-treatment were not statistically significant. Values of base saturation increased to nearly 98 percent in the Oi horizon and 94 percent in the Oe horizon. Even the Oa horizon experienced a 20 percent increase in base saturation. Values of base saturation decreased slightly in mineral horizons due to an increased proportion of exchangeable acidity on cation exchange sites.

Results from one pit located in subcatchment II (Figure 1) corroborate results discussed above which were aggregated from all soil pits. The effects of the calcite addition appear to be migrating down-profile over time. The large increase in exchangeable calcium in the Oe horizon during the second year of sampling is attributed to the relative downward movement of the treated horizon with each year's subsequent litterfall.

Results from soil bags were inconclusive. It is unclear how complete a hydraulic connection was made between the soil bag and surrounding soil. David et al. (1990) cited this as a cause of concern in a buried bag study in Maine. Fifty-four samples were collected in October 1990 and 44 in August 1991. Samples from the treated catchments were pooled for statistical analysis (Table 3). The average cation exchange capacity increased from 1.12 to 1.52 $cmol_c$ kg^{-1}, agreeing with trends observed in soils collected from pits, where an increased CEC in mineral horizons was filled with an increase in exchangeable aluminum. Significant differences were found for exchangeable aluminum which increased from 0.81 to 1.32 $cmol_c$ kg^{-1}, and exchangeable hydrogen ion which decreased from 0.17 to 0.02 $cmol_c$ kg^{-1}. Although exchangeable calcium increased from 0.09 to 0.14 $cmol_c$ kg^{-1} for the two samplings, the differences were not significant. Base saturation did not change (12.4 versus 12.2%) because of the observed small increase in exchangeable calcium and decrease in exchangeable hydrogen ion.

Discussion

Dissolution of applied material

Under laboratory conditions dissolution rates for limestone are partially dependent on the composition of the limestone and the particle size, both of which were presumed constant for the watershed experiment. Additional controls which could result in different rates of dissolution include the degree of mixing and moisture levels (Thomas & Hargrove 1984). Mixing in the field

Table 2. Pre- and post-treatment concentrations of soil exchangeable cations from soil pit samples (in cmol$_c$ kg^{-1}). Standard deviations from the mean are shown in parentheses. Post-treatment values followed by an asterisk were significantly different from the pre-treatment sample when compared by unpaired t-tests to a 95% significance level.

