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The effects of liming an Adirondack lake watershed on downstream water chemistry

Effects of liming on stream chemistry

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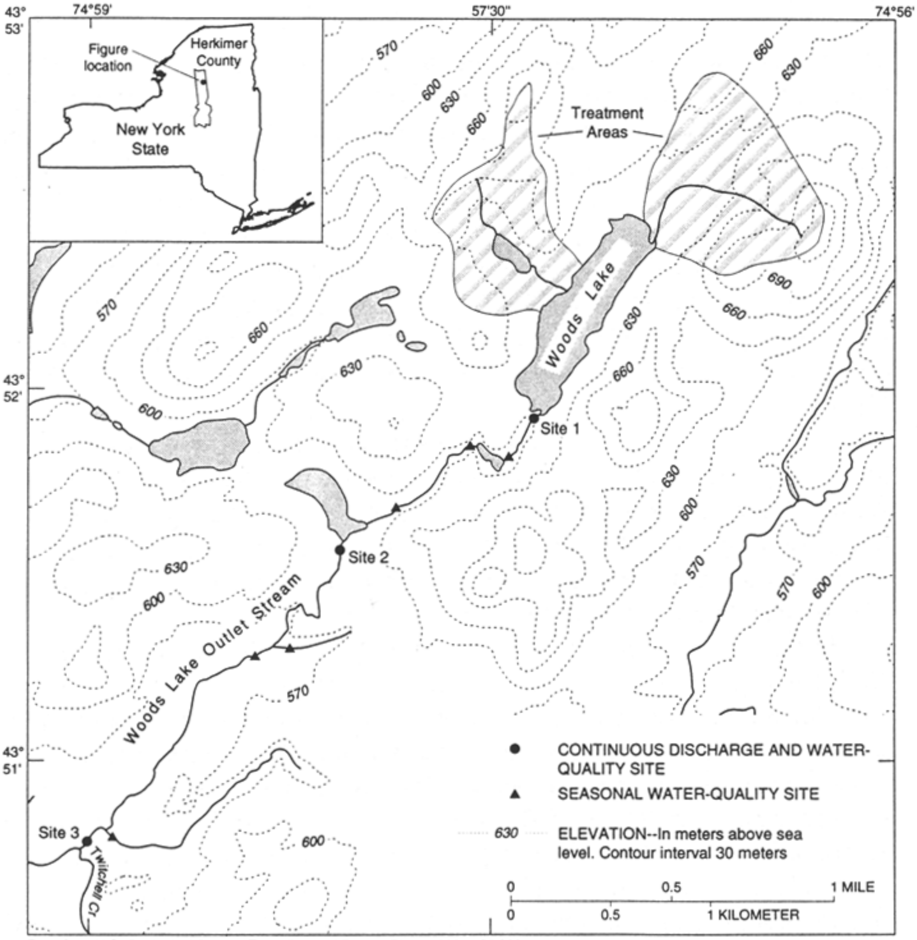
Abstract. Calcite treatment of chronically acidic lakes has improved fish habitat, but the effects on downstream water quality have not previously been examined. In this study, the spatial and temporal effects of watershed $CaCO_3$ treatment on the chemistry of a lake outlet stream in the Adirondack Mountains of New York were examined. Before $CaCO_3$ treatment, the stream was chronically acidic. During spring snowmelt before treatment, pH and acid-neutralizing capacity (ANC) in the outlet stream declined, and NO_3^- and inorganic monomeric aluminum (Al_{IM}) concentrations increased sharply. During that summer, SO_4^{2-} and NO_3^- concentrations decreased downstream, and dissolved organic carbon (DOC) concentrations and ANC increased, in association with the seasonal increase in decomposition of organic matter and the attendant SO_4^{2-}-reduction process. A charge-balance ANC calculation closely matched measured downstream changes in ANC in the summer and indicated that SO_4^{2-} reduction was the major process contributing to summer increases in ANC. Increases in Ca^{2+} concentration and ANC began immediately after $CaCO_3$ application, and within 3 months, exceeded their pretreatment values by more than 130 μeq/L. Within 2 months after treatment, downstream decreases in Ca^{2+} concentration, ANC, and pH, were noted. Stream mass balances between the lake and the sampling site 1.5 km downstream revealed that the transport of all chemical constituents was dominated by conservative mixing with tributaries and ground water; however, non-conservative processes resulted in significant Ca^{2+} losses during the 13-month period after $CaCO_3$ treatment. Comparison of substrate samples from the buffered outlet stream with those from its untreated tributaries showed that the percentage of cation-exchange sites occupied by Ca^{2+}, as well as non-exchangeable Ca, were higher in the outlet-stream substrate than in tributary-stream substrate. Mass-balance data for Ca^{2+}, H^+, Al_{IM}, and DOC revealed net downstream losses of these constituents and indicated that a reasonable set of hypothesized reactions involving Al_{IM}, HCO_3^-, Ca^{2+}, SO_4^{2-}, NO_3^-, and DOC could have caused the measured changes in stream acid/base chemistry. In the summer, the sharp decrease in ANC continued despite significant downstream decreases in SO_4^{2-} concentrations. After $CaCO_3$ treatment, reduction of SO_4^{2-} was only a minor contributor to ANC changes relative to those caused by Ca^{2+} dilution from acidic tributaries and acidic ground water, and Ca^{2+} interactions with stream substrate.

Introduction

The role of atmospheric deposition in the acidification of surface waters has been well documented in the Adirondack Mountains of New York (Driscoll & Newton 1985; Asbury et al. 1989), throughout eastern North America (Dillon et al. 1987; Baker et al. 1991), and in Europe (Henriksen & Seip 1980). Waters that have become acidic from atmospheric deposition are generally in areas where steep slopes provide rapid runoff, and where thin soils that lack carbonate minerals limit the release of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and provide incomplete neutralization of acidic precipitation. In such waters, a combination of low pH (less than 5.5) and high aluminum concentrations (greater than 5 μmol/L) adversely affect biological communities (Baker & Christensen 1991).

One method of mitigating surface-water acidity is direct addition of a base to the water body. This method has been used extensively in Sweden (Bengtsson et al. 1980) and to a limited extent in the United States (Kretser & Colquhon 1984). Research on the effects of base addition to lakes and optimal treatment methods has been done throughout Europe and North America (Hultberg & Andersson 1982; Booth et al. 1986).

While bases have been added to lakes to improve biological habitat, particularly for fish, none of the reported studies have discussed the chemical effects downstream from the lake. Lake or lake-watershed treatment with bases such as $CaCO_3$ could potentially create downstream conditions with high enough pH and low enough aluminum concentrations for survival and reproduction of fish, particularly brook trout (Salvelinus fontinalis). The objective of the study described herein was to examine the processes controlling the spatial and temporal patterns of water chemistry downstream from a limed lake watershed (Woods Lake) in the Adirondack region of New York. The initial assumption was that the stream under study would progressively acidify downstream from the lake. The hypothesis tested in the investigation was that the dominant process affecting acidification of the stream would be conservative mixing with acidic tributaries and ground water. Considering the sudden chemical changes expected in the stream from liming, however, processes occurring in the stream channel and in the wetlands/beaver ponds through which the stream passes were also anticipated to affect stream chemistry both temporally and spatially. This investigation was performed as part of the Experimental Watershed Liming Study (EWLS), a comprehensive ecosystem study of the response of an upland watershed and interconnected wetlands and drainage lake to an experimental addition of $CaCO_3$. Details of the $CaCO_3$ application to the lake watershed including a description of the other investigations performed during the EWLS is contained in Driscoll et al. (1996).



