

The Experimental Watershed Liming Study: Comparison of lake and watershed neutralization strategies

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Received 28 October 1994; accepted 4 October 1995

Key words: acidification, acid neutralizing capacity, calcite, lake chemistry, liming

Abstract. The Experimental Watershed Liming Study (EWLS) was initiated to evaluate the application of CaCO_3 to a forested watershed in an effort to mitigate the acidification of surface water. The objective of the EWLS was to assess the response of the Woods Lake watershed to an experimental addition of CaCO_3 . During October 1989, 6.89 Mg CaCO_3/ha was applied by helicopter to two subcatchments comprising about 50% (102.5 ha) of the watershed area. The EWLS involved individual investigations of the response of soil and soil water chemistry, forest and wetland vegetation, soil microbial processes, wetland, stream and lake chemistry, and phytoplankton and fish to the CaCO_3 treatment. In addition, the Integrated Lake/Watershed Acidification (ILWAS) model was applied to the site to evaluate model performance and duration of the treatment. The results of these studies are detailed in this volume. The purposes of this introduction and synthesis paper are to: 1) present the overall design of the EWLS, 2) discuss the linkages between the individual studies that comprise the EWLS, and 3) summarize the response of the lakewater chemistry to watershed addition of CaCO_3 and compare these results to previous studies of direct lake addition. An analysis of lake chemistry revealed the watershed treatment resulted in a gradual change in pH, acid neutralizing capacity (ANC) and Ca^{2+} in the water column. This pattern was in contrast to direct lake additions of CaCO_3 , which were characterized by abrupt changes following base addition and subsequent rapid reacidification. Over the three-year study period, the supply of ANC to drainage waters was largely derived from dissolution of CaCO_3 in wetlands. Relatively little dissolution of CaCO_3 occurred in freely draining upland soils. The watershed treatment had only minor effects on forest vegetation. The watershed treatment eliminated the episodic acidification of streamwater and the near-shore region of the lake during snowmelt, a phenomenon that occurred during direct lake treatments. Positive ANC water in the near-shore area may improve chemical conditions for fish reproduction, and allow for the development of a viable fish population. The watershed CaCO_3 treatment also decreased the transport of Al from the watershed to the lake, and increased the concentrations of dissolved organic carbon (DOC) and dissolved silica (H_4SiO_4) in stream and lakewater. The watershed treatment appeared to enhance soil

nitrification, increasing concentrations of NO_3^- in soilwater and surface waters. However, the acidity associated with this NO_3^- release was small compared to the increase in ANC due to CaCO_3 addition and did not alter the acid-base status of Woods Lake. Acid neutralizing capacity (ANC) budgets for 12-month periods before and after the watershed treatment showed that the lake shifted from a large source of ANC to a minor source due to retention of SO_4^{2-} , NO_3^- , Al and the elevated inputs of Ca^{2+} associated with the watershed CaCO_3 application. In contrast to the direct lake treatments, Ca^{2+} inputs from the watershed application were largely transported from the lake.

Introduction and background

Surface water acidification by atmospheric deposition of strong acids has impacted aquatic resources in large regions of North America (Jeffries et al. 1986; Charles 1991) and Europe (Henriksen et al. 1989). In the U.S., the Adirondack region of New York has a large number of acidic lakes. Kretser et al. (1989) reported that 352 of 1469 lakes sampled (24%) in the Adirondack region had pH values below 5.0.

A critical parameter used to assess the sensitivity of waters to strong acid inputs is acid neutralizing capacity (ANC). Acidic lakes are typically characterized by ANC less than $0 \mu\text{eq/L}$. Biogeochemical processes that involve the transfer of ionic solutes can alter ANC (Stumm & Morgan 1981). Acid neutralizing capacity can be defined as:

$$\text{ANC} = C_B + [\text{NH}_4^+] + n[\text{Al}^{n+}] + 2[\text{Fe}_{\text{tot}}] + 2[\text{Mn}_{\text{tot}}] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-] - [\text{F}^-] - n[\text{A}_s^{n-}], \quad (1)$$

$$= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + n[\text{A}_w^{n-}] + [\text{Al}(\text{OH})^{2+}] + 2[\text{Al}(\text{OH})_2^+] + 4[\text{Al}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+], \quad (2)$$

where C_B is the sum of basic cation concentrations ($2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+]$; concentration units in $\mu\text{mol/L}$); and A_w^{n-} and A_s^{n-} represent weakly and strongly acidic organic anions, respectively, associated with dissolved organic carbon (DOC; Driscoll et al. 1994).

Since Ca^{2+} and SO_4^{2-} are typically the dominant ions in dilute acidic surface waters in the Adirondacks, the expression for ANC can be simplified to:

CaCO_3
addition

SO_2 emission
reduction

↓

↑

$$\text{ANC} = 2[\text{Ca}^{2+}] - 2[\text{SO}_4^{2-}]$$

(3)

This simplified expression illustrates the options available to resource managers to mitigate the effects of acidic deposition. One option is to decrease SO_4^{2-} concentration in surface waters through controls on SO_2 emissions which result in acidic deposition (equation 2). Marked reductions in emissions of SO_2 have occurred since 1970 largely due to New Source Performance Standards associated with the Clean Air Act Amendments of 1970 (Husar et al. 1991). Declines in SO_2 emissions over the last 15 to 25 years have resulted in decreases in the concentration and deposition of SO_4^{2-} in precipitation (Hedin et al. 1987; Butler & Likens 1991) and surface waters throughout the northeastern U.S. and southeastern Canada (Dillon et al. 1987; Driscoll et al. 1989a; Morgan 1990; Driscoll & van Dreaseon 1993; Driscoll et al. 1995). Unfortunately, this decline has not resulted in widespread increases in the ANC of these surface waters. In addition to decreases in SO_4^{2-} , declines in concentrations of basic cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) have been reported for the United States and Europe (Driscoll et al. 1989a, 1995; Hedin et al. 1994). This decrease in inputs of basic cations appears to coincide with control of particulate emissions and may increase the sensitivity of base-poor forested ecosystems to acidic deposition. The response of surface water ANC to future reductions in emissions of SO_2 and NO_x ($\text{NO} + \text{NO}_2$), anticipated following the 1990 Amendments of the Clean Air Act, await the results of long-term monitoring studies.

Surface water ANC can also be increased by the addition of basic materials, such as CaCO_3 , increasing the Ca^{2+} concentration (equation 2). While weathering and atmospheric deposition naturally supply basic cations to water, human manipulation of ANC can be accomplished by a strategy commonly called "liming." Base addition has been widely practiced to mitigate surface-water acidification in Norway (Wright 1985), Sweden (Bengtsson et al. 1980; Hultberg & Andersson 1982), Canada (Dillon & Scheider 1984) and the U.S. (Porcella 1989; Olem 1990; Smallidge et al. 1993). In the U.S., one of the more detailed and long-term study sites for the application of base to neutralize the effects of acidic deposition is Woods Lake, located in the Adirondack Mountain region of New York. Research at this site has included studies of various direct lakewater-column treatments of CaCO_3 (Porcella 1989; Gubala & Driscoll 1991), as well as the Experimental Watershed Liming Study (EWLS), which is the focus of the series of papers in this volume. The objectives of this introductory paper are to: 1) describe the Woods Lake watershed and summarize the results of previous direct lakewater-column CaCO_3 additions; 2) describe the logistics of the watershed application of CaCO_3 (EWLS) and the associated field instrumentation and monitoring; 3) present lake water-column chemistry as well as solute mass balances and ANC budgets, comparing and contrasting these results with the previous direct base

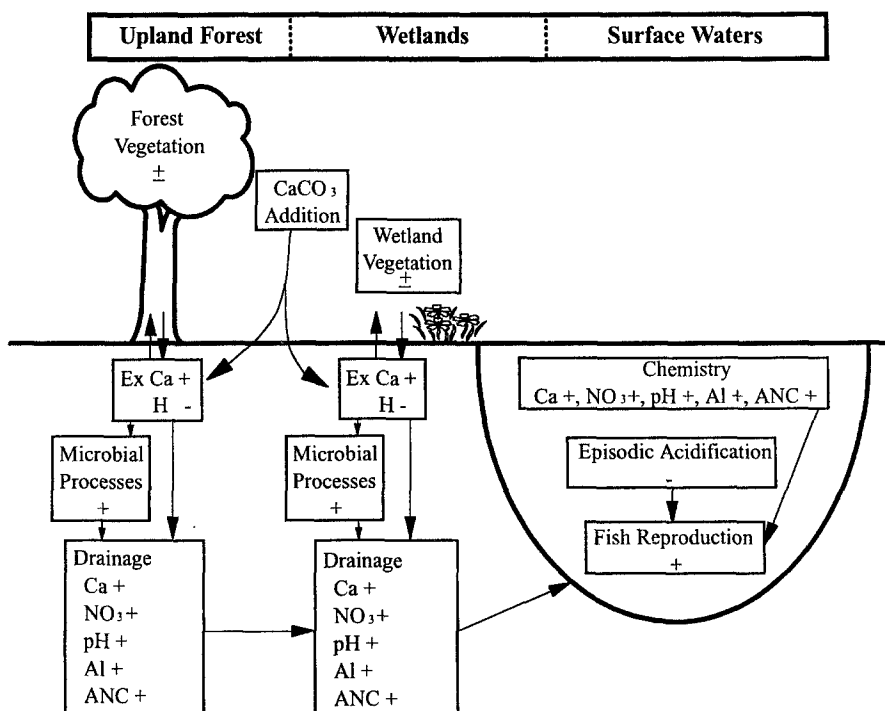


Fig. 1. Conceptual diagram illustrating the hypothesized response of the forest/wetland/surface water at Woods Lake to experimental addition of CaCO_3 . A plus sign (+) represents a hypothesized increased response to the manipulation; a minus sign (-) represents a decreased response to the manipulation. Ex represents exchangeable soil pool.

additions; and 4) summarize and provide a synthesis of the detailed studies which comprise the EWLS and are included in this series of articles.