Horizon	Sodium	Potassium	Calcium	Magnesium	SBC	Total acidity	Aluminium	Hydrogen	CEC	% Base sat.	n
Oi-pre	0.10(0.06)	0.98(0.59)	16.8(5.07)	2.16(0.85)	20.0(4.98)	5.08(0.91)	0.84(0.53)	4.23(0.76)	26.0(4.94)	79.7(6.62)	5
Oi-post	0.04(0.02)	1.18(0.40)	37.4(6.10)*	2.05(0.94)	40.7(6.99)*	0.92(0.36)*	0.00(0.00)*	0.92(0.36)*	41.5(7.27)*	97.8(0.60)*	13
Oe-pre	0.05(0.02)	1.04(0.16)	8.53(1.75)	1.49(0.24)	11.1(1.92)	7.06(1.78)	1.15(0.86)	5.91(1.69)	18.2(2.07)	61.2(7.79)	7
Oe-post	0.05(0.02)	0.88(0.19)	35.6(10.1)*	2.27(0.03)*	38.8(10.2)*	1.98(0.66)*	0.05(0.10)*	1.93(0.69)*	40.8(9.84)*	94.6(2.94)*	16
Oa-pre	0.05(0.04)	0.39(0.16)	5.83(2.59)	1.12(0.69)	7.39(3.05)	8.10(1.07)	2.16(0.94)	5.93(0.78)	15.5(3.01)	46.0(11.8)	12
Oa-post	0.04(0.01)	0.43(0.12)	10.4(5.21)	1.24(0.55)	12.1(5.62)	5.82(1.61)*	1.70(0.37)	4.12(1.29)*	18.0(5.51)	64.3(14.6)*	30
E-pre	0.05(0.03)	0.03(0.01)	0.14(0.09)	0.04(0.02)	0.26(0.11)	1.77(0.49)	0.84(0.26)	0.93(0.27)	2.03(0.58)	13.0(3.59)	9
E-post	0.03(0.02)	0.04(0.01)	0.34(0.28)	0.05(0.02)	0.45(0.29)	2.96(1.44)	1.72(1.15)	1.25(0.51)	3.41(1.57)	13.9(5.46)	10
Bh,Bhs-pre	0.06(0.04)	0.06(0.03)	0.36(0.29)	0.08(0.06)	0.56(0.39)	6.94(2.67)	4.34(1.96)	2.60(1.10)	7.50(2.90)	7.43(3.05)	11
Bh,Bhs-post	0.03(0.02)	0.07(0.02)	0.48(0.50)	0.08(0.04)	0.67(0.50)	7.64(3.57)	5.36(2.52)	2.28(1.63)	8.31(3.71)	8.91(7.13)	24
Bs,B2,B3-pre	0.04(0.03)	0.03(0.02)	0.09(0.06)	0.03(0.02)	0.20(0.10)	3.85(2.51)	3.08(2.10)	0.78(0.60)	4.05(2.60)	5.47(1.89)	25
Bs,B2,B3-post	0.02(0.01)*	0.05(0.02)*	0.17(0.12)	0.05(0.02)	0.30(0.14)	6.00(2.06)	4.34(1.54)	1.66(1.39)	6.30(2.14)	4.9(1.87)	20

SBC = Sum Base Cations, CEC = Cation Exchange Capacity, n = number of samples.

Table 3. Concentrations of exchangeable cations obtained from mineral soil bag samples ($\mathrm{cmol_c\ kg^{-1}}$), with the standard deviation of the mean shown in parentheses. Bulk samples of B horizon collected from the perimeter of the watershed used as an initial value. Soil bags were collected from treated subcatchments II and IV and reference subcatchments I and V. The collection date is noted for each group. Values followed by an asterisk were significantly different from the pre-treatment (i.e. 'bulk') sample.

Horizon	Sodium	Potassium	Calcium	Magnesium	SBC	Total acidity	Aluminum	Hydrogen	CEC	% Base sat.	n
Bulk B	0.04	0.02	0.05	0.02	0.13	1.20	1.00	0.20	1.23	9.77	
Collected 3/90	0.07(0.00)	0.02(0.00)	0.14(0.16)	0.01(0.00)	0.25(0.16)	1.07(0.20)	0.96(0.17)	0.11(0.05)	1.32(0.17)	18.6(9.76)	52
Collected 10/90	0.01(0.01)*	0.02(0.00)	0.09(0.07)	0.01(0.00)	0.14(0.08)*	0.99(0.17)	0.81(0.15)*	1.12(0.09)*	1.12(0.17)*	12.4(6.54)*	54
Collected 8/91	0.01(0.00)*	0.02(0.00)	0.14(0.10)	0.01(0.01)	0.18(0.10)	1.34(0.31)*	1.32(0.27)*	1.52(0.06)*	1.52(0.31)*	12.2(6.97)	44
Reference 3/90	0.06(0.02)	0.03(0.01)	0.08(0.02)	0.02(0.01)	0.19(0.03)	1.05(0.13)	0.95(0.12)	1.24(0.05)	1.24(0.14)	15.3(1.64)	12
Reference 10/90	0.01(0.00)	0.02(0.01)	0.03(0.00)*	0.01(0.00)*	0.06(0.01)*	0.86(0.08)*	0.85(0.06)	0.92(0.09)*	0.92(0.09)	6.49(0.49)*	9

SBC = Sum Base Cations, CEC = Cation Exchange Capacity, n = number of samples.