Base from U.S. Geological Survey, Eagle Bay and Beaver River, 1989, 1:25,000

Fig. 1. Locations of streamflow gaging sites, water-quality-sampling sites, and the areas that were treated with $CaCO_3$.

Woods Lake (43°52′ N, 74°58′ W) is a 24-ha, chronically acidic lake (pH 4 to 5) in the west-central Adirondack region of New York State (Fig. 1). The Woods Lake outlet stream passes through several wetlands and five beaver ponds (two of which are large enough and old enough to appear on the U.S. Geological Survey's Big Moose quadrangle, 1:62,500, 1954) along the 3.5 km from the lake to its confluence with Twitchell Creek (Fig. 1). A description of the physical and chemical characteristics of the Woods Lake watershed is contained in Driscoll et al. (1996).

Methods

Stream stage was recorded at 15-minute intervals at three locations on the outlet stream (Site 1, USGS ID 04256485; Site 2, USGS ID 04256486; and Site 3, USGS ID 0425648805, in downstream order) from January 1989 through October 1990. Site 1 had a 90° v-notch weir, and natural controls were used at sites 2 and 3. The watershed areas at sites 1, 2, and 3 are 207 ha, 339 ha, and 630 ha, respectively. Grab samples of stream water were collected for analysis of pH, ANC, major solutes, and aluminum fractions at the three gages from January 1989 until August 1991 at 3-week intervals and more frequently during spring snowmelt. Chemical analyses were done at Syracuse University in accordance with analytical procedures described in Driscoll et al. (1996). Seven water samples were collected along the length of the stream, and two to six samples were collected from tributaries and seeps in the watershed on 10 occasions from May 1989 through September 1991; all were analyzed at the USGS laboratory in Albany, N.Y. (except for aluminum fractions, which were analyzed at Pennsylvania State University) by methods similar to those used at Syracuse University. Bicarbonate (HCO_3^-) concentrations were calculated from pH and dissolved inorganic carbon concentrations with the thermodynamic equilibrium program ALCHEMI (Schecher & Driscoll 1987).

Acid-neutralizing capacity (ANC) is a measure of the ability of a solution to neutralize added H^+. In this study, ANC was determined by a Gran titration (Gran 1952), a technique that measures the sum of all H^+ accepting species minus the sum of all H^+ donating species:

$$\mathrm{ANC} = [\mathrm{H^+\ acceptors}] - [\mathrm{H^+\ donors}] \tag{1}$$

Bicarbonate is the dominant contributor to ANC in most natural waters in the pH range of 6–8. In low ANC waters such as those commonly found in the Adirondacks, however, the concentration of other H^+ acceptors becomes significant and includes organic acids, aluminum, and other species (Driscoll et al. 1994). An alternative and mathematically equivalent way to represent ANC is (in equivalents):

$$\begin{aligned}\mathrm{ANC} = \ & (\mathrm{Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+ + Al(OH)_2^+ +} \\ & \mathrm{Al(OH)_4^-) - (SO_4^{2-} + NO_3^- + Cl^- + Al^{3+})}\end{aligned} \tag{2}$$

This expression is often referred to as the charge balance ANC.

In this paper, results for measured Gran ANC will be presented, but in the discussion, charge balance ANC will be invoked to describe the processes affecting spatial and temporal variability of acid/base chemistry. Note that, theoretically, the two expressions for ANC should be equal, but often are not due to analytical errors (Schaefer et al. 1990).

Table 1. Concentrations of chemical constituents used in winter and summer mass-balance calculations to represent water entering the upper reach of the Woods Lake outlet stream (between sites 1 and 2).

Constituent	Winter (n = 18) (October–May)	Summer (n = 9) (June–September)
pH	4.5	4.74
ANC (μeq/L)	−32.0	−9.1
Ca^{2+} (μeq/L)	63.9	63.9
Mg^{2+} (μeq/L)	19.7	19.7
Na^{+} (μeq/L)	21.3	21.3
K^{+} (μeq/L)	8.4	8.4
SO_4^{2-} (μeq/L)	120	94.5
NO_3^- (μeq/L$^{-)}$	47.4	5.0
Cl^- (μeq/L)	8.6	8.6
DOC (μmol/L)	484	788
Aluminum (μmol/L):		
Total monomeric	19.4	16.5
Organic monomeric	6.5	8.0
Inorganic monomeric	12.9	8.5

Mass balances for each constituent measured in the reach between sampling sites 1 and 2 were calculated for the 9-month pretreatment period (January 1 through September 30, 1989) and the 13-month posttreatment period (October 1, 1989 through October 20, 1990, when stream-gage operation at site 2 was discontinued). Mass balances were not calculated for the reach between sampling sites 2 and 3 because the tributaries in this reach were not sampled extensively enough to provide an adequate balance. The mass balances were calculated by: (1) assigning the measured concentration of a constituent to each day succeeding and preceding collection up to the point halfway to the next sample-collection date, and (2) multiplying the assigned daily concentration by the total daily discharge (derived from the mean daily discharge) to obtain a daily mass flux for the constituent at each site. Although Johnson (1979) suggests that regression of concentration in relation to discharge gives accurate estimates of solute flux for constituents in which concentration is correlated with discharge, the method described above is more appropriate in a study such as this, in which many constituents showed treatment-dependent changes independent of discharge. Because only the stream, not the watershed, between sites 1 and 2 was altered by $CaCO_3$, the mass-balance differences in flux could be attributed to within-stream processes. Tributaries and seeps along the stream's upper reach were sampled on several occasions during the study, and the samples were assumed to be representative of water entering the stream. The increase in discharge between sites 1 and 2 was multiplied by the mean summer or winter concentration of each constituent (except for base cations and Cl^-, which were multiplied by a median annual concentration because they did not show strong summer-to-winter differences) to calculate the mass input along the stream reach (hereafter referred to as the tributary input). The concentrations used in these calculations are shown in Table 1.

Samples of stream substrate were collected at depths of 0 to 10 cm from the outlet streambed ($n = 8$) and two tributaries ($n = 10$) in July 1990. The samples included sandy stream sediment and organic-rich streambank material, much of which contained abundant Sphagnum spp. The objective was to identify chemical differences that could be attributed to the interaction of substrate material with $CaCO_3$-treated water. Substrate samples were analyzed for weight loss on ignition, total base cations (nitric-perchloric acid digestion), pH (1:1 deionized water), exchangeable acidity, exchangeable bases, and cation-exchange capacity at the Colorado State University Soil Testing Laboratory by methods described in Black et al. (1965).

Results

Pretreatment period

In 1984–85, before the introduction of $CaCO_3$ to Woods lake, the chemical characteristics of the outlet stream were typical of chronically acidic Adirondack lakes in which strong mineral acids predominate (Table 2). Sulfate was the dominant anion, Ca^{2+} the dominant cation, and ANC was generally negative. Samples for the current study were not collected regularly at the outlet stream until January 1989, 9 months before $CaCO_3$ was applied to the lake watershed. During this 9-month period, lake-outlet chemistry showed residual effects from the previous $CaCO_3$ application to the lake (fall 1986), and from 2,000 kg of $CaCO_3$ added to the lake in November 1988 to maintain the brook trout population. Calcium concentrations, ANC, and pH were greater than during 1984–85, and SO_4^{2-} and NO_3^- concentrations were slightly higher (Table 2). Despite the residual effects from previous $CaCO_3$ applications, the 9 months preceding October 1989 are herein referred to as the pretreatment period.