Objectives and hypotheses of the experimental watershed liming study

The EWLS was a comprehensive ecosystem investigation of the response of a forested watershed, and interconnected wetlands, streams and drainage lake to an experimental addition of CaCO_3 . The overall objective of the study was to determine the viability of watershed base treatment as a strategy to mitigate the acidification of lake ecosystems, primarily through the successful development of a reproducing fishery. Prior to the experiment, we hypothesized that the application of CaCO_3 to Woods Lake watershed would alter the structure and function of this upland forest/wetland/surface water ecosystem (Fig. 1). It was anticipated that terrestrial application of CaCO_3

would result in the release of Ca^{2+} and ANC to soil and drainage waters in both upland soils and wetlands. Because of the ambient acidity of the forest soils at the Woods Lake watershed, it was hypothesized that base application would enhance microbial activity increasing the mineralization of organic C and associated elements in soil. Increased mineralization of organic N and subsequent nitrification would increase NO_3^- leaching and acidify drainage water, possibly offsetting increases in ANC and pH and decreases in Al concentrations resulting from the CaCO_3 treatment. While we did not anticipate major effects to forest and wetland vegetation, an assessment of this response was a critical component of our evaluation of CaCO_3 as a mitigative strategy. We expected that the watershed treatment would increase stream and lake ANC and pH and decrease concentrations of Al. Moreover, it was hypothesized that this application would eliminate episodic acidification of inlet streams and the near-shore region of Woods Lake. These chemical changes were hypothesized to allow for the reproduction of brook trout and to improve the water quality of downstream waters.

To test these hypotheses, a series of studies that are described in the manuscripts that follow this introductory paper were initiated to provide an integrated assessment of the impacts of CaCO_3 treatment on the abiotic and biotic components of the upland/wetland/lake ecosystem (Table 1). The manuscripts are sequenced along the hydrologic flowpath through the Woods Lake watershed. Terrestrial components and processes are discussed in the first three papers, including the response of the soils, and soil solutions (Blette & Newton 1996a, this issue; Geary & Driscoll 1996, this issue), and soil microbial processing of N (Simmons et al. 1996, this issue). Wetland and stream studies include the effects of CaCO_3 treatment on wetland peat and peat porewaters (Yavitt & Fahey 1996, this issue), the biogeochemistry of tributary streamwater and beaver-impoundment/wetland waters (Cirino & Driscoll 1996, this issue) and the response of stream chemistry to episodic hydrologic events (Newton et al. 1996, this issue). Schofield & Keleher (1996, this issue) assess the response of brook trout to changes in surface water chemistry in Woods Lake and Burns (1996, this issue) describes the impact of watershed base treatment on the chemistry of downstream waters.

Although the EWLS was a comprehensive analysis of the effects of a watershed application of CaCO_3 to mitigate the acidity of surface waters, a limitation was the relatively short period of post-treatment investigation (three years). The success of base treatment as a management technique should ideally be assessed over many years, even decades. To quantify the duration and long-term ecosystem effects of the CaCO_3 treatment, Blette & Newton (1996b, this issue) conducted 9 and 50 year simulations using the Integrated Lake Watershed Acidification Study (ILWAS) model.

Table 1. Manuscripts comprising the Experimental Watershed Liming Study (EWLS).

Paper	Citation	Aspects Studied
1.	This manuscript	Introduction to the EWLS and comparison of changes in lake chemistry in response to water column (WC), water column/ sediment (WC/S) and watershed (WS) treatments.
2.	Blette & Newton 1995a	Effects of CaCO_3 treatment on soil exchange complex and calcite mass balance on the watershed.
3.	Geary & Driscoll 1995	Response of soil water to watershed CaCO_3 treatment.
4.	Simmons et al. 1995	Response of forest floor nitrogen dynamics to watershed CaCO_3 treatment, including net N mineralization and nitrification.
5.	Yavitt & Fahey 1995	Effects on peat and peat porewater chemistry in littoral and beaver pond wetlands. Includes impacts on microbial respiration and sulfate reduction rates.
6.	Cirno & Driscoll 1995	Impacts of a beaver pond and wetlands on stream chemistry and efficiency of calcite mobilization. In-pond chemistry, pond mass balances, ANC and Ca^{2+} budgets.
7.	Newton et al. 1995	Chemical response of tributary streams to episodic rainfall and snowmelt events.
8.	Schofield & Keleher 1995	Response of fish dynamics and structure in Woods Lake to watershed CaCO_3 treatment.
9.	Burns 1995	Effects on lake outlet and downstream chemistry for 3 km below the lake, including mass balances on Ca and ANC.
10.	Blette & Newton 1995b	Predictions of the watershed response to the CaCO_3 treatment using the ILWAS model.

Methods

Study site description

The Woods Lake watershed (42°52' N, 71°58' W) is located in the west-central section of the Adirondack Park in New York (Fig. 2). The lake and watershed were originally investigated as part of the ILWAS project (Goldstein et al. 1984, 1985). Results of these studies were used to formulate the ILWAS simulation model describing the biogeochemical lake-watershed processes that regulate the acid-base status of drainage waters and lake sensitivity to acidic deposition (Gherini et al. 1985). This model was used to evaluate potential CaCO_3 treatment dosages for the EWLS (Davis 1988) and subsequently to investigate the long-term response of the watershed to base treatment (Blette & Newton 1996a, this issue).

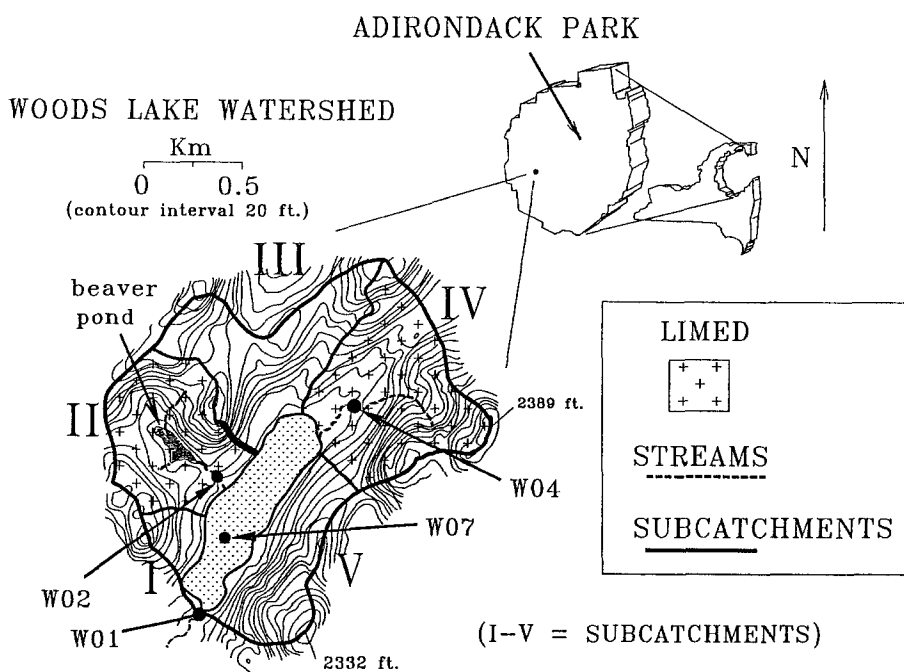


Fig. 2. Map of Woods Lake watershed. Subcatchments II and IV were treated with CaCO_3 .

The Woods Lake watershed covers an area of 207 ha (Table 2, after Staubitiz & Zariello 1989). Surficial deposits consist mainly of thin till, although seismic refraction surveys have revealed depths to bedrock of up to 10 m on the northwest shore of the lake. Numerous small bedrock outcrops of hornblende granitic gneiss occur mainly on the southeast side of the lake, as well as on ridgetops and topographic highs. The soils of the watershed are relatively young (<12,000 yr), and exhibit the Spodosol profile typical of the region (April & Newton 1985). Forest communities that have developed following various timber harvests during the past 100 years are dominated by *Acer rubrum* L. (red maple), *Fagus grandifolia* Ehrh. (American beech), *Betula alleghaniensis* Britton (yellow birch), and *Picea rubens* Sarg. (red spruce). Plant community composition and structure are described in detail in Cronan et al. (1987), Brach & Raynal (1992), and Smallidge & Leopold (1994, 1995). Wetlands occur around the lake and in association with a large beaver pond upstream of one of the main tributaries (W02; Fig. 2). Wetland vegetation is characterized by weakly minerotrophic shrub, graminoid and herbaceous species, (Mackun et al. 1994; Rossell et al. 1994, 1995; Yavitt & Fahey 1996, this issue).

Table 2. Watershed and lake characteristics of Woods Lake, New York (after Staubitz & Zariello 1989).

<i>Watershed Characteristics</i>	
Basin area (ha)	207
Watershed area (ha)	184
Maximum basin relief (m)	122
Forest cover (%)	98 .1
Open wetland coverage (%)	1 .9
Mean thickness of surficial deposits (m)	2.3
Area of surficial deposits greater than 3 m thick (%)	9.2
Range of total annual precipitation (cm)	110–140
Mean annual precipitation (cm)	123
Mean annual snow depth (cm)	76 .2
Mean annual evapotranspiration (% of mean annual precipitation)	40
Lake to watershed area ratio	0.13
<i>Lake Characteristics</i>	
Lake surface area (ha)	23
Lake volume (*10 ⁵ m ²)	8
Maximum lake depth (m)	12
Mean lake depth (m)	3.5
Lake surface altitude above msl (m)	606
Mean lake hydraulic residence time (d)	174

Woods Lake is dimictic and normally ice-covered from mid-December to mid-April. It is a relatively small, shallow lake with a mean hydraulic residence time of approximately 6 months (Table 2). Major surface water inputs to the lake include two nearly-perennial tributary streams located in the northwest and northeast subcatchments of the watershed (II and IV, respectively; Fig. 2). Diffuse inputs from ephemeral streams are common, particularly during large hydrologic events, and subsurface inputs have been estimated to contribute approximately 31 to 38% of total inflow to the lake, on an annual basis (Staubitz & Zariello 1989).