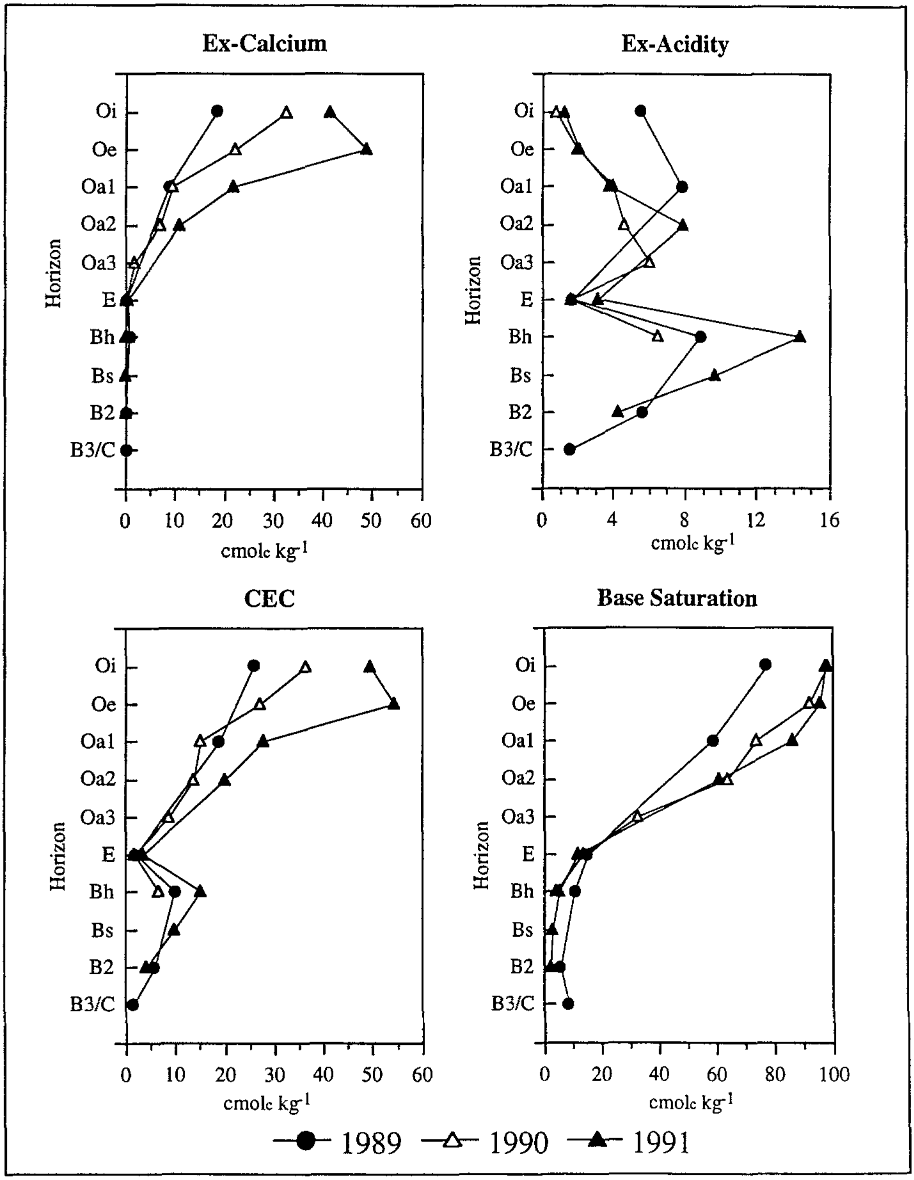

Fig. 1. Exchangeable calcium, exchangeable acidity, cation exchange capacity and base saturation for Pit-2 in subcatchment II. Pre-treatment samples were collected in 1989. Note the increase in CEC in the Oe horizon two years after treatment.

does not suggest mixing in the classic sense, as there was no mechanical distribution of calcite throughout the soil. Instead water serves as a mixing agent, facilitating the movement of calcite over the surface of leaf litter. Physical movement down slopes also could occur. Moisture levels differ depending on the saturation conditions of the soil and the relative amount of canopy cover.