Temporal chemistry

In the spring of 1989, during the period of greatest snowmelt, ANC, SO_4^{2-}, and Ca^{2+} concentrations in the stream decreased at all three sampling sites, and

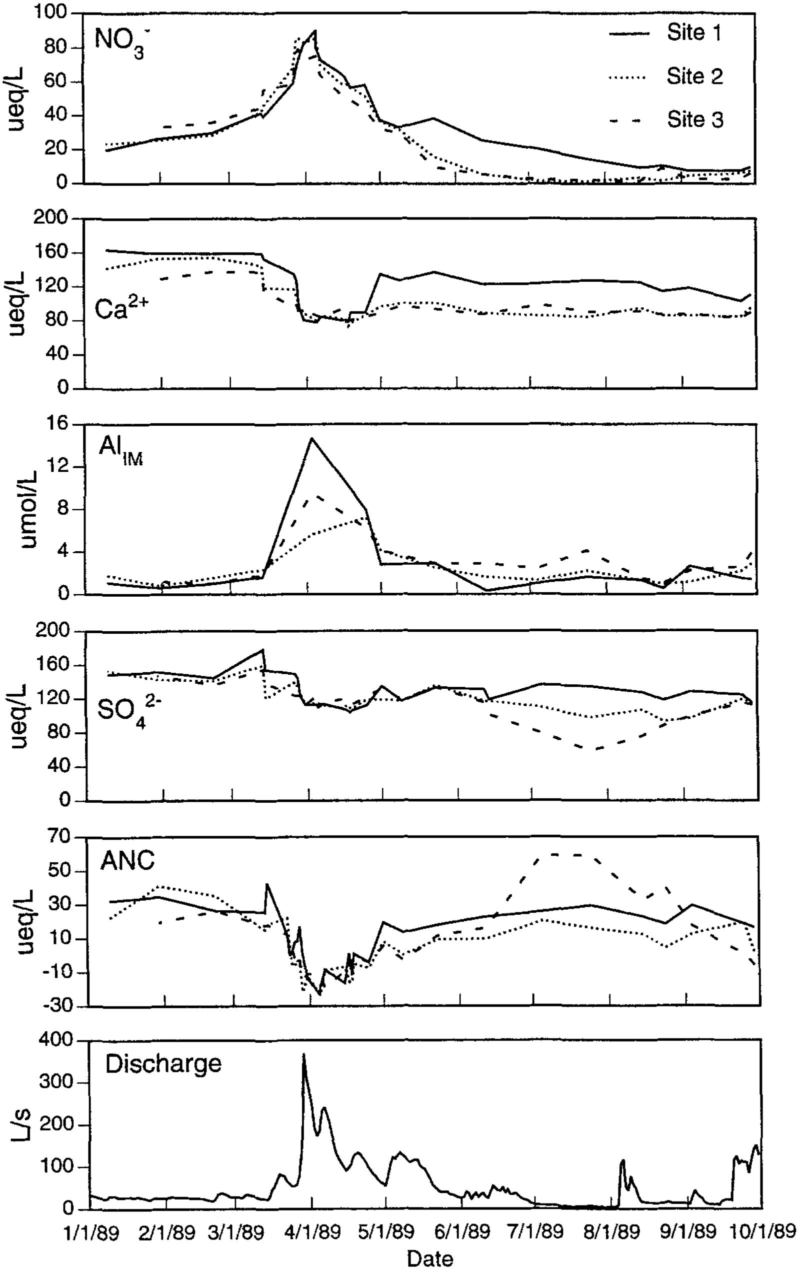


Fig. 2. Nitrate, Ca^{2+}, AL_{IM}, and SO_4^{2-} concentrations, ANC, and discharge of the Woods Lake outlet stream at sampling sites 1, 2, and 3, January through September 1989, before $CaCO_3$ application. Discharge is shown for Site 1 only. (Site locations shown in Fig. 1.)

Table 2. Chemical characteristics of the Woods Lake outlet at sampling site 1, January 1984 through May 1985, before $CaCO_3$ application to the lake or watershed, and from January 1989 through September 1989, just before watershed $CaCO_3$ treatment [Values are mean plus or minus standard deviation; 1984–85 data from Driscoll et al. 1989].

Constituent	1984–85 (n = 23)	1989 (n = 14)
pH	4.8 ± 0.3	5.57 ± 0.57
ANC (μeq/L)	−8 ± 14	16 ± 18
Ca^{2+} (μeq/L)	68 ± 7	124 ± 32
Mg^{2+} (μeq/L)	17 ± 2	19 ± 2.6
Na^+ (μeq/L)	21 ± 2	25 ± 6.1
K^+ (μeq/L)	7 ± 2	9.3 ± 3.7
NH_4^+ (μeq/L)	7.8 ± 3.6	3.0 ± 1.1
SO_4^{2-} (μeq/L)	119 ± 6	134 ± 16
NO_3^- (μeq/L)	26 ± 17	39 ± 30
Cl^- (μeq/L)	6 ± 2	7.2 ± 2.1
DOC (μmol/L)	220 ± 59	213 ± 67
Monomeric Al (μmol/L)	7.5 ± 5.1	6.8 ± 6.0

NO_3^- and inorganic monomeric aluminum (Al_{IM}) concentrations increased (Fig. 2). For a short period before and just after peak runoff, NO_3^- and SO_4^{2-} concentrations (in μeq/L) were nearly equivalent, as were Al_{IM} and Ca^{2+} concentrations. During winter and summer base-flow periods, ANC and Ca^{2+} concentrations reached their highest values of the year, and Al_{IM} concentrations reached their lowest. Nitrate concentrations at the three sampling sites followed a seasonal pattern; they increased from late fall into early April when they reached maximum values of 80 to 95 μmol/L, then declined to minimum concentrations of 0 to 10 μmol/L by late summer. Sulfate concentrations increased and reached their maximum values in the late winter, and then decreased during snowmelt. At sampling sites 2 and 3, SO_4^{2-} concentrations decreased from spring through mid-summer, and then increased through the fall. At sampling site 1, SO_4^{2-} concentrations were nearly constant throughout the summer and fall.

Spatial chemistry

Downstream from the lake, Ca^{2+} concentrations decreased successively from sampling site 1 to 3 throughout the year, except during the spring snowmelt period when there was little difference between the three sites (Fig. 2).

Table 3. Mean concentration of selected constituents in samples collected during summer 1989 and summer 1990 at three sampling sites in the Woods Lake outlet stream [All values are in μeq/L, except DOC, in μmol/L]

A. Summer 1989 (July 4, July 24, August 15)

	ANC	SO_4^{2-}	NO_3^-	DOC	NH_4^+	Ca^{2+}
Site 1	26.1	133	14.6	188	2.5	125
Site 2	16.2	105	1.1	339	2.8	87.9
Site 3	50.3	71.2	2.0	800	3.8	92.9

B. Summer 1990 (June 26, July 16, and August 7)

	ANC	SO_4^{2-}	NO_3^-	DOC	NH_4^+	Ca^{2+}
Site 1	171	110	18.7	344	4.9	274
Site 2	94.2	89.7	7.7	475	8.0	163
Site 3	62.7	73.9	6.1	679	5.3	117

Nitrate concentrations were similar at all three sites except during the summer when there was a sharp decline from sampling site 1 to 2, and little to no decline downstream (Table 3A). Sulfate concentrations showed a successive downstream decrease throughout the summer (Table 3A), and were similar throughout the remainder of the year (Fig. 2). In the summer, ANC decreased from sampling site 1 to 2, and then increased between sites 2 and 3 (Table 3A). During the remainder of the year, ANC differences between sites were generally less than 20 ueq/L (Fig. 2) Inorganic monomeric aluminum concentrations were generally low and similar at all three sites except at the peak of snowmelt, when they decreased from sampling site 1 to 2, and then increased from site 2 to 3 (Fig. 2). Dissolved organic carbon concentrations increased successively from sites 1 to 3 in the summer (Table 3A).