Water-column base addition history

In 1984, Woods Lake was selected as one of three lakes studied as part of the Lake Acidification Mitigation Project (LAMP; Porcella 1989). The LAMP was designed to quantify the effects of the application of CaCO₃ directly to the water column of an acidic lake. The water column of Woods Lake was

initially treated on 30 and 31 May 1985 with a 23 Mg dose of a 71% CaCO_3 slurry (442 keq Ca^{2+} , median particle size of 2 μm). This small particle size treatment is referred to as the “water-column only” (WC) manipulation. The duration of this treatment (period of positive water column ANC) was approximately 15 months. Woods Lake was treated again in September of 1986 with a 34.3 Mg dose (686 keq Ca^{2+}) using a combination of fine (6 to 44 μm particle size, 19.9 Mg) and coarse (40 to 400 μm particle size, 23.4 Mg) CaCO_3 particles. This “water column/sediment” (WC/S) treatment was designed to allow penetration of the larger particles of CaCO_3 to the sediments, with subsequent release of a slow diffusive flux of ANC across the sediment/water interface in an attempt to lengthen the treatment period (Gubala & Driscoll 1991). The duration of positive ANC conditions following the WC/S treatment was approximately 20 months.

The Experimental Watershed Liming Study (EWLS): Watershed CaCO_3 application

In 1989, the EWLS project was initiated with the application of CaCO_3 to the Woods Lake watershed. Two subcatchments of the Woods Lake watershed (II and IV, Fig. 2), comprising approximately 50% of the watershed area (102.5 ha), were selected for treatment with CaCO_3 based on their large hydrologic contribution to the lake and the presence of two perennial tributaries. The manipulation is referred to as the watershed (WS) treatment. The treated subcatchments were amended with pelletized limestone, 1.41 to 4.00 mm in diameter. This limestone was quarried near Watertown, NY, pulverized to a consistency of fine sand, and pelletized using a water-soluble calcium lignosulfonate binder. The binder allowed the pellets to disintegrate to their original grain size in the presence of moisture after application. The elemental composition of the limestone was approximately 82% CaCO_3 , 8% MgCO_3 and 4% organic binder, the balance consisting of inorganic salts and insoluble silicate minerals.

The CaCO_3 was applied by helicopter from 2 to 19 October 1989. The treatment was conducted after leaf-fall in order to provide more immediate contact of added CaCO_3 with the forest floor. The target application rate was 10 Mg/ha of limestone. Weather was generally good, but variable winds likely caused some non-uniform application to the target areas. To quantify the actual CaCO_3 application over the whole watershed, collectors were placed along six transects within the treated subcatchments (designated 2100, 2200, 4100, 4200, 4300, 4400; Fig. 3), with “limefall” plots of 10 m $\times$ 10 m located every 15 m along the transects (Simmons 1993). Two sets of samples were taken from each collector, including initial limefall obtained the day of the aerial application to that transect (direct limefall), and limefall collected three weeks

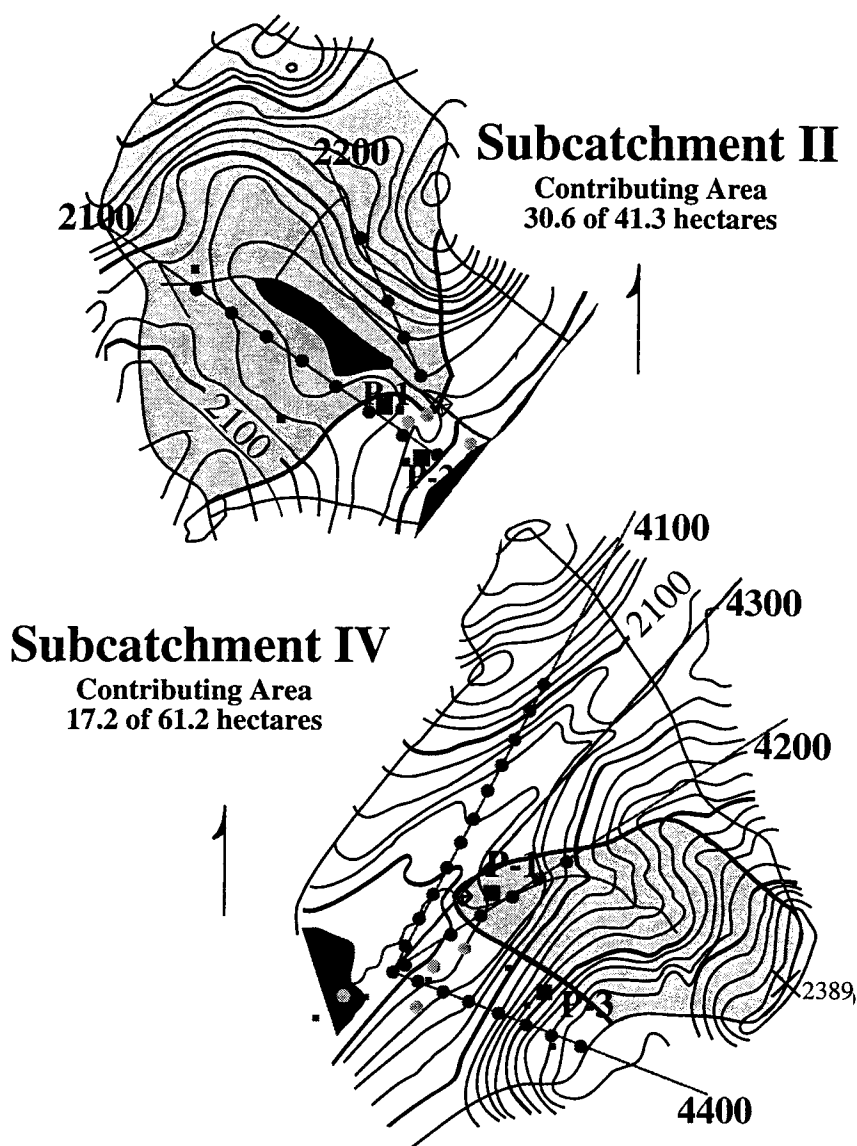


Fig. 3. Map showing transects of limefall collectors for treated subcatchments.

after the application (intercepted limefall). The direct limefall samples were analyzed gravimetrically and total CaCO_3 input was calculated assuming an 82% CaCO_3 content (see above). Intercepted limefall samples were acidified with 6N HCl and analyzed for Ca^{2+} by atomic absorption spectrophotometry (Simmons 1993). Estimates of total CaCO_3 input to specific locations in

Woods Lake watershed were made by individual EWLS investigators and are discussed in the individual papers in this series.

Terrestrial and aquatic field instrumentation and measurement

The watershed and lake were instrumented to monitor surface and ground-water chemistry, soil solution and solid phase soil chemistry, peat and peat porewater chemistry, and snow chemistry. Surface-water hydrology was monitored using United States Geological Survey (USGS) stream gauging stations at both major inlet streams (site W02, USGS ID code 04256480; site W04, USGS ID code 04256470; Fig. 2) and at the lake outlet stream (site W01, USGS ID code 04256485). The inlet gauging stations were used to monitor surface drainage of 74% (site W02) and 28% (site W04) of the total surface discharge from subcatchments II and IV, respectively (Fig. 3). Samples were routinely collected for chemical analysis at the lake inlets, outlet and within the water column (described below). Additional water sampling included use of zero tension soil lysimeters for soil water (Geary & Driscoll 1996, this issue), groundwater wells for shallow and deep groundwater (Newton et al. 1996, this issue), peat porewater sampling (Yavitt & Fahey 1996, this issue) and beaver pond and wetland monitoring (pond inlet, outlet, and in-pond depth profiles; Cirno & Driscoll 1996, this issue). Hydrometric and chemical measurements were made during episodic hydrologic events and during snowmelt conditions. The location and description of sites for specific investigations during the EWLS are described in the accompanying papers (Table 1).

The methods used for chemical analysis of drainage water and soil are summarized in Table 3. The chemical equilibrium model ALCHEMI (version 4.0, Schecher & Driscoll 1995) was used to calculate the equivalence of inorganic monomeric Al ($\text{Al}^{\text{n}+}$) from measured total monomeric Al (Al_{tm}) and organic monomeric Al (Al_{om}). Inorganic monomeric Al (Al_{im}) is calculated as Al_{tm} less Al_{om} . Particulate Al (Al_{p}) is calculated as total Al (Al_{t}) – Al_{tm} . ALCHEMI was also used to calculate the equivalence of organic anions ($\text{A}^{\text{n}-}$), using measured dissolved organic carbon (DOC), pH and other chemical parameters (Schecher & Driscoll 1995).

The responses of soils and vegetation to CaCO_3 addition were assessed by comparing element concentrations in the forest floor, soil and plant tissue in treated and reference plots (Brach & Raynal 1992; Mackun et al. 1994; Rossell et al. 1994, 1995; Smallidge & Leopold 1994, 1995).

Table 3. Chemical analytical methods used in the Experimental Watershed Liming Study (EWLS).