The amount of calcite in post-treatment samples was less than the amount of calcite in the application (Driscoll et al. 1996, this issue). After two years it appeared that 35–50% of the applied calcite dissolved. Although much of the calcite dissolved, some was still visible in the soil five years after treatment. Variability of calcite content among post-treatment sites was great. Some of the variability may be explained by soil moisture conditions. In areas of the watershed where wetter conditions prevailed (e.g. wetlands, near-shore areas, areas with shallow bedrock), the calcite was not visible or detectable in post-treatment samples. The response of the stream and lake chemistry in the two years after treatment was probably largely due to dissolution of calcite from these areas which also serve as variable sources areas for streamflow (Newton et al. 1995).

The pH of organic horizons in the watershed were normally less than 4.5, which would favor dissolution of calcite. In response to the calcite applied to the forest floor, pH increased to greater than 6 (Brach, unpublished data), which undoubtedly slowed subsequent dissolution of calcite. Conditions of oversaturation which may have existed at the calcite/water interface could also impede dissolution (Amrhein & Suarez 1987). The calcite physically migrated deeper into the forest floor with the addition of litterfall each year (Figure 1). Concentrations of exchangeable calcium were greater in the Oe horizon than the Oi horizon in the second year after treatment. It is expected that organic acids produced in the decomposition of litter above the calcite and wetter conditions enhance the subsequent dissolution process.

Response of soil exchange complex

The soil exchange complex exhibited a marked response to the watershed treatment. Traditionally, the cation exchange capacity is assumed to be constant, with only the distribution of exchangeable cations changing over time. However, cation exchange sites in forest soil are largely associated with soil organic matter which has an abundance of pH-dependent exchange sites (Kalisz & Stone 1980; Ross et al. 1991; Santore et al. 1994). As pH increases, acidic functional groups (primarily carboxyl or phenol groups) dissociate, donating hydrogen ions to solution and providing negatively charged cation exchange sites. Due to the presence of pH-dependent exchange sites in these soils, the CEC increased following treatment in the organic horizons (Table 2). As the predominant cation in solution, calcium readily sorbed to these available sites. Increases in base saturation suggest that much of the calcium released from dissolution of the calcite was retained on exchange sites in the organic horizons of the soil.

The increase in pH also facilitated aluminum hydrolysis reactions which created additional exchange sites for calcium. Exchangeable aluminum decreased to nearly 0 $\text{cmol}_c\ \text{kg}^{-1}$ in the Oi and Oe horizons. Exchangeable hydrogen ion, the predominant form of exchangeable acidity in soils with abundant organic matter, decreased by more than half in the Oi and Oe horizons. Hydrogen ions released during the dissociation of functional groups and aluminum hydrolysis reactions may have been consumed by reaction with bicarbonate or hydroxyl ions in solution or subsequent dissolution of calcite. It is possible that excess hydrogen ion not consumed in these reactions could leach to mineral horizons and thus might account for the slightly higher exchangeable hydrogen ion concentrations observed in post-treatment E horizon samples.

While the increase in CEC was largely associated with increases in exchangeable calcium in the organic horizons, a different response was evident in mineral horizons. There appears to have been a slight increase in CEC in mineral horizons. Although exchangeable calcium concentrations increased slightly, the additional exchange sites were primarily associated with exchangeable aluminum (Figure 2). Aluminum is the dominant cation associated with the mineral soil exchange complex. If excess hydrogen ion were to leach to the mineral horizons from the organic horizon, lowering the pH, the dissolution of mineral aluminum could supply an increase in exchangeable aluminum. This pattern might suggest that over the short-term, calcite addition to the watershed could have an adverse effect on water routed through deeper soil horizons. This water would be neutralized less effectively, with more aluminum available for release to drainage waters. However, no consistent increase in monomeric aluminum was noted in either soil solutions (Geary & Driscoll 1995) or stream samples (Cirmo & Driscoll 1995). Soil bags collected two years after treatment did not yield useful results for determination of the effects at depth.