Posttreatment period

Temporal chemistry

Chemical changes at the lake outlet (site 1) were noted within 2 days after application of $CaCO_3$ to the watershed began on October 2, 1989. By October 10, the day after the treatment was completed, Ca^{2+} concentration and ANC had increased to 144 μeq/L and 80.8 μeq/L from 111 μeq/L and 17.6 μeq/L, respectively, 3 days before the beginning of the treatment. Concentrations of Al_{IM} declined from 1.4 μmol/L to below detection limits during the same period. Calcium concentration and ANC continued to increase for 3 months and, by early January, reached values of 266 and 150 μeq/L, respectively (Fig. 3). At the downstream sampling sites 2 and 3 (Fig. 3), the chemical changes after $CaCO_3$ application paralleled those at the lake outlet (site 1), although they were smaller and lagged by several days. The exception were Al_{IM} concentrations, which decreased the most at the mouth (site 3). During the spring 1990 snowmelt after $CaCO_3$ treatment, Ca^{2+} and SO_4^{2-} concentrations and ANC decreased at all three sampling sites, and NO_3^- and Al_{IM} concentrations increased, as they did in the 1989 spring snowmelt (before $CaCO_3$ treatment). The minimum ANC values in the 1990 snowmelt, however, were higher (17.7 μeq/L) than in the 1989 snowmelt (-23.6 μeq/L), despite higher flows during the 1990 snowmelt (Fig. 3). After spring turnover of the lake in April 1990, ANC and Ca^{2+} concentrations in the stream increased sharply, particularly at the lake outlet (site 1), and remained elevated until the following winter.

During the 1991 snowmelt period, 18 months after $CaCO_3$ treatment, Ca^{2+}, SO_4^{2-}, and ANC concentrations decreased, and increases in NO_3^- and Al_{IM} concentrations were less than during the previous spring. Samples were collected less frequently during the 1991 melt period than during the 1990 melt period, however; thus, the highest concentrations might not have been measured. Additionally, the peak flow during March and April of 1991 was less than during the same period in 1990 (Fig. 3).

Spatial chemistry

Calcite treatment of the lake watershed significantly altered the pattern of downstream chemical changes in the outlet stream. Within 3 months after treatment, a downstream pattern of decreasing pH, ANC, and Ca^{2+} concentrations was established (Fig. 4). In the first summer (1990) after $CaCO_3$ application, SO_4^{2-} and NO_3^- concentrations decreased downstream as in the previous year, but ANC also decreased downstream (Table 3B), instead of increasing as it had in the previous summer. The downstream decreases in pH, ANC, and Ca^{2+} concentrations continued through the remainder of the study.

Downstream chemical changes through the summer of 1991 were similar to those in 1990, except that Ca^{2+} concentrations and ANC decreased less. For example, the last summer sample collected in this study, on August 16, 1991, indicated a downstream (between sites 1 and 3) ANC decrease of only 43.9 μeq/L – less than half the mean ANC decrease of 108 μeq/L during the summer of 1990.

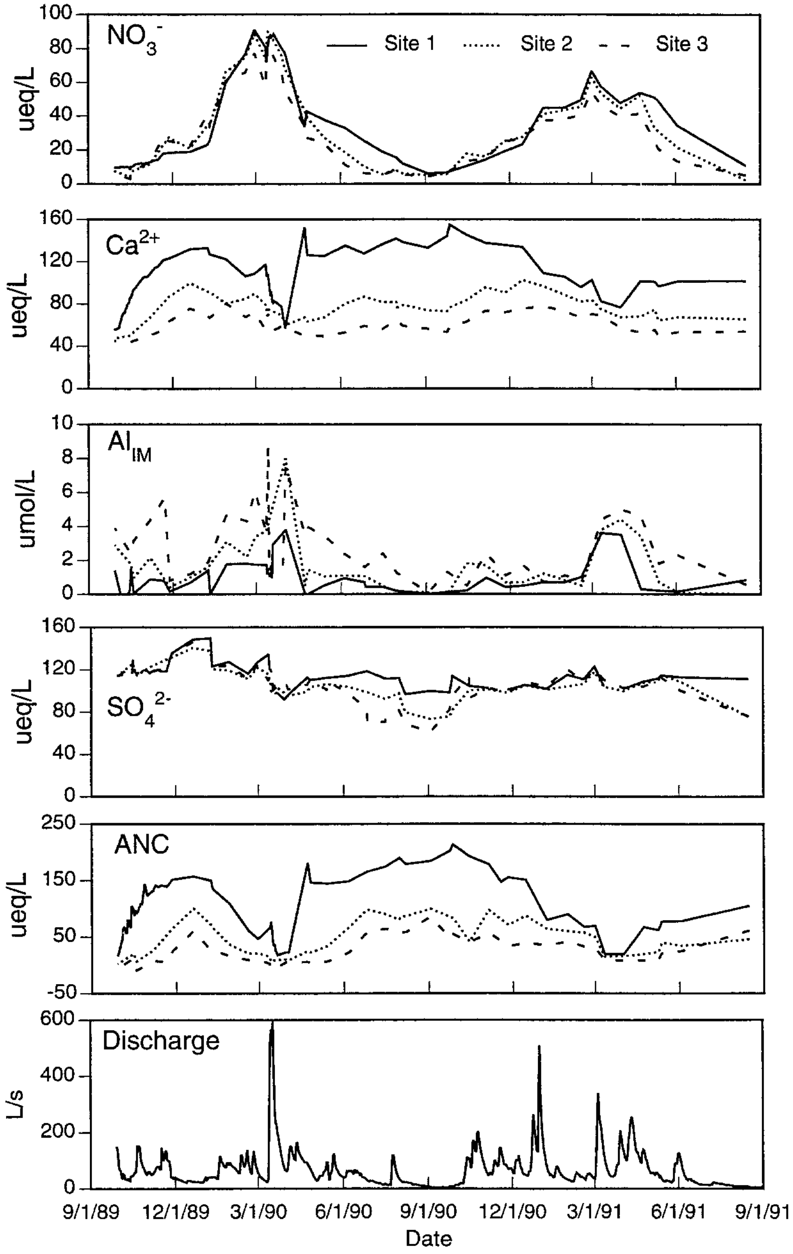


Fig. 3. Nitrate, Ca^{2+}, AL$_{IM}$, and SO$_4^{2-}$ concentrations, ANC, and discharge of the Woods Lake outlet stream at sampling sites 1, 2, and 3, October 1989 through August 1991, after CaCO$_3$ application. Discharge is shown for Site 1 only. (Site locations shown in Fig. 1.)