Analyte	Method	Investigators (keyed to references in Table 1)	Reference
<i>Aqueous Phase</i>			
pH	Potentiometric, glass combination electrode	1,2,3,4,5,6,7,8,9	APHA 1985
Ca^{2+} , Mg^{2+}	Atomic absorption spectroscopy (AAS), flame	1,2,3,4,5,6,7,9	Slavin 1968
K^{+} , Na^{+}	Atomic emission spectroscopy (AEM), flame	1,2,3,5,6,7,9	Slavin 1968
Fe_{tot} , Mn_{tot}	AAS, graphite furnace	1	Slavin 1968
Fe^{2+}	o-phenanthroline complexation, absorption spectroscopy	6	APHA 1985
SO_4^{2-} , NO_3^{-} , Cl^{-}	Ion chromatography (IC)	1,3,4,5,6,7,9	Tabatabai & Dick 1983
Total F^{-}	Potentiometric, ion selective electrode after TISAB addition	1,3,6	Orion 1976
NH_4^{+}	Phenate colorimetry	1,3,4,5,6	Cappo et al. 1987
Acid Neutralizing Capacity (ANC)	Strong acid titration, Gran plot analysis	1,2,3,6,7,9	Gran 1952
Dissolved Inorganic Carbon (DIC)	Acid purge, infrared (IR) CO_2 detection	1,3,5,6,9	Dohrman 1984
Dissolved Organic Carbon (DOC)	UV enhanced persulfate oxidation, infrared (IR) CO_2 detection	1,3,5,6,7,9	Dohrman 1984
Dissolved H_4SiO_4	Heteropoly blue colorimetry	1,3,6,7	Cappo et al. 1987
Total Al	Acidification, AAS analysis, graphite furnace	1	Driscoll 1984
Total monomeric Al (Al_{tm})	Pyrocatechol violet (PCV), automated analysis	1,2,3,5,6,7,9	Driscoll 1984; McAvoy et al. 1990
Organic (non-labile) monomeric Al (Al_{om})	Ion exchange, PCV, automated analysis	1,3,5,6,7,9	Driscoll 1984; McAvoy et al. 1990
Dissolved Oxygen (DO)	Modified Winkler titration	1,6	APHA 1985
<i>Solid Phase</i>			
Calcite (CaCO_3)	Acidification with HCl, CO_2 detection	2,5	Gross 1971
pH (soils and sediments)	Potentiometric, glass combination electrode, 1:1 or 2:1 deionized water/soil	2,4,5,9	Black et al. 1965

Table 3 (continued)

Analyte	Method	Investigators (keyed to references in Table 1)	Reference
Forest floor pH	10:1 (vol:air dried mass) slurry w/DI water	4	Cappo et al. 1987
Soil exchangeable bases	NH ₄ Cl extraction, AES for Ca ²⁺ , Mg ²⁺ ; AEM for Na ⁺ , K ⁺	2,6,9	Cappo et al. 1987
Soil exchangeable acidity	KCl extraction, analysis for H ⁺ and Al	2,9	Cappo et al. 1987
Soil NH ₄ ⁺ , NO ₃ ⁻ , NO ₂ ⁻	Extraction with KCl, phenol nitroprusside-cadmium followed by diazotization, colorimetric analysis	4	Weatherburn 1967; Keeney and Nelson 1982
Soil organic content	Loss on ignition at 550 °C	4,9	Black et al. 1965
Soil C	Direct combustion and IR detection	4	Cappo et al. 1987

Mass balances and ANC budget calculations

Precipitation, surface water hydrology and surface water chemistry were used to calculate mass solute mass balances for Woods Lake in an effort to assess the effects of the various base treatment strategies. The detailed hydrologic studies of Staubitz & Zariello (1989) for the period June 1984 to May 1986 were used to develop hydrologic and solute budgets for Woods Lake over the entire study period (June 1984 to December 1992). Inlet discharge was not measured during the period following the WC/S treatment (October 1986–September 1987) because gauging stations were not operated. During this period, total inflow was estimated from the water budget using the known outlet discharge, precipitation inputs and estimated evaporation, assuming that outseepage was minimal (Staubitz & Zariello 1989). Precipitation amount and wet deposition chemistry were estimated for Woods Lake based on measurements at Nick's Lake (20 km southwest), operated by the New York State Department of Environmental Conservation (New York State Acid Deposition Monitoring Program 1987–1991). Evaporation was estimated using the method of Hamon (1961).

Lake inlet streams (sites WO2 and WO4) and the lake outlet (site WO1) were sampled for the concentrations of major solutes and selected trace metals

from the initiation of the LAMP project until the completion of the EWLS in 1992. Sites were sampled throughout the year on a three-week interval, with more intensive sampling during spring snowmelt and major rainfall events. Lake chemistry profiles were also constructed from data collected at an in-lake site (WO7, Fig. 2), which included sample collections at seven depths.

Watershed mass balances and ANC budgets were estimated using the approach described by Driscoll et al. (1989b). Both subcatchments II and IV are drained by perennial streams, while subcatchments I, III and V drain into Woods Lake by ephemeral streams and diffuse groundwater discharge (Staubitz & Zariello 1989). These ungauged subcatchments are characterized by shallow deposits of glacial till (April & Newton 1985). For the period prior to the WS treatment, the concentrations of chemical constituents in the inlet streams were flow-weighted based on the discharge record of the streams. The water quality of stream WO2 was assumed to contribute 30.8% of the flux calculated for chemical inputs from the entire gauged and ungauged area of the watershed (including diffuse surficial and subsurface inputs), while the water quality of stream WO4 was assumed to contribute 69.2% of the chemical inputs from the watershed (Staubitz & Zariello 1989). The discharge of the two streams was pro-rated to the entire watershed, based on these percentages. These percentages reflect the relative area of the watershed underlain by different depths of till, with stream WO2 assumed to be representative of flow through deep till (>3 m) and stream WO4 representative of flow through shallow till (<3 m). For stream inlet flux calculations performed for the post-WS treatment period, the flux from the CaCO_3 -treated subcatchments was treated separately from the untreated areas, calculated from "baseline" concentrations used for the inlet fluxes during the year prior to CaCO_3 treatment. Direct inputs of dry deposition were estimated from dry/wet ratios for the Adirondack region (Shepard et al. 1989; Baker 1990). Drainage fluxes were calculated by multiplying measured concentrations times the cumulative flow for the period midway between the preceding and subsequent sampling dates. Lake inputs included drainage inflow, direct precipitation to the lake surface and dry deposition to the lake surface. Outfluxes were assumed to be due solely to losses calculated at the lake outlet (WO1, Fig. 1). The inherent error in these flux estimates is directly related to uncertainties in hydrologic estimates as detailed in Staubitz & Zariello (1989). Our lake mass balances indicate that inputs of relatively conservative solutes like Cl^- , F^- and Na^+ were close to the measured fluxes from the lake outlet (see Results and Discussion), suggesting that assumptions used for this analysis were appropriate.

Table 4. Mass balances for pre- (A) and post- (B) water column (WC) treatment of Woods Lake. STREAM INFLUX = inlet stream flux, PPT IN = wet precipitation inputs, DRY DEP = total dry deposition inputs, LAKE OUTFLOW = lake outlet flux and RET COEFF = retention coefficient $[(\text{STREAM INFLUX} + \text{PPT IN} + \text{DRY DEP}) - (\text{LAKE OUTFLOW})]/(\text{STREAM INFLUX} + \text{PPT IN} + \text{DRY DEP})$. “-” indicates net release and “+” indicates net retention. Charged species are expressed as eq/ha-yr, all other species as moles/ha-yr. # includes CaCO_3 added in treatment.

A. Pre-WC TREATMENT (June 1, 1984–May 31, 1985)						
	STREAM INFLUX	PPT IN	DRY DEP	LAKE OUTFLUX	NET	RET COEFF
Ca^{2+}	4410	104	123	5000	-363	-0.08
Mg^{2+}	1096	33.9	26.1	1230	-74	-0.06
Na^+	1560	35.2	13	1450	158	0.10
K^+	425	26.1	57.4	517	-8.50	-0.02
DOC	23700			15600	8100	0.34
A^{n-}	765			530	235	0.31
SO_4^{2-}	7670	704	352	8270	456	0.05
Cl^-	504	49.1	11.7	461	104	0.18
NO_3^-	2500	398	159	2340	717	0.23
F^-	126			135	-9.00	-0.07
NH_4^+	63.0	267	90.4	613	-193	-0.46
Al_t	1160			652	508	0.44
Al_{tm}	887			509	378	0.43
Al_{im}	687			429	258	0.38
Al_{om}	201			80.0	121	0.60
Fe_{tot}	204			93.0	111	0.54
Zn_{tot}	42.2			30.0	12.2	0.29
Mn_{tot}	55.2			67.8	-12.6	-0.23
B. Post-WC TREATMENT (June 1, 1984–May 31, 1986)						
Ca^{2+}	24200#	120	143	19800	4660	0.19
Mg^{2+}	1140	38.3	28.7	1450	-243	-0.20
Na^+	1730	40.9	15.2	1590	196	0.11
K^+	309	18.3	40.0	534	-168	-0.46
DOC	22000			19900	2100	0.10
A^{n-}	687			1950	-1260	-1.84
SO_4^{2-}	8960	698	350	8960	1050	0.10
Cl^-	543	64.4	15.6	643	-20.0	-0.03
NO_3^-	1630	500	200	1460	870	0.37
F^-	162			183	-20.0	-0.13
NH_4^+	107	269	91.3	539	-71.7	-0.15
Al_t	1120			522	698	0.57
Al_{tm}	783			97	686	0.88

Table 4 (continued)

	STREAM INFLUX	PPT IN	DRY DEP	LAKE OUTFLUX	NET	RET COEFF
Al _{im}	591			33	558	0.94
Al _{om}	193			63.9	129	0.67
Fe _{tot}	163			280	-117	-0.72
Zn _{tot}	42.2			16.1	26.1	0.62
Mn _{tot}	62.2			43	19.2	0.31

Table 5. Mass balances for post-water column/sediment (WC/S) treatment of for Woods Lake. STREAM INFLUX = inlet stream flux, PPT IN = wet precipitation inputs, DRY DEP = total dry deposition inputs, LAKE OUTFLUX = lake outlet flux and RET COEFF = retention coefficient [(STREAM INFLUX + PPT IN + DRY DEP) - (LAKE OUTFLUX)/(STREAM INFLUX + PPT IN + DRY DEP)]. “-” indicates net release and “+” indicates net retention. Charged species are expressed as eq/ha-yr, all other species as moles/ha-yr. # includes CaCO₃ added in treatment.