The question remains as to whether significant amounts of calcium will reach the mineral horizons in the long term. If the cation exchange capacity of the organic horizon continues to increase, most of the calcium added will be sequestered in that horizon. However, if the exchange capacity of the organic horizon stabilizes, then calcium ions will likely migrate into mineral horizons as they are leached from the forest floor. The increase in exchangeable calcium in organic horizons should stimulate vegetative uptake of calcium. Brach (unpublished data) observed an increase in levels of calcium of leaf litter collected after treatment. This could potentially enhance the cycling of calcium, as calcium ions dissolved from calcite or removed

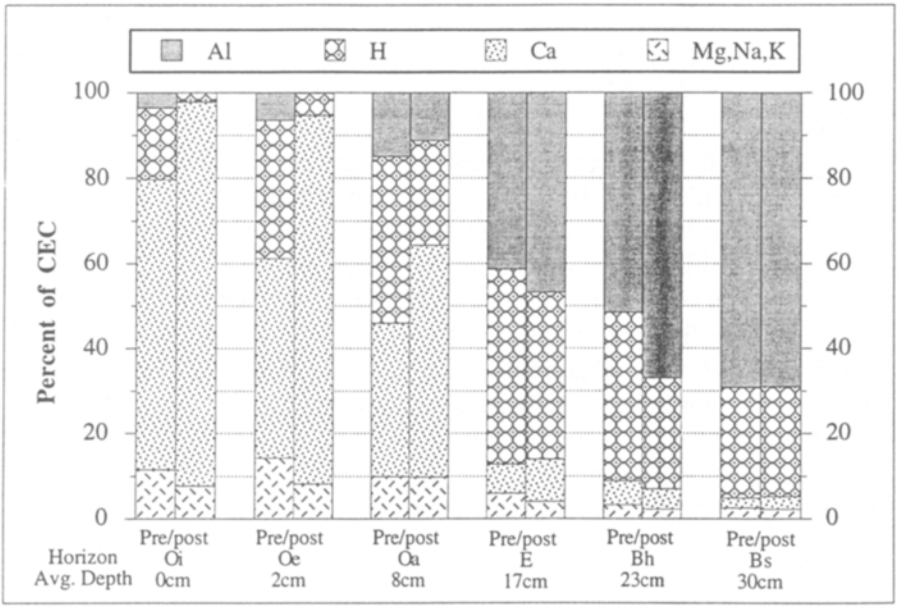

Fig. 2. Components of the cation exchange capacity for pre- and post-treatment soil samples in the organic and mineral horizons.

from exchange sites are taken up by vegetation which eventually returns calcium to the soil by the decomposition of leaf litter.

Surface water chemistry

The chemical response of the streams to liming was immediate. Calcium concentrations increased to greater than 500 μeq/l in WO2 and 100 μeq/l in WO4 and remained elevated relative to pre-liming levels through the summer of 1991 (Cirmo & Driscoll 1995). Concentrations of calcium also increased in the lake after liming, from 120 μeq/l in June, 1989 to 260 μeq/l in June 1990 (Cirmo & Driscoll 1995). During the LAMP liming program in the mid-1980's it was observed that the effects of lake liming were negligible fifteen months following treatment (Driscoll et al. 1989). In June, 1991, twenty months following lake and watershed liming, calcium concentrations of 200 μeq/l were still 80 μeq/l higher than pre-liming concentrations, suggesting that some calcium from the application of calcite to watershed soils is being transported to drainage waters.