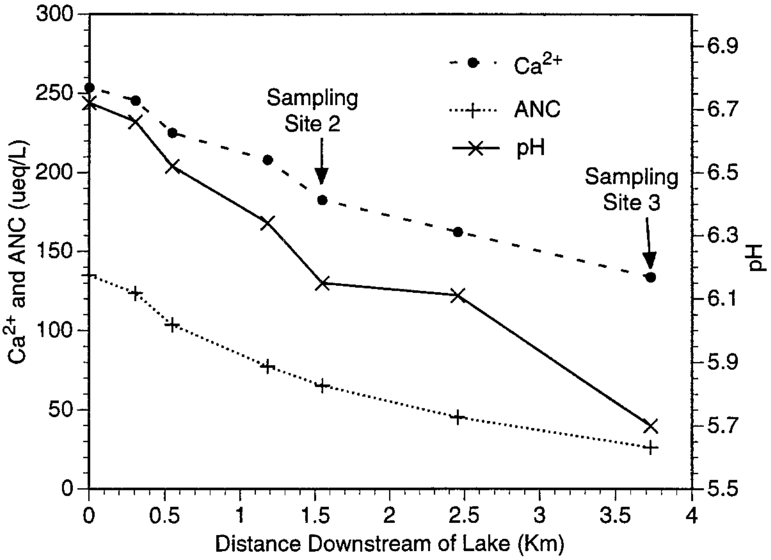


Fig. 4. Acid-neutralizing capacity, pH, and Ca^{2+} concentrations in the Woods Lake outlet stream as a function of distance downstream from the lake, January 10, 1990, 3 months after treatment.

Mass balances

The relative influence of conservative mixing on stream chemical transport was determined by comparing the tributary input to the non-conservative mass for chemical constituents:

$$\text{Conservative mixing factor} = \frac{\text{Tributary input}}{(\text{Tributary input} + |\,\text{Non} - \text{conservative mass}\,|)} \tag{3}$$

where

$$\text{Non-conservative mass} = \text{Mass at site 2} - \text{Mass at site 1} - \text{Tributary input} \tag{4}$$

A negative non-conservative mass value implies that mass was lost as the constituent was transported downstream. The conservative mixing factor can vary from 0 to 1.0, with conservative mixing dominating the mass transport of a constituent at values greater than 0.50.

Results of the mass balance calculations for the pretreatment period (Table 4A) show that conservative mixing dominates the transport of all the constituents measured. The lower conservative mixing factor values of

Table 4. Mass balances for chemical constituents before and after liming between sampling sites 1 and 2. The ΔMass for reach = Mass at bottom of reach - Mass at top of reach. The Non-conservative mass = ΔMass for reach - Trib. input. Conservative mixing factor = Trib. input / (Trib. input + |Non-conservative mass|). All constituent mass values are in Keq except DOC and Al_{IM} which are in Kmol.

A. Pretreatment period (January 1, 1989 through September 30, 1989).

Constituent(s)	ΔMass for reach	Trib. input	Non-conservative mass	Conservative mixing factor
Ca^{2+}	54	45.7	8.3	0.85
$Mg^{2+} + Na^{+} + K^{+}$	33.5	35.3	−1.8	0.95
SO_4^{2-}	81	81.8	−0.8	0.99
DOC	293	393	−100	0.80
H^{+}	14.9	20.6	−5.7	0.78
NO_3^{-}	29.1	27.3	1.8	0.94
Al_{IM}	6.2	8.5	−2.3	0.79
Cl^{-}	4.7	6.1	−1.4	0.81

B. Posttreatment period (October 1, 1989 through October 20, 1990)

Constituent(s)	ΔMass for reach	Trib. input	Non-conservative mass	Conservative mixing factor
Ca^{2+}	29	80.6	−51.6	0.61
$Mg^{2+} + Na^{+} + K^{+}$	62	62.3	−0.3	1.00
SO_4^{2-}	127	157	−30.0	0.84
DOC	538	628	−90.0	0.87
H^{+}	5.2	39.1	−33.9	0.54
NO_3^{-}	62.6	57.4	5.2	0.92
Al_{IM}	10.1	16.0	−5.9	0.73
Cl^{-}	10.9	10.8	0.1	0.99

0.78 to 0.81 for DOC, H^{+}, Al_{IM}, and Cl^{-} indicate that non-conservative losses of these constituents may have occurred during stream transport. In the posttreatment period (Table 4B), Ca^{2+}, H^{+}, and Al_{IM} showed proportionally greater non-conservative transport than before treatment. The greatest change in transport behavior between the pre- and posttreatment periods was for Ca^{2+} and H^{+}.

Substrate analyses

The mean cation exchange capacity (CEC) and percent organic matter content (as determined by weight loss on ignition) were both greater in tributary substrate than in substrate from the outlet stream (Table 5). The difference between the two sample locations for these measurements could be accounted for, in part, by the linear relation between CEC and percent organic matter (CEC = dependent variable, slope = 0.88, $r^2 = 0.79$). The data also suggest that percent base saturation and exchangeable Ca^{2+} were greater in outlet substrate than in tributary substrate, however, these differences were not statistically significant (Mann-Whitney Rank Sum Test, $p > 0.025$). The absolute concentration of each exchangeable base cation is, in part, a function of CEC, and therefore, percent organic matter content as discussed above. If exchangeable concentrations are normalized by dividing by CEC (Fig. 5A), then exchangeable Ca^{2+} saturation was significantly greater in outlet substrate than tributary substrate, while there was no significant difference between the two sampling sites for the other three base cations.

For the total cation analyses, both Ca and Mg concentrations were significantly greater in outlet substrate than tributary substrate (Table 5). Like CEC, however, total cation concentrations were related to organic matter content, except in an inverse manner (linear regressions between individual cation concentrations and percent organic matter content all had $r^2 > 0.68$). Additionally, total cation concentrations include the exchangeable fraction. If the exchangeable fraction is subtracted from the total fraction, the resulting non-exchangeable fraction is representative of the sum of cations incorporated in living cells, some mineral-bound cations (hydrofluoric acid was not part of the digest, and so the silicate lattice was likely not completely broken down during digestion), and organically-bound cations. To account for the negative relations between organic matter content and total cation concentrations, the non-exchangeable fraction was divided by organic matter content (Fig. 5B). In this comparison, the values for each base cation appear to be greater in outlet substrate than tributary substrate, but only for Ca and Mg were the differences between the two locations statistically significant. The Na and K values were affected by two high values for the outlet substrate.

Discussion

Immediate effects of $CaCO_3$ treatment on ANC

The changes in outlet chemistry after $CaCO_3$ treatment of the lake watershed began are consistent with the observation that some of the $CaCO_3$ pellets fell