Post-WC/S TREATMENT (October 1, 1986–September 30, 1987)						
	STREAM INFLUX	PPT IN	DRY DEP	LAKE OUTFLUX	NET	RET COEFF
Ca ²⁺	37800#	335	398	21300	17200	0.45
Mg ²⁺	896	403	302	1420	181	0.11
Na ⁺	1510	143	53.0	1610	96.0	0.06
K ⁺	470	7.39	2.61	465	15.0	0.03
DOC	25900			20800	5100	0.2
A ⁿ⁻	857			530	327	0.38
SO ₄ ²⁻	6480	870	436	6960	826	0.11
Cl ⁻	452	53.5	12.6	522	-3.90	-0.01
NO ₃ ⁻	1440	470	187	2030	67.0	0.03
F ⁻	133			202	-69.0	-0.52
NH ₄ ⁺	153	237	80.4	509	-38.6	-0.08
Al _t	1000			496	504	0.51
Al _{tm}	604			106	498	0.83
Al _{im}	422			2.17	420	0.99
Al _{om}	180			84.8	95.2	0.53
Fe _{tot}	232			158	74.0	0.32
Zn _{tot}	23.0			12.6	10.4	0.45
Mn _{tot}	50.9			35.2	15.7	0.31
H ₄ SiO ₄	4590			4091	479	0.10

Table 6. Mass balances for pre- (A) and post- (B) watershed (WS) treatment of Woods Lake. STREAM INFLUX = inlet stream flux, PPT IN = wet precipitation inputs, DRY DEP = total dry deposition inputs, LAKE OUTFLUX = lake outlet flux and RET COEFF = retention coefficient $[(\text{STREAM INFLUX} + \text{PPT IN} + \text{DRY DEP}) - (\text{LAKE OUTFLUX})]/(\text{STREAM INFLUX} + \text{PPT IN} + \text{DRY DEP})$. “-” indicates net release and “+” indicates net retention. Charged species are expressed as eq/ha-yr, all other species as moles/ha-yr.

A. Pre-WS TREATMENT (October 1, 1988–September 30, 1989)						
	STREAM INFLUX	PPT IN	DRY DEP	LAKE OUTFLUX	NET	RET COEFF
Ca ²⁺	4820	335	398	10000	-4400	-0.78
Mg ²⁺	1200	403	302	1520	385	0.20
Na ⁺	1900	143	53.0	1840	256	0.12
K ⁺	578	7.39	16.1	639	-37.5	-0.06
DOC	23600			18500	5100	0.21
A ⁿ⁻	591			500	91.0	0.15
SO ₄ ²⁻	9130	498	250	9740	138	0.01
Cl ⁻	500	112	27.0	600	39.0	0.06
NO ₃ ⁻	3260	282	113	2650	1000	0.27
F ⁻	196			238	-42.0	-0.22
NH ₄ ⁺	157	237	80.4	224	250	0.53
Al _t	1520			643	877	0.58
Al _{lm}	1320			535	785	0.59
Al _{im}	987			323	664	0.67
Al _{om}	327			212	115	0.35
Fe _{tot}	181			169	12.0	0.06
Zn _{tot}	33.9			21.7	12.2	0.36
Mn _{tot}	87.0			50.4	36.6	0.42
H ₄ SiO ₄	5610			4390	1220	0.22
B. Post-WS TREATMENT (October 1, 1989–September 30, 1990)						
Ca ²⁺	18700	201	239	18700	440	0.20
Mg ²⁺	1900	122	91.3	1890	227	0.11
Na ⁺	2250	33.9	12.6	1840	457	0.20
K ⁺	780	5.22	11.7	639	158	0.20
DOC	30800			25400	5400	0.17
A ⁿ⁻	1730			1320	410	0.24
SO ₄ ²⁻	10500	644	323	9570	1900	0.16
Cl ⁻	705	66		783	-12.0	-0.01
NO ₃ ⁻	4420	382	153	4060	895	0.18
F ⁻	176			199	-23.0	-0.13
NH ₄ ⁺	367	347	118	461	371	0.45

Table 6 (continued)

	STREAM INFLUX	PPT IN	DRY DEP	LAKE OUTFLUX	NET	RET COEFF
Al _t	1180			748	432	0.37
Al _{tm}	876			308	568	0.65
Al _{im}	593			98.3	495	0.83
Al _{om}	283			210	73.0	0.26
Fe _{tot}	227			158	69.0	0.31
Zn _{tot}	23.8			13.5	10.3	0.43
Mn _{tot}	63.8			37.4	26.4	0.41
H ₄ SiO ₄	8030			5910	2120	0.26

Table 7. Limefall statistical data, by transect and subcatchment. All values in Mg CaCO₃/ha. Subcatchments refer to Fig. 2 and transects refer to those shown in Fig. 3.

Transect	Mean	sd	se	cv	n
2100	7.25	2.75	0.49	35.95	32
2200	8.88	8.58	3.50	73.67	6
4100	1.91	1.57	0.20	82.15	61
4200	4.17	1.98	0.48	47.62	17
4300	3.10	1.47	0.74	47.50	4
4400	8.47	5.38	1.35	63.55	16
Subcatchments					
II	7.85	4.06	0.66	51.77	38
IV	3.42	3.53	0.36	89.71	98
II and IV	4.66	4.18	0.36	89.71	136
Subcatchments (excluding transect 4100)					
IV	5.91	4.39	0.72	74.17	37
II and IV	6.89	4.31	0.50	62.50	75

Results and discussion

Water-column CaCO₃ treatments (WC and WC/S, 1985 and 1986)

Prior to CaCO₃ addition, Woods Lake was highly acidic, with low water-column pH (volume-weighted mean of 4.8), ANC (volume-weighted mean

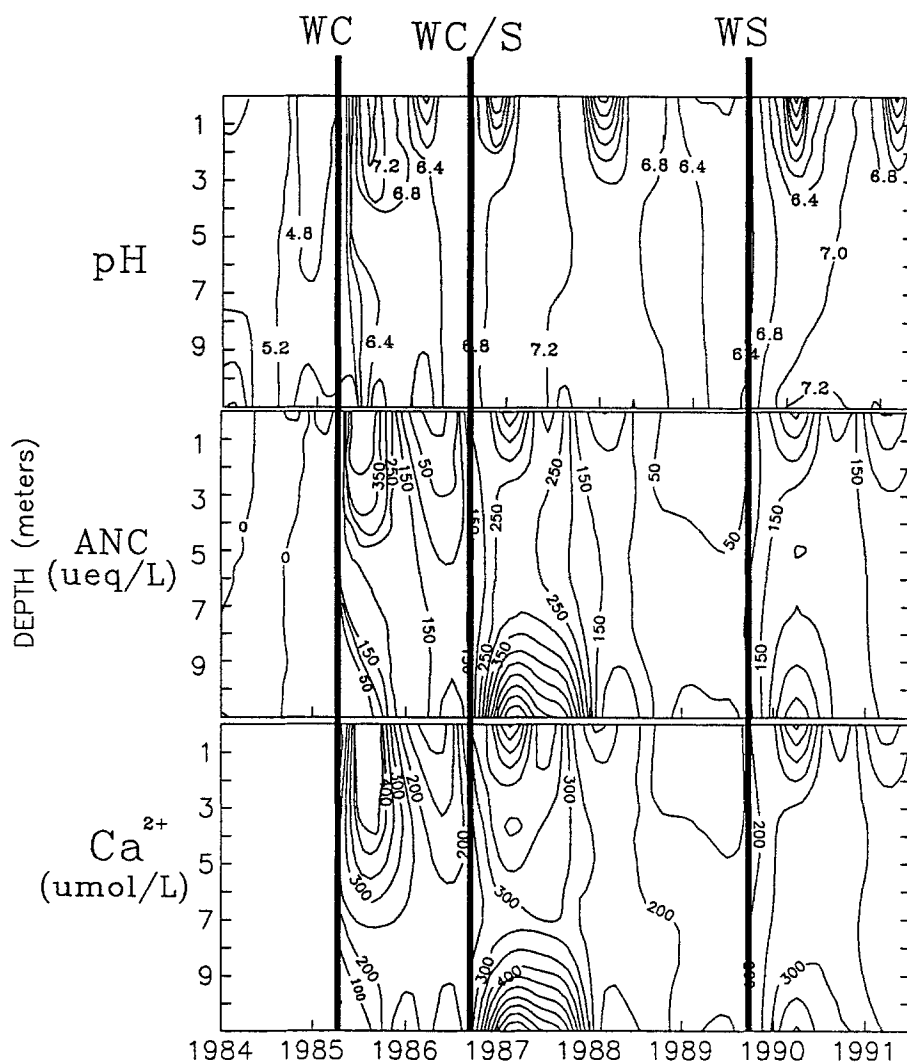


Fig. 4. Isopleths of pH, acid neutralizing capacity (ANC) and Ca^{2+} of the water column of Woods Lake prior to base treatment, and after water column (WC), water column/sediment (WC/S) and watershed (WS) treatments of CaCO_3 . Prior to base treatment, the volume-weighted mean concentration of Ca^{2+} was $34 \mu\text{mol/L}$. Isopleths are shown for calendar years.