Mass balance of calcium

In order to determine whether the addition of calcite to a watershed is a viable option for mitigating soil and drainage water acidification, it is important to determine the duration of effects. To this end, the calcium flux due to the watershed treatment was calculated for the two streams draining subcatchments II and IV and for the lake outlet using concentration data from both three-week and episodic samples (Burns, unpublished data). Measured calcium fluxes were corrected for natural pre-treatment levels using the long-term (1984–1989) database for the watershed. The calcium flux determined for WO2 during the 1990 and 1991 water years was 289 keq, 85 percent greater than the pre-treatment flux. The flux from WO4 was 74 keq or 65 percent greater than pre-treatment levels. The measured flux from the lake for the same period, 890 keq, was 68 percent greater than pre-treatment levels. Subtraction of pre-treatment from post-treatment fluxes yielded the amount of calcium added in response to the calcite manipulation. The net flux due to treatment was 247 keq from WO2, 48 keq from WO4 and 605 keq from the lake. Some of the flux from WO2 can be attributed to the beaver pond, which received approximately 175 keq (Cirmo & Driscoll 1995). Forty-nine percent of the flux to the lake can be accounted for by the gauged streams, whose contributing areas made up 46 percent of the total area of the treated subcatchments. The remaining 51 percent of the calcium flux to the lake is presumed to have come from the 54 percent area of the subcatchments not drained by the gauged streams. Subcatchment IV had at least one other major stream and non-contributing areas in both subcatchments border the lake.

The observed fluxes allow one to determine how much of the applied calcium has left the lake. Assuming the observed application of 6.89 Mg ha^{-1}, or 14117 keq, (Driscoll et al. 1996, this issue), 4.3 percent of the applied calcium left the watershed through the outlet in the two years following treatment, leaving approximately 96 percent in the terrestrial component of the watershed.

A mass balance of calcium for the lake/watershed system was conducted to determine whether observed calcium fluxes from the outlet could be explained by observed changes in the soil exchange chemistry after calcite application. Because most of the observed effects of treatment were restricted to the organic horizon, the mineral horizon chemistry was ignored in calculating mass balances. The mass of the Oi, Oe and Oa horizons was calculated using soil thickness and bulk density data. The amount of exchangeable calcium added to exchange sites was determined by subtracting pre-treatment concentrations from post-treatment concentrations. Amounts of calcite applied (Driscoll et al. 1996, this issue) and remaining in each subcatchment were averaged from the database. These parameters allowed for the calculation

Table 4. Input parameters used for the calculation of a calcium mass balance for the watershed.

Subcatchment	Thickness cm	Bulk density g/cm^3	Mass of horizon kg/ha	Pre-liming Ex-Ca eq/kg		Post-liming Ex-Ca eq/kg	
				II	IV	II	IV
Oi horizon	2	0.09	18000	0.175	0.168	0.359	0.397
Oe horizon	6	0.22	132000	0.090	0.079	0.326	0.394
Oa horizon	10	0.40	400000	0.089	0.031	0.113	0.082

	Ca applied keq/ha	Ca remaining keq/ha
Subcatchment II	157	102
Subcatchment IV	118	50

of the total amount of calcium applied to, and the total amount of calcium remaining in, the soil. The amount of calcium dissolved was obtained by difference. The amount of calcium added to exchange sites was subtracted from the amount dissolved to obtain the calcium flux which was transported to streams, groundwater and presumably, ultimately, to the lake.

Input data for the analysis were obtained from catchment averages (Table 4). The same inputs were used for contributing and non-contributing parts of each subcatchment. The amounts of calcite applied and undissolved, calcium added to exchange sites, and calcium transported to the gauged stream within each subcatchment are shown in Table 5. While this analysis cannot be considered definitive, because results are sensitive to small changes in many of the input parameters, it does document the primary pools of dissolved calcium. Using inputs shown in Table 4, it was estimated that 47.0 percent of the calcite applied to the watershed dissolved by 1992 (Table 5). Of this dissolved fraction, 91.2 percent of the calcium was sequestered on soil exchange sites and the remaining 8.8 percent was transported to surface waters. Of the total calcium applied to the watershed, 4.1 percent was estimated to have left the basin through the outlet. This calculated value compares favorably with the observed flux from the watershed of 4.3 percent. Both the calculated and observed values show the importance of the soil exchange complex as a sink for the applied calcium.