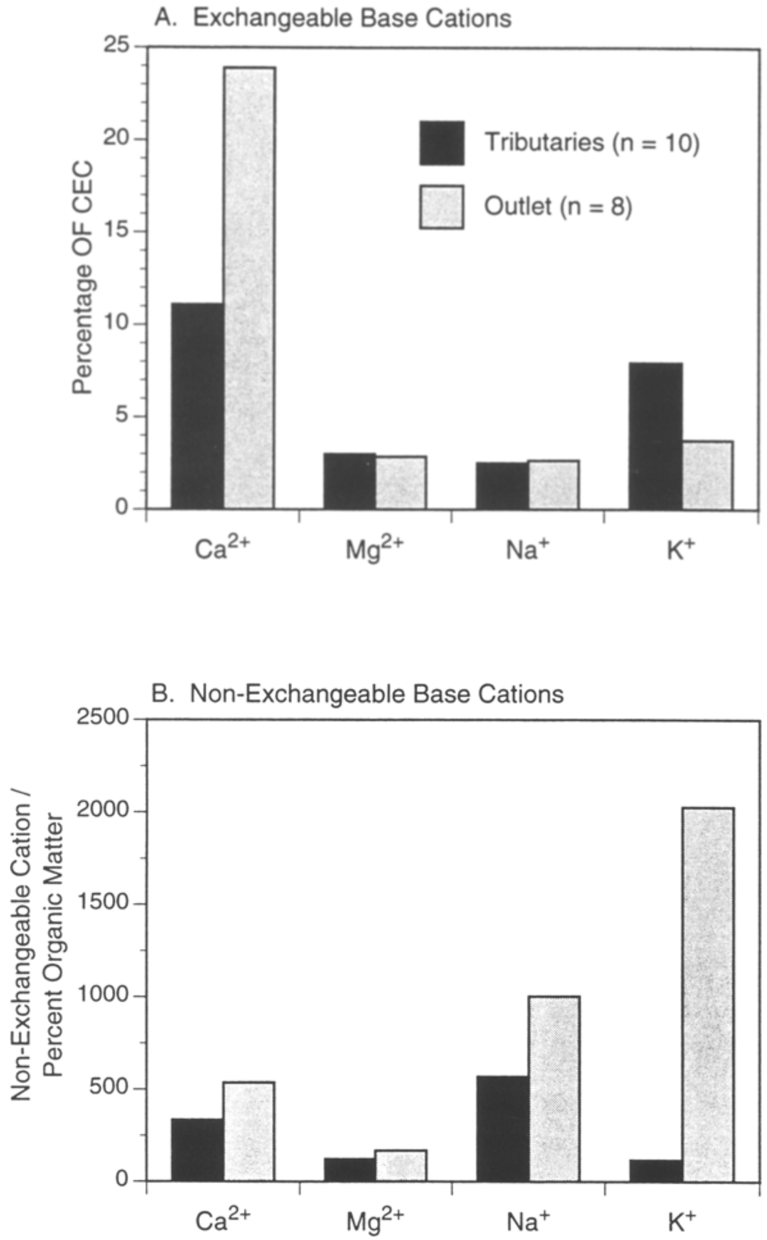


Fig. 5. Base cation (Ca, Mg, Na, and K) values in substrate material from the outlet stream (in contact with $CaCO_3$-treated water) and from tributaries (not in contact with $CaCO_3$-treated water). The samples were collected between July 15 and August 1, 1990. A. Mean exchangeable base saturation. B. Mean non-exchangeable concentrations normalized for sample organic matter content.

Table 5. Concentrations in substrate samples collected from the Woods Lake outlet stream and its tributaries. Exchangeable fractions are in units of milliequivalents/100 g, and total fractions are in weight percent of digested sample. All values are mean plus or minus 1 standard deviation. Sample groups were compared with a Mann-Whitney Rank Sum Test in which differences were considered to be significant if $p \leq 0.025$.

	Outlet substrate (n = 8)	Tributary substrate (n = 10)	Statistical comparison
CEC	51.9 ± 32.7	80.8 ± 31.8	T > 0
Percent base saturation	33.2 ± 18.1	23.8 ± 17.2	No difference
Exchangeable Ca^{2+}	13.9 ± 12.6	7.1 ± 7.1	No difference
Exchangeable Mg^{2+}	1.9 ± 2.4	2.1 ± 1.9	No difference
Exchangeable Na^{+}	1.2 ± 1.0	1.8 ± 1.1	No difference
Exchangeable K^{+}	3.1 ± 4.4	6.5 ± 6.0	No difference
pH	5.3 ± 0.5	5.0 ± 0.7	No difference
Percent weight loss on ignition	40.4 ± 31.8	73.7 ± 29.4	T > 0
Percent Ca	0.739 ± 0.159	0.285 ± 0.329	0 > T
Percent Mg	0.170 ± 0.058	0.095 ± 96	0 > T
Percent Na	0.664 ± 0.712	0.232 ± 0.524	No difference
Percent K	1.36 ± 1.30	0.650 ± 0.839	No difference
Percent K	1.36 ± 1.30	0.650 ± 0.839	No difference

in shallow parts of the lake, near the shore, and in adjacent wetlands. The rapid dissolution of some of these pellets and transport toward the outlet was probably responsible for the chemical changes noted within 48 hours after the application began. The steady increase in outlet stream pH, ANC, and Ca^{2+} concentrations over the next 3 months was attributed to the dissolution of $CaCO_3$ that fell directly into the channels (and beaver pond) of the two streams that drain the treated areas of the watershed and subsequent transport to the lake and the outlet (Cirmo & Driscoll 1996). The transport of higher ANC water from the lake inlets to the lake outlet was facilitated by the inability of lake water to mix below depths of 1 to 2 m in winter, when the lake is thermally stratified (Gubala et al. 1991).

Changes in processes that affect ANC during snowmelt

Lakes in the Adirondack region typically undergo a depression in ANC, pH, and base-cation concentrations, and an increase in NO_3^- and Al_{IM} concentrations during spring snowmelt (Schaefer et al. 1990); similar chemical changes can occur in winter during periods with above-freezing temperatures. In 1978–80, before any $CaCO_3$ application at Woods Lake, outlet ANC decreased by 10 to 50 μeq/L during snowmelt, and the sum of NO_3^- and Al_{IM} concentrations increased by 30 to 50 μeq/L (Schofield et al. 1985). During the last snowmelt before watershed treatment in 1989, outlet ANC decreased 59.0 μeq/L from mid-winter to the peak snowmelt runoff, slightly more than typically observed before the mid-1980s, although the minimum pH (4.65) and ANC (-24.4 μeq/L) in 1989 were close to those of the last spring snowmelt before lake treatment (4.49 and -30.0 μeq/L) (C.T. Driscoll, unpublished data). Before the mid-1980s, base-cation concentrations at the outlet changed little during snowmelt, but in 1989, before treatment, they declined by 96.0 μeq/L from mid-winter to spring snowmelt – about 30 percent greater than the increase in NO_3^- concentration (73.6 μeq/L).

The greater decline in ANC and base cation concentrations during the snowmelt of 1989 than in the previous years was likely caused by elevated pre-melt ANC and Ca^{2+} concentrations in the lake from previous $CaCO_3$ applications. In the spring of 1990, 6 months after $CaCO_3$ application, ANC declined by 127 μeq/L from mid-winter to snowmelt, more than twice the decline of the preceding year. The concentration of Ca^{2+} also decreased over the same time period, by 111 μeq/L – more than twice the increase in NO_3^- concentration (52 μeq/L). The minimum pH and ANC in the spring of 1990 were significantly greater than the year before – 5.63 and 17.7 μeq/L, respectively.