of $-8 \mu\text{eq/L}$) and Ca^{2+} (volume-weighted mean of $34 \mu\text{mol/L}$), and high concentrations of Al_{im} (volume-weighted mean $6.2 \mu\text{mol/L}$; Figs. 4, 5). Solute mass-balance calculations (Table 4) revealed that Woods Lake retained NO_3^- (717 eq/ha-yr), SO_4^{2-} (456 eq/ha-yr), total organic anions ($\text{A}^{\text{n-}}$; 235 eq/ha-yr) and released C_B (288 eq/ha-yr). The net retention of $\text{A}^{\text{n-}}$ was

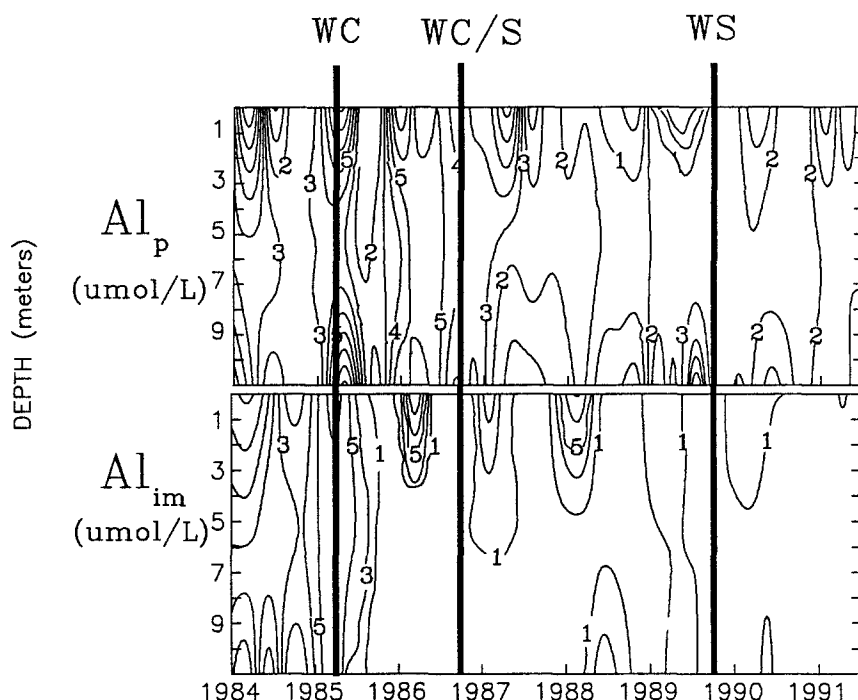


Fig. 5. Isoleths of particulate Al (Al_p) and inorganic monomeric Al (Al_{im}) of Woods Lake prior to base treatment, and after water column (WC), water column/sediment (WC/S) and watershed (WS) treatments of $CaCO_3$. Isoleths are shown for calendar years.

consistent with the net retention of dissolved organic carbon (DOC) in the lake (8100 mol C/ha-yr). These ANC production processes (equation 1) were offset by the consumption of ANC associated with Al hydrolysis (i.e., retention, 1330 eq/ha-yr), resulting in net production of ANC (406 eq/ha-yr; Fig. 6). Prior to base treatment, a non-stoichiometric relationship was evident between ANC and Ca^{2+} in the water column ($ANC = -216 + 3.0 \cdot Ca^{2+}$, in $\mu eq/L$, $r^2 = 0.54$).

Immediately following the WC treatment (<24 h), lake pH increased from 4.9 to 9.4 due to the rapid dissolution of the small $CaCO_3$ particles coupled with low initial concentrations of dissolved inorganic carbon (DIC; Fordham & Driscoll 1989). The WC treatment occurred early during summer stratification, and the applied base was thus restricted to the upper mixed layer until fall turnover. Within 1 to 2 months after base addition concentrations of Al declined by about an order of magnitude, largely through decreases in Al_{im} and particulate Al (Al_p) forms (Fig. 5; Driscoll et al. 1989c).

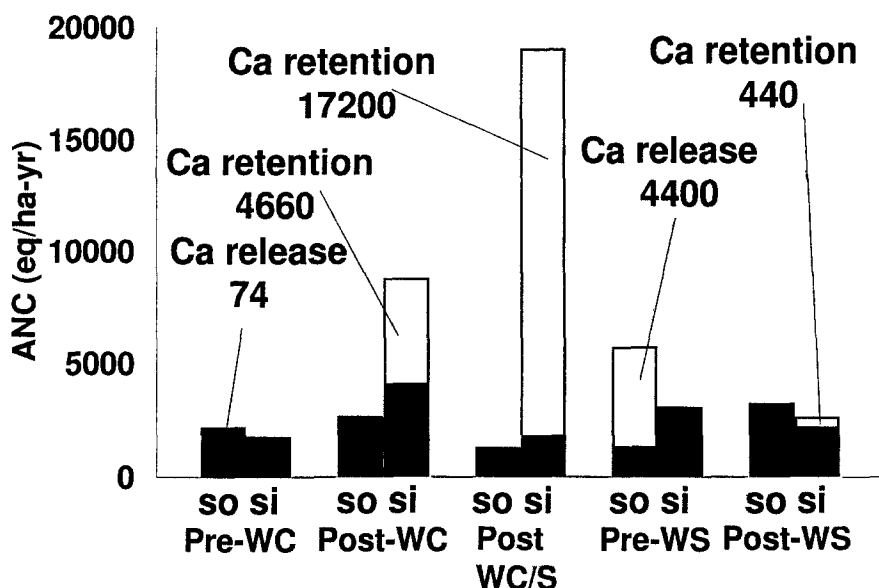


Fig. 6. Annual acid neutralizing capacity (ANC) budgets of Woods Lake prior to base treatment (pre-WC), after direct water column treatment (post-WC), after the water column/sediment treatment (WC/S), prior to the watershed treatment (pre-WS) and after the watershed treatment (post-WS). Sources (SO) and sinks (SI) of ANC are shown, and the role of Ca in the ANC budget is indicated by shading.

The water column addition of CaCO_3 resulted in a marked shift in the acid-base status of Woods Lake. Solute mass balance calculations for the 12 month period after the manipulation (Table 4) reveal that the lake became a large sink of ANC (6100 eq/ha-yr) due in large part to the retention of added CaCO_3 (4660 eq/ha-yr, Fig. 6). The WC treatment increased ANC consumption through enhanced retention of Al^{n+} (2550 eq/ha-yr) and a shift to a net release of A^{n-} (1260 eq/ha-yr) from the lake. This release of A^{n-} occurred despite continued retention of DOC (2100 mol C/ha-yr), and was likely due to the deprotonation of naturally occurring organic acids in the water column of the lake in response to the increase in pH associated with base addition. Hypothetical calculations using a triprotic organic acid model for Adirondack surface waters show that increases in pH from 5.0 to 7.0 result in a 265 percent increase in the concentration of organic anions (in $\mu\text{eq/L}$) for a given concentration of DOC (Driscoll et al. 1994). Increases in SO_4^{2-} retention (1050 eq/ha-yr) were also observed. The acid-base chemistry of the lake was virtually entirely regulated by the supply of ANC through Ca^{2+} release from CaCO_3 dissolution, as variations in ANC were nearly stoichiometric with changes in Ca^{2+} in the water column of Woods Lake after the WC treatment ($\text{ANC} = -101 + 1.02 \cdot \text{Ca}^{2+}$, in $\mu\text{eq/L}$, $r^2 = 0.99$).

Most of the added CaCO_3 dissolved (81%) within 1 month following the WC treatment. As a result of the rapid dissolution and short hydraulic residence time, the added ANC was readily flushed from Woods Lake. Values of measured ANC approached 0 $\mu\text{eq/L}$ and lake pH was 5.9 within 15 months after the treatment. At this time, virtually all (97.5%) of the added Ca was accounted for in the mass balance (i.e., flushed from the lake), with approximately 2.5% (11 keq) presumably retained in sediments.

The WC/S addition of CaCO_3 resulted in a more gradual increase in lake pH (from 5.9 to 6.8 immediately after the additions), reflecting the higher DIC concentration in the lake prior to the manipulation and the slower dissolution rate of the larger CaCO_3 particle sizes added. Concentrations of Ca^{2+} and ANC increased, and Al_{im} concentration decreased in the water column (Figs. 4 and 5). As with the WC treatment, changes in ANC values closely corresponded to changes in Ca^{2+} concentrations ($\text{ANC} = -101 + 1.02 \cdot \text{Ca}^{2+}$, in $\mu\text{eq/L}$, $r^2 = 0.99$). Sediment release of ANC and Ca^{2+} was evident after the WC/S treatment by elevated concentrations ($\text{ANC} > 650 \mu\text{eq/L}$, $\text{Ca}^{2+} > 700 \mu\text{eq/L}$) in the deepest waters during stratification periods (Fig. 4).

Mass balance calculations for the year following the WC/S treatment showed the system to be a large ANC sink (17,800 eq/ha-yr; Fig. 6), primarily associated with retention of CaCO_3 in the water column and sediments. Aluminum hydrolysis also contributed to the consumption of ANC (1270 eq/ha-yr). Sulfate retention was the predominant process supplying ANC (826 eq/ha-yr), while, as was evident under pretreatment conditions, DOC (5100 mol C/ha-yr) and $\text{A}^{\text{n-}}$ (327 eq/ha-yr) were retained in the lake. Since the change in pH in response to the WC/S treatment was small in comparison to the change in pH that occurred after the initial WC treatment, deprotonation of natural organic acids was not important in the acid-base response to the manipulation.