Conclusion

The Woods Lake watershed was treated with an observed application of 6.89 Mg ha^{-1} of $CaCO_3$ in October 1989 in an attempt to improve the pH

Table 5. Calcium mass balance calculation for the Woods Lake watershed.

Subcatchment	II Non-contrib area	II inlet	IV Non-contric area	IV inlet	Totals to lake
Area of catchment (ha)	10.7	30.6	44.0	17.2	102.5
Ca applied (keq)	1676	4793	5192	2030	13691
Ca remaining (keq)	1089	3115	2196	858	7258
Ca dissolved (keq)	587	1678	2996	1172	6433
Ca added to exchange sites (keq)	472	1348	2908	1137	5865
Ca exported to streams/lake (keq)	115	330	88	35	568
Summary:					
Amount of calcium added (keq)	13691				
Percent undissolved	53.01	Percent dissolved			46.99
Percent added to soil	42.84	% of dissolved added to soil			91.17
Percent exported to water	4.15	% of dissolved exported			8.82

and ANC of Woods Lake and its inlets, with the ultimate goal of enhancing brook trout populations in the lake. Forest floor samples collected one and two years following treatment showed that approximately 48% of the applied calcite remained undissolved within the Oe horizon. Dissolution was impaired by relatively dry conditions of the forest floor, short contact time with precipitation, caking of the calcite which has reduced the surface area available for dissolution, and alkaline conditions near the calcite/water interface.

Calcium ions derived from calcite dissolution have moved into the organic horizons of the soils, resulting in significant changes within the soil exchange complex. Cation exchange capacities increased significantly with levels of exchangeable calcium roughly doubling in the Oi and Oe horizons, and base saturations increased to nearly 100 percent. The CEC increase was due to the pH-dependent characteristics of organic matter. As pH increases, organic carboxyl ions dissociate, donating hydrogen ion to solution and creating cation exchange sites. Effects in the mineral horizons were not as prominent, likely due to limited changes in soil pH from the treatment. Exchangeable calcium increased only slightly while there was a large increase in exchangeable acidity, primarily filled by an increase in exchangeable aluminum. The applied calcite migrated downward through the forest floor during the study, due to the relative downward movement of the limed horizon with the annual input of litterfall.

Although zero-tension lysimeters placed below Oa and Bs horizons have shown some increase in calcium concentrations (Geary & Driscoll 1995), the effects were not consistent between sites. Groundwater wells showed no increase in concentrations within the first year of treatment. A small amount of calcite-derived calcium does appear to be reaching the streams and the lake. It is hypothesized that calcium is being transported to the streams by flow through the organic horizons.

Approximately 4 percent of the calcium applied to the watershed was exported through the lake outlet during the two year period following application of calcite to the watershed. Approximately 96 percent of the applied calcium remained within the watershed as undissolved calcite, on exchange sites in the soil, or stored in the vegetation, groundwater or surface waters. It is uncertain whether effects of the calcite addition will migrate to mineral horizons. If the removal rate of calcium from the watershed outlet continued at the 2% per year rate observed in the two years after treatment, all calcium added to the watershed during the experiment would be expected to be removed in approximately 50 years. Computer simulations conducted by Davis & Goldstein (1988) using the ILWAS model (Gherini et al. 1985), suggested that the duration of treatment effects could be greater than 50 years. Additional ILWAS model results for this study (Blette & Newton 1996) also suggest a duration of greater than 50 years. Only future monitoring of the lake and soils will show whether watershed calcite addition has proven to be an effective means of lake acidity mitigation. However, thus far the beneficial effects of calcite addition to the watershed have exceeded those derived from application of calcite to the lake.

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