The dissolution of $CaCO_3$ pellets and the transport of buffered water to the lake resulted in gradual increases in pH, ANC, and Ca^{2+} concentrations at the outlet through the winter of 1989–90. During spring snowmelt, however, the rapid inflow of meltwater to inlet streams by overland flow and shallow subsurface runoff through the thin soil, and rapid transport to the lake outlet with little downward mixing, resulted in dilution of Ca^{2+} and decreases in pH and ANC at the outlet. Before the introduction of $CaCO_3$ to the lake, declines in ANC during snowmelt were caused largely by increases in strong-acid NO_3^- concentrations. In 1989, before treatment, the ANC decline was slightly greater than the increase in NO_3^- concentration, and the decrease in Ca^{2+} concentration nearly equal to it. By 1990, after watershed treatment, decreased Ca^{2+} concentrations were largely responsible for a much greater spring ANC decline. Although the outlet stream pH decreased during snowmelt in 1990, it did not reach low enough values to cause high Al_{IM} concentrations. The maximum measured Al_{IM} concentration in 1990 was 3.8 μmol/L – one-fourth that of the year before (15.2 μmol/L). During the spring snowmelt of 1991, however, ANC declined barely half as much as in the previous year, although the dominant contributor to the decline was still dilution of Ca^{2+}. The minimum pH and ANC values in 1991 – 5.42 and 19.7 μeq/L – were similar to those in 1990, and the outlet did not become acidic at the lake. As mentioned previously, however, the smaller peak flow in spring 1991 than in 1990, and the less frequent collection of samples, made a direct comparison of ANC and pH seasonal patterns in the 2 years difficult.

Changes in processes that affect ANC during summer

Anoxia in wetland and beaver-pond sediments has the potential to affect the downstream chemical evolution of the Woods Lake outlet stream. As water temperature increases in the summer, decomposition rates and oxygen depletion increase concurrently, releasing DOC into the water column and causing anoxia to spread from the sediments and bottom water toward the surface (Cirmo & Driscoll 1993). In the winter, water passes through these ponds without significant chemical changes, but in summer, SO_4^{2-} and NO_3^- are removed from solution by reduction processes, and some NO_3^- is likely taken up by phytoplankton and aquatic macrophytes as well. The reduction of SO_4^{2-} and NO_3^- generates ANC, as reflected in measured increases in ANC downstream and at site 3 throughout the summer (Fig. 2, Table 3A). These longitudinal and temporal increases are not balanced by equivalent decreases in SO_4^{2-} and NO_3^- concentrations, however. For example, the mean increase in ANC along the length of the stream for three summer sampling dates during the pretreatment period was 24.2 μeq/L, but SO_4^{2-} and NO_3^- concentrations declined by 61.8 and 12.6 μeq/L, respectively (Table 3A). Increases in DOC concentrations generally cause decreases in ANC through the dissociation of strong organic acids (Hemond 1990). Data from a large survey of Adirondack lakes (Munson & Gherini 1993) reveal that ANC decreases by an average of 4.5 to 5.0 μeq/mg of DOC. Applying this relation to the increase in DOC along Woods Lake outlet, in combination with the effect of concentration changes in base cations, SO_4^{2-}, and NO_3^- (NH_4^+, Cl^- and Al are negligible in this calculation), yields a charge-balance ANC increase of 24.7 μeq/L, close to the measured increase. Therefore, the net effect of base-cation dilution, reduction of SO_4^{2-} and NO_3^-, uptake of NO_3^-, and generation of DOC along the outlet stream in the summer before treatment was an increase in ANC. Of these four processes, the reduction of SO_4^{2-} affected the ANC most strongly.

The application of $CaCO_3$ to the watershed sharply altered the downstream pattern of ANC along the outlet stream. Acid-neutralizing capacity decreased more than 100 μeq/L from the lake to the mouth in the first summer (1990), instead of increasing, as in the summer before treatment (Table 3B), mainly through dilution of Ca^{2+} by acidic ground water and tributaries that enter the outlet stream. If the base-cation concentrations in the outlet stream had not decreased downstream in the summer of 1990, a charge-balance ANC calculation reveals that ANC would have increased by a mean of 28.6 μeq/L, similar to that in the summer of 1989 before treatment. By the summer of 1991, a new pattern of downstream changes had developed. On August 16, 1991 (the only sampling that summer), the downstream ANC decrease was only 43.9 μeq/L, less than half that of the previous summer. Calcium dilution was still the dominant process, but had a lesser effect than in 1990. A charge-balance ANC calculation shows that, in the absence of changes in base-cation concentrations, ANC would have increased by 19.7 μeq/L along the outlet stream on that date. As Ca^{2+} concentrations in the lake declined, the effect of Ca^{2+} dilution on downstream ANC decreased. With time, reduction of SO_4^{2-} will again become the dominant process and cause downstream ANC increases in summer.

The mass-balance calculations indicate nearly conservative transport of SO_4^{2-} and NO_3^- in the upper reach of the outlet stream during the pre- and posttreatment periods (except for a possible loss of SO_4^{2-} during the latter period) (Table 4). Even though SO_4^{2-} and NO_3^- were lost through reduction and (or) uptake in summer, the mass transport of these constituents during summer (June through September) was only 5 to 10 percent of the annual mass transport, and the significant downstream losses of these constituents in the summer do not contribute greatly to annual mass balances. The ability of SO_4^{2-} reduction and NO_3^- uptake and reduction to affect ANC in the summer despite the lack of significant annual downstream losses is probably typical of streams in the northeastern United States that have wetlands and beaver ponds (Cirmo & Driscoll 1993) and whose dominant runoff periods are during the spring snowmelt and the fall (Peters & Murdoch 1985; Driscoll et al. 1987).

Ca^{2+}-H^+ ion exchange and Ca^{2+} uptake

The mass-balance calculations for the upper reach of the outlet stream, and the chemical data from substrate samples, indicate that, in addition to Ca^{2+} dilution, NO_3^- uptake, and SO_4^{2-} reduction in the stream and its beaver ponds and wetlands, other processes were affecting downstream acid/base chemistry as well. The apparent net loss of Ca^{2+} in the upper reach of the outlet stream (Table 4B), and the elevated concentrations of exchangeable Ca^{2+} from the substrate in the same stream reach (Fig 5A), indicate that exchange of Ca^{2+} with H^+ and Al could have affected downstream decreases in pH and ANC. The mean non-exchangeable Ca concentration normalized for organic matter content was greater in outlet substrate than in the tributaries, as was Mg. This suggests that some of the increased Ca^{2+} transported along the outlet stream may have been taken up by Sphagnum spp. and organisms in the periphytic and benthic communities from which the samples were collected. At least some of this enhanced uptake may have resulted from lime applications to Woods Lake in the mid-1980s. Calcium uptake, like Ca^{2+}-H^+ exchange, results in a net decrease in ANC.

Effects of in-stream losses of Al_{IM}, H^+, and DOC

The mass-balance calculations reveal losses of Al_{IM} along the upper reach of the outlet, an observation consistent with the direct relation between Al_{IM} concentrations and pH in surface waters of the Adirondack region (Driscoll et al. 1984) and the response of aluminum at mixing zones where sharp pH increases from acidic to circumneutral occur (Theobald et al. 1963; Wright & Skogheim 1983). The pH of the outlet stream at the lake (site 1) was about 5.5 during the pretreatment period and, after $CaCO_3$ treatment, was generally greater than 6, with Al_{IM} concentrations of 1 to 3 μmol/L. The pH of tributaries and ground-water seeps entering the upper stream reach generally ranged from 4.5 to 4.8, with Al_{IM} concentrations from 8 to 13 μmol/L. As acidic water entered the stream, its pH increased, causing aluminum hydrolysis and precipitation of aluminum hydroxide minerals – a process that would account for the net loss of Al_{IM} along the reach. Alternatively, some aluminum could have been lost from solution through ion-exchange reactions. The non-conservative loss of Al_{IM} in the upper reach (between sites 1 and 2) was proportionally greater during the posttreatment period than during the pretreatment period (Table 4), when stream pH was lower, providing further evidence for a pH-dependent precipitation control on aluminum transport.