Mass balance calculations suggested a slow release of Ca^{2+} and ANC from the sediments during the post WC/S treatment period. Of the 686 keq CaCO_3 added to the lake during the WC/S treatment, approximately 8% (55 keq) was lost from the system, presumably retained in sediments. The retention in the sediments, as well as the greater dose (about 50% more than the WC treatment alone), prolonged the period of positive ANC in the water column of Woods Lake to 20 months. The WC/S treatment approach may be effective in delaying reacidification in lakes with moderate hydraulic retention times. Unfortunately, lakes in the Adirondack region typically have short hydraulic residence times (< 0.5 yr; Kretser et al. 1989).

Since direct lake treatment did not alter the chemistry of inflowing streams or shallow groundwater, pH, ANC and Ca^{2+} were low, and Al was high in

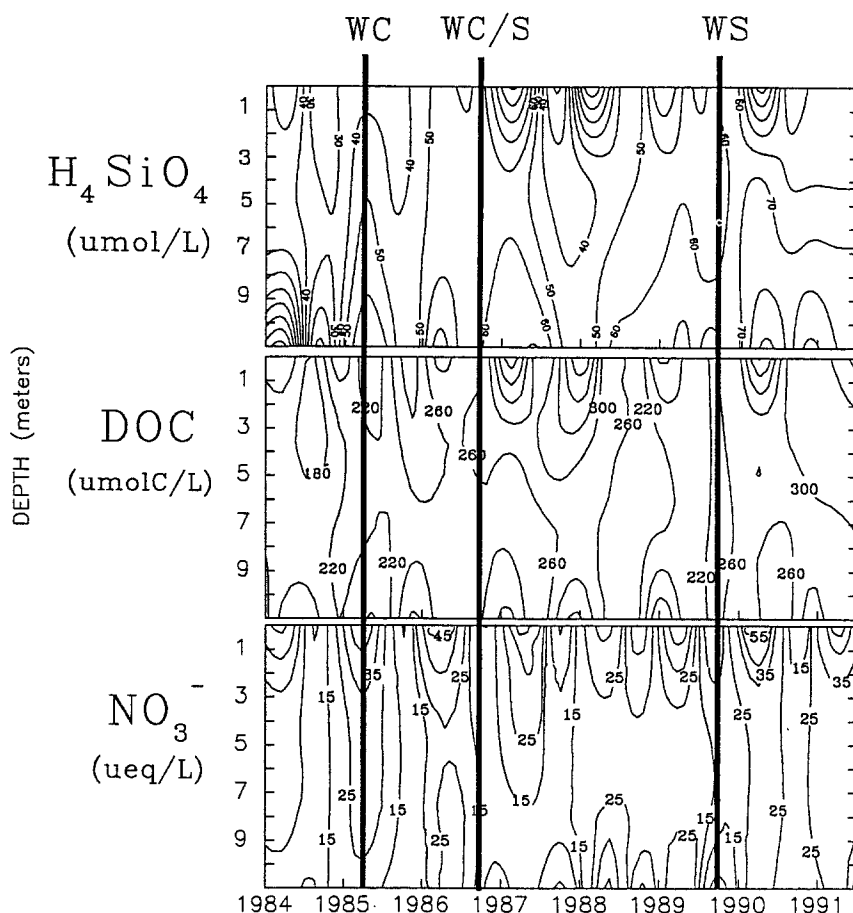


Fig. 7. Isopleths of H_4SiO_4 , dissolved organic carbon (DOC) and NO_3^- of Woods Lake prior to base treatment, and after water column (WC), water column/sediment (WC/S) and watershed (WS) treatments of CaCO_3 . Isopleths are shown for calendar years.

the upper meter of the water column during spring snowmelt (Figs. 4, 5, 8). Spring snowmelt resulted in the acidification of the upper water column and near-shore region after both WC and WC/S treatments. For example, in the upper 1 m of the water column during mid-March, pH values were 4.86 and 4.51, ANC values were -6 and $-11 \mu\text{eq/L}$ and Ca^{2+} concentrations were 85 and $17 \mu\text{eq/L}$ following the WC and WC/S treatments, respectively. This acidification was associated with fluxes of NO_3^- during snowmelt in the watershed, with increased NO_3^- concentrations evident in near-shore zones and under the ice during spring episodes (Fig. 7). High concentrations of Al_{im} were also observed after the WC and WC/S treatments (15 and 10

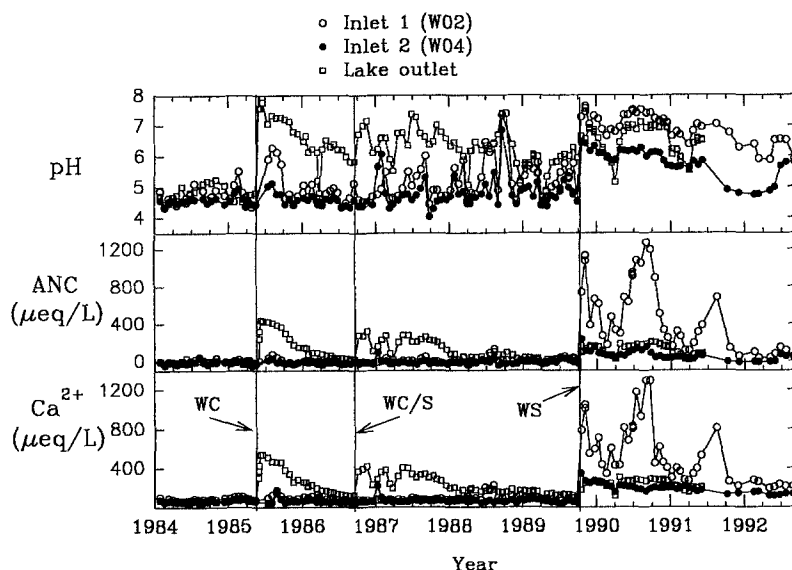


Fig. 8. Time series of pH, acid neutralizing capacity (ANC) and Ca^{2+} for inflowing streams (WO2, WO4) and the outlet of Woods Lake.

$\mu\text{mol/L}$, respectively). This supply of Al_{im} from acidic stream and shallow groundwater hydrolyzed in the lake, resulting in the formation of Al_p and the production of H^+ . Temporary acidification of the upper waters during spring snowmelt may limit fish reproduction in lakes with suitable physical conditions for spawning in the near-shore regions. As a result of the limited success with both direct lake treatment strategies, the EWLS project was initiated.

EWLS watershed base treatment (WS, 1989)

Calcite application rate and areal coverage

Based on the in-situ collectors, we estimate average loading rates of $7.85 \text{ Mg CaCO}_3/\text{ha}$ and $3.42 \text{ Mg CaCO}_3/\text{ha}$ in subcatchments II and IV, respectively (Table 7). Variations in application rates were large, however, within plots, along transects and between transects. Average total “limefall” collections along transect 4100 (the first to be treated) were very low ($1.91 \text{ Mg CaCO}_3/\text{ha}$). These low values were due to our inability to effectively deploy collectors on the first day of treatment as a result of adverse weather conditions. If these initial collections, which represent less than 1% of added CaCO_3 , are excluded from the analysis, a much higher application rate to subcatchment IV is obtained ($5.91 \text{ Mg CaCO}_3/\text{ha}$; Table 7). When the values

obtained from the initial transect collections are eliminated, a mean watershed application rate of 6.89 Mg CaCO_3/ha (137,000 eq/ha) is estimated.

Water-column chemistry affected by the WS CaCO_3 treatment

Changes in the water column of Woods Lake in response to the WS treatment were more subtle than patterns observed for direct-lake additions (Figs. 4, 5, 7). Mean volume-weighted lake pH increased from 6.36 to 6.68. Concentrations of ANC and Ca^{2+} following WS treatment increased from 52.7 $\mu\text{eq/L}$ to 138 $\mu\text{eq/L}$ and 80 $\mu\text{eq/L}$ to 119 $\mu\text{eq/L}$, respectively. These values remained relatively constant through the 2-year water column monitoring period that followed the WS treatment. These patterns of solute concentrations contrasted markedly with the abrupt changes in water chemistry that accompanied the base addition for the WC and WC/S treatments and subsequent rapid reacidification. The input of Ca^{2+} (from inlet streams and shallow groundwater input) derived from terrestrial CaCO_3 dissolution (Cirmo & Driscoll 1996, this issue; Newton et al. 1996, this issue) helped maintain relatively uniform water chemistry with positive values of ANC. Like the WC and WC/S treatments, the lakewater chemistry exhibited a close stoichiometric relationship between ANC and Ca^{2+} ($\text{ANC} = -132 + 1.14 \cdot \text{Ca}^{2+}$, in $\mu\text{eq/L}$, $r^2 = 0.96$). Concentrations of Al_p were greatly diminished in the water column of the lake after the WS treatment (Fig. 5), due likely to decreases in stream inputs of Al_im and in-lake Al hydrolysis, with less subsequent formation of Al_p .

The most distinct change in water column chemistry following the WS treatment occurred in the upper 1 to 2 m of the water column during spring snowmelt, under ice-cover conditions. The WS CaCO_3 treatment altered the pattern of snowmelt acidification of the upper water column of the lake, that was characteristic of the direct lake treatments. Rather than dilution of Ca^{2+} concentrations, the upper waters of the lake showed increases in Ca^{2+} during snowmelt after the WS manipulation.