Mass-balance calculations reveal a loss of H^+ along the outlet stream equivalent to about one-fourth of the tributary input for the stream reach during the pretreatment period and just slightly less than the tributary input during the posttreatment period (Table 4). The large in-stream loss of H^+ during the posttreatment period appears inconsistent with the calculated mass losses of Ca^{2+} and Al_{IM}, both of which should result in net gains of H^+. When all major H^+-consuming or H^+-producing reactions are combined in a proton mass balance as in equation (5), however, the theoretical and measured mass loss of H^+ in the stream reach are in close agreement (Fig. 6):

$$\begin{aligned} H^+ \text{ change} = {} & (\text{Loss of } Al_{IM} \times 3) + \text{Loss of } Ca^{2+} - \\ & \text{Loss of } (NO_3^- + SO_4^{2-}) - \text{Loss of } HCO_3^- - \\ & (\text{Loss of DOC} \times .06). \end{aligned} \qquad (5)$$

In the above equation, it is assumed that Al_{IM} and DOC are in units of Kmol, and all other constituents are in Keq.

The greatest mass loss of H^+ occurred by the following reaction:

$$HCO_3^- + H^+ \rightarrow H_2CO_3, \qquad (6)$$

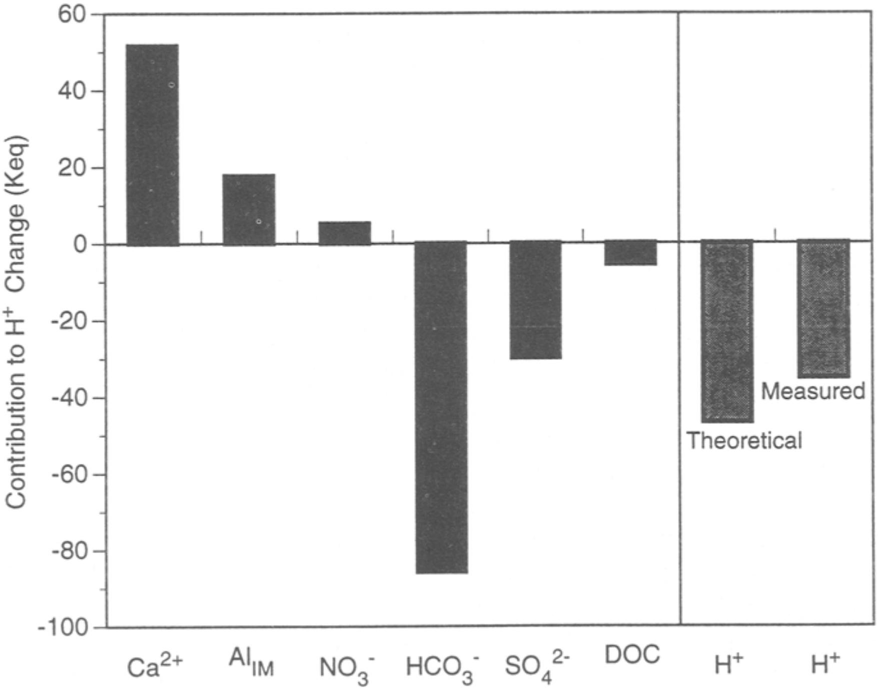


Fig. 6. Contribution of mass gains or losses of Ca^{2+}, AL_{IM}, NO_3^-, HCO_3^-, SO_4^{2-}, and DOC between sites 1 and 2 during the posttreatment period to the mass loss of H^+ based on pH measurements. Note that a negative value indicates a contribution to H^+ loss and a positive value indicates a contribution to H^+ gain.

as pH decreased along the stream reach. A difference of 11.5 Keq between the theoretical and measured H^+ loss was evident (Figure 6). This difference is small, however, because the calculated H^+ balance has a potential error based on the sum of the errors of all six constituents in the equation. Alternatively, if the pH values used in Table 1 to calculate tributary input along the stream reach were just 0.08 lower, the theoretical and measured H^+losses would be identical.

Some of the apparent loss of H^+ in the upper reach of the stream could have been the result of some combination of precipitation and adsorption of DOC with H^+. The mass-balance calculations indicate potential non-conservative losses of DOC during the pretreatment period and posttreatment periods, despite generally increasing downstream concentrations (Table 4). Although naturally occurring DOC contains molecules of widely differing sizes and structures, carboxylic acids are probably the most abundant group of acids in natural DOC (Perdue 1985). The pK_a values of these acids are typically between 4 and 5; thus, complexation of H^+ and precipitation would be expected to result when pH declines below 6 in water containing these acids. Carboxylic acids and naturally occurring DOC, in general, also have the ability to form complexes with cations such as Ca^{2+} and Al^{3+}. Thus, the net loss of DOC along the outlet stream could have played a role in the removal of H^+, Ca^{2+}, and Al_{IM} from solution.

Biological implications

Results of this study indicate that, in addition to lake neutralization, a benefit of watershed $CaCO_3$ treatment is the potential creation of several kilometers of less acidic outlet stream that might be suitable habitat for brook trout and other acid-sensitive aquatic organisms. Within three months after $CaCO_3$ treatment of the Woods Lake watershed, outlet pH increased above the levels considered critical for the survival and reproduction of many freshwater fish species, and Al_{IM} concentrations decreased below critical concentrations (Baker & Christensen 1991). These new conditions were maintained along the entire 3.5-km length of the stream throughout the 24-month posttreatment study period, except during the few weeks of snowmelt each spring. This study made no attempt to assess other characteristics of fish habitat, such as the extent of anoxia and the presence of suitable spawning habitat. However, the creation of additional suitable habitat downstream of a $CaCO_3$-treated lake could be a consideration in fish-management decisions.

Conclusions

The distance over which an outlet stream from a $CaCO_3$-treated lake becomes reacidified depends mainly on the chemistry of water entering the stream through ground-water seepage and from tributaries, although the stream substrate can increase the rate of acidification through ion exchange and biological uptake of Ca^{2+}. Streams with abundant wetlands and beaver ponds and, thus an organic-rich substrate with high CEC, would become acidified over a shorter distance than a stream channel with sandy substrate (other conditions being equal). Streams that pass through wetlands and beaver ponds that produce sufficiently strong reducing conditions to decrease downstream SO_4^{2-} concentrations would remain well-buffered farther downstream than well-oxygenated streams. In the Woods Lake outlet stream, SO_4^{2-} reduction affected ANC and pH from June through September.

Conservative mixing was the dominant process affecting downstream chemical changes in the Woods Lake outlet stream after watershed liming; however, cation exchange, reduction, biological uptake, and other in-channel processes affected pH, ANC, and Ca^{2+} concentrations as well. These processes include the loss of H^+ through the conversion of bicarbonate to carbonic acid, hydrolysis and precipitation of Al, and precipitation of DOC as organic acids or as Ca-organic matter complexes. These processes are inferred solely from in-stream mass balances, although the loss of Ca^{2+} by ion exchange is supported by data on the chemistry of the stream substrate. Most of the processes within the stream that affect acid/base chemistry are, in turn, affected by changes in acid/base chemistry; thus, their effect on downstream water quality would depend on how much the pH of the treated lake is increased. If the exchange and(or) uptake of Ca^{2+} by substrate material is reversible, the substrate could act as a buffer and delay the stream's return to pretreatment chemical conditions. The study was not continued long enough to address this question, however.

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