Other changes in water-column chemistry were evident in response to the WS treatment (Fig. 7). Volume-weighted concentrations of DOC (from 244 to 292 $\mu\text{mol C/L}$) and dissolved H_4SiO_4 (from 53 to 64 $\mu\text{mol/L}$) increased after the WS treatment. Increases in lakewater DOC may have been due to dieback of littoral zone vegetation associated with elevated pH (Bukaveckas 1988). Alternatively, the increase in water column DOC may have resulted from increased flux of DOC from stream WO2 after CaCO_3 treatment (Cirmo and Driscoll 1996; this issue). The stream influx of DOC to Woods Lake for the 12 month period after the WS treatment (30,800 mol C/ha-yr), was higher than values observed prior to the manipulation (mean 25,200 mol C/ha-yr, Tables 4–6). Increases in the concentration of H_4SiO_4 may reflect the enhanced dissolution of silicate minerals by complexation by organic anions), which

occurs at circumneutral pH conditions (Bennett et al. 1991; Hiebert & Bennett 1992). Indeed, stream influx of H_4SiO_4 to the lake was higher after the WS treatment (8,350 mol/ha-yr) than prior to the WS manipulation (mean 5,090 mol/ha-yr). Concentrations of NO_3^- also increased in the water column of the lake after the WS treatment (a volume-weighted mean of 29 $\mu\text{eq/L}$ after WS treatment compared to 23 $\mu\text{eq/L}$ before treatment).

A comparison of solute mass balances for the 12 month periods immediately before and after the WS manipulation shows that the treatment resulted in a shift in the ANC budget of Woods Lake (Fig. 6, Table 6). Prior to the WS CaCO_3 treatment, the lake was a net source of ANC (2,640 eq/ha-yr), largely associated with the release of Ca^{2+} from sediments following the WC/S treatment in 1986 (4,400 eq/ha-yr). In-lake retention of NO_3^- also contributed to ANC production (1,000 eq/ha-yr). The production of ANC by these processes was offset, in part, by the ANC consumption associated with Al hydrolysis (2,040 eq/ha-yr).

After the WS treatment, the lake returned to near steady-state conditions with respect to Ca^{2+} inputs (i.e., retention of 440 eq/ha-yr), and became a net source of ANC (591 eq/ha-yr). Most (98%) of the Ca^{2+} influx was transported through the lake outlet. Consumption of ANC due to Al^{3+} hydrolysis (735 eq/ha-yr) continued to be important, while SO_4^{2-} and NO_3^- retention (1900 eq/ha-yr and 895 eq/ha-yr, respectively) also contributed to ANC production.

Summary and synthesis of the experimental watershed liming study

In the EWLS, a series of integrated field experiments were initiated (Table 1) to test our hypotheses concerning the response of the Woods Lake watershed to CaCO_3 application (Fig. 1). Over the time-frame of the EWLS, there were clear improvements in the acid-base status of Woods Lake (Figs. 4, 5; Burns 1996, this issue), enabling populations of brook trout stocked in the lake after the WC treatment to reproduce (Schofield & Keleher 1996, this issue). The relatively low application of CaCO_3 (6.89 Mg CaCO_3/ha) to the Woods Lake watershed dissolved at a moderate rate, supplying Ca^{2+} to the upland forest and downstream wetland/lake ecosystem. Approximately 50% of the added CaCO_3 dissolved within two years (Blette & Newton 1996a, this issue), but Ca^{2+} added to the upland forest was largely restricted to the forest floor (Blette & Newton 1996a, this issue). Increases in pH associated with the base treatment resulted in deprotonation of functional groups associated with soil organic matter, increasing the cation exchange capacity (CEC) of the forest floor. This perturbation enhanced Ca^{2+} retention in the forest floor (Blette &

Newton 1996a, this issue) and restricted drainage fluxes of Ca^{2+} and ANC to the mineral soil (Geary & Driscoll 1996, this issue).

Despite the limited penetration of added CaCO_3 to upland mineral soils and relatively small increases in ANC of waters draining this large fraction of the watershed, marked increases in Ca^{2+} and ANC, and decreases in Al were evident in peat pore water (Yavitt & Fahey 1996, this issue), streamwater (Cirmo & Driscoll 1996, this issue) and lakewater (Figs. 4, 5, 8). Indeed over the two years following the WS treatment, the increased supply of ANC largely occurred through the dissolution of CaCO_3 applied to saturated soils and wetland areas, most prominently in subcatchment II which drains a beaver impoundment (Fig. 8; Cirmo & Driscoll 1996, this issue). Mass balance calculations showed that 60% of the CaCO_3 added to the beaver impoundment and associated wetland dissolved within two years. There was no evidence that the WS CaCO_3 treatment altered microbial processes in wetlands, such as respiration or SO_4^{2-} reduction (Yavitt & Fahey 1996, this issue).

Treatment of the watershed with CaCO_3 stimulated Ca uptake by forest vegetation and weakly minerotrophic wetland plants (Rossell et al. 1994; Smallidge & Leopold 1995). However, on a mass basis, foliage of upland forest species during the growing season following treatment was a minor sink ($\sim 0.05\%$) for the added Ca. Sequestration of Ca by vegetation and its gradual release through leaching and decomposition will contribute to the long-term neutralization of surface water at Woods Lake. The treatment enhanced the growth of some species in both forest and shrub-graminoid wetlands but inhibited the growth of others (Brach & Raynal 1992; Rossell et al. 1995; Smallidge & Leopold 1995). Responses of growth and foliar elemental change were species specific; predictably, the growth of acid tolerant (calcifuge) species was suppressed. As we hypothesized, short-term effects of CaCO_3 treatment on plant community structure and composition in the watershed were slight. However, future changes in forest vegetation could be substantial, particularly in wetlands, if species composition and competitive relationships shift in response to altered substrate chemistry (Rossell et al. 1995).

When the EWLS was initiated, we hypothesized that base application would stimulate mineralization of soil organic matter and subsequent nitrification of NH_4^+ (Fig. 1). Nitrification in acidic forest soils is generally thought to be limited by low-pH conditions (Aber & Melillo 1991). Base addition might be expected to increase nitrification and leaching of NO_3^- to drainage waters. The H^+ associated with this process would counteract increases in ANC in the lake resulting from the CaCO_3 treatment. Simmons et al. (1996, this issue) observed that the addition of CaCO_3 indeed enhanced nitrification in the forest floor, but root uptake minimized NO_3^- loss in drainage

water. Increases in NO_3^- concentrations were evident in soil water (Geary & Driscoll 1996, this issue), streamwater (Cirmo & Driscoll 1996, this issue) and lakewater (Fig. 7) in response to the WS base treatment. Nevertheless, the magnitude of the NO_3^- increase in lakewater ($\sim 5 \mu\text{eq/L}$) was small in comparison to the increase in ANC associated with the CaCO_3 treatment ($\sim 100 \mu\text{eq/L}$). Thus, increases in lakewater acidity associated with enhanced NO_3^- inputs did not have an appreciable effect on the change in ANC resulting from base addition.

A critical hypothesis of the EWLS was that the watershed CaCO_3 treatment would mitigate episodic acidification during spring snowmelt and fall rain events. Newton et al. (1996, this issue) observed pulsed increases in Ca^{2+} during snowmelt associated with the movement of waters along shallow flow-paths, coupled with the supply of Ca^{2+} from CaCO_3 dissolution and cation exchange in the organic soil horizons. The WS treatment also diminished the mobilization of Al from the soil (Geary & Driscoll 1996, this issue), resulting in much lower Al concentrations in streamwater and, subsequently, lower inputs to Woods Lake (Fig. 5, Table 6; Cirmo & Driscoll 1996, this issue). As a result, concentrations of Al_{im} were low in the upper waters and near-shore zone of the lake during snowmelt. The mitigation of snowmelt acidification and the improvement of water chemistry conditions in the near-shore region of the lake are major benefits associated with the WS CaCO_3 treatment. These changes created suitable chemical conditions for fish spawning in the near-shore zones where there is suitable groundwater discharge and physical substrate (Gubala et al. 1991; Schofield 1993; Schofield & Keleher 1996, this issue).

Increases in pH and Ca^{2+} concentrations, and decreases in Al_{im} concentrations in streamwater after the WS treatment allowed for successful reproduction of brook trout in WO2, a stream with suitable physical conditions for spawning (Schofield & Keleher 1996, this issue). The WS treatment not only resulted in positive ANC conditions for inlet streams and the lake, but also improved the water chemistry for a 3 km reach of the lake outlet stream (Burns 1996, this issue).

A critical management issue associated with watershed amendments of CaCO_3 is the duration of the treatment. Lake/watershed mass balances show only 4% of the Ca^{2+} associated with the CaCO_3 treatment was lost from the lake outlet within two years following base treatment (Blette & Newton 1996b, this issue). Most (96%) of the added Ca^{2+} remained in the watershed as undissolved CaCO_3 or associated with the soil exchanger, vegetation or soil/groundwater. This slow response of the WS treatment contrasts starkly with the direct lake applications of CaCO_3 , which were readily flushed from the lake over a 2-year period (Gubala & Driscoll 1991). The ILWAS model

was applied to Woods Lake watershed to project the duration of treatment effects (Blette & Newton 1996b, this issue). Model calculations suggest that under current loadings of acidic deposition, positive ANC conditions will occur in Woods Lake as long as the inputs of ANC associated with CaCO_3 dissolution exceed strong acid input from the atmosphere. Under the CaCO_3 loading of the WS treatment, positive ANC conditions in Woods Lake would persist for approximately 50 yr. These predictions are tempered by uncertainty associated with important observations made during the EWLS that are not considered in the model formulation, including: 1) the role of wetlands and saturated soil conditions in facilitating the dissolution of CaCO_3 , and 2) the effects of increases in soil CEC, that occurred in response to base addition, on Ca^{2+} retention/loss by the soil exchange complex.

Acknowledgements

Funding for the EWLS was provided by Living Lakes, Inc., the Empire State Electric Energy Research Corporation, the U.S. Fish and Wildlife Service, the U.S. Geological Survey and the Electric Power Research Institute. We thank G. Fordham, R. Geary, J. Simmons, P. Smallidge, A. Brach, I. Rossell, W. Ayling, L. Oliver, J. Blaisdell, B. Aulenbach, K. Postek and D. Long for their help. This is contribution number 141 of the Upstate Freshwater Institute.

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