Biogeochemistry **32:** 265–297, 1996.

The impacts of a watershed $CaCO_3$ treatment on stream and wetland biogeochemistry in the Adirondack Mountains

CHRISTOPHER P. CIRMO[1] & CHARLES T. DRISCOLL
Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244; [1] *Current address: Department of Geological and Environmental Science, Susquehanna University, Selinsgrove, PA 17870*

Received 28 October 1994; revised 30 June 1995

Key words: acid neutralizing capacity, biogeochemistry, liming, *Sphagnum*, watershed, wetland

Abstract. Temporal and longitudinal variations in the chemistry of two tributary streams of Woods Lake in the Adirondack Mountains of New York were monitored before and after a watershed $CaCO_3$ application. One subcatchment of the lake had a large beaver pond and wetland at its headwaters, while the second was free-flowing. Treatment of both subcatchments with $CaCO_3$ resulted in an immediate increase in acid neutralizing capacity (ANC) associated with Ca^{2+} release. The extent and duration of the response to the treatment were greater in the wetland-impacted stream. Aluminum was retained and complexed with organic solutes generated within the beaver-pond. In the free-flowing stream, NO_3^- concentration increased significantly after the manipulation; this pattern was not evident in the wetland-impacted stream. Net retention of SO_4^{2-} was evident in the beaver pond prior to and following treatment, and this response was enhanced after the watershed liming. Comparisons of beaver pond inlet/outlet concentrations, mass balance calculations, and in-pond profiles of chemical parameters revealed patterns of retention of SO_4^{2-}, NO_3^- and Al, and release of Fe^{2+}, dissolved organic carbon (DOC) and NH_4^+ in the wetland during the summer before $CaCO_3$ treatment. Post-treatment releases of Ca^{2+} from the near-sediment zone in the beaver pond corresponded to anoxic periods in mid- to late-summer and under ice in winter. These findings demonstrate the importance of increased microbial processing of organic matter, along with high partial pressure of CO_2 (P_{CO_2}) in facilitating the dissolution of the applied $CaCO_3$. Dissolved silica (H_4SiO_4) was retained in the wetland during the summer prior to treatment but was released after the manipulation. This phenomenon may reflect the dissolution of diatom frustules or silicate minerals in the wetland at higher pH and DOC concentrations. Within two years of the $CaCO_3$ treatment 60% of the $CaCO_3$ applied to the beaver pond and surrounding wetland was dissolved and transported from the pond, in contrast to only 2.2% of the $CaCO_3$ applied to the upland subcatchment draining into the wetland. These results, coupled with high quantities of exchangeable Ca^{2+} found in sediments and on *Sphagnum* mosses in the pond, demonstrate the importance of hydrologic source areas and wetlands in facilitating the dissolution of added $CaCO_3$, and in regulating the production of chemical species important in ANC generation.

Abbreviations. ANC = acid neutralizing capacity, DIC = dissolved inorganic carbon, DOC = dissolved organic carbon, EWLS = Experimental Watershed Liming Study, P_{CO_2} = partial pressure of carbon dioxide, SI = saturation index

Introduction

Calcium carbonate application to hydrologic source areas and wetlands

Recent studies have shown that when $CaCO_3$ is applied as an acid neutralizing agent in hydrologic source areas within watershed subcatchments (e.g., wetlands, saturated zones, discharge zones) and in upland soils adjoining streams and drainage flowpaths (i.e., riparian zones), both the efficiency of dissolution of the base and the duration of the acid neutralization response are enhanced (Davis & Goldstein 1988; Grieve 1990; Jenkins et al. 1991). While the effects of $CaCO_3$ additions on upland and wetland soils in forested catchments have been investigated (Matzner et al. 1983; Persson et al. 1989; Yavitt & Newton 1990/91), there is relatively little information available concerning the impact of $CaCO_3$ treatments on acid neutralizing capacity (ANC) production within sediments and peat (Young et al. 1989; Gubala & Driscoll 1991). Yavitt & Newton (1990/91) observed higher rates of $CaCO_3$ dissolution in the surface layers of wetland soils as compared to upland mineral soils. Surface peat and wetland soils were also shown to contain higher concentrations of exchangeable Ca^{2+} following $CaCO_3$ dissolution. Nye & Amelko (1987) demonstrated an enhancement of the rate of $CaCO_3$ dissolution in soils with low pH (<5.0), high partial pressure of carbon dioxide (Pco_2) and high soil moisture content. It is believed that elevated concentrations of dissolved inorganic carbon (DIC) and high Pco_2 facilitates $CaCO_3$ dissolution in moist or saturated organic-rich soils and sediments (DePinto et al. 1989). Processes which facilitate the storage of applied Ca^{2+} in sediments, soil, or peat (e.g., high biological productivity, high sediment and peat cation exchange capacity (CEC), pH dependent CEC increase, active *Sphagnum* exchange of basic cations, etc.) would be expected to enhance the release of Ca^{2+} upon subsequent reacidification. Limited sediment/water interaction is expected with most surface waters in lakes (except perhaps during turnover periods), whereas sediment/water contact (both spatially and temporally) is greater in shallow ponds and wetlands. This condition could facilitate the dissolution and movement of sediment-bound Ca^{2+} in these systems. Burial of applied $CaCO_3$, surface deactivation by iron oxides or siderite, and coating by organic materials (Plummer et al. 1979; Sverdrup et al. 1984) could make further dissolution dependent upon sediment/porewater processes like diffusion, diagenesis, and bioturbation (Aller 1980; Berner 1980). Such processes dominate shallow wetland sediments which are warm, exposed to sunlight, and microbiologically active. Increased benthic or sediment microbial activity has been observed subsequent to $CaCO_3$ treatments in Europe (Ivarson 1977; Raddum et al. 1986; Persson et al. 1989).

Hydrological and biogeochemical impacts of wetlands and beaver ponds

The importance of wetlands and beaver ponds in controlling surface water hydrology and biogeochemical cycling has recently been demonstrated in a number of studies (Naiman et al. 1988; Johnston & Naiman 1990; Woo & Waddington 1990; Cirmo & Driscoll 1993). Hydrological consequences of the damming and flooding of stream valleys include elevated water tables, lower stream velocity and increased hydraulic residence times (Parker et al. 1985; Apple 1985; Szaro & DeBano 1985; Parker 1986; Dahm et al. 1987; Woo & Waddington 1990). The accumulation of allocthonous particulate organic matter in beaver ponds also results in increased organic content of sediments. Carbon accretion, along with increased hydraulic residence time, enhances O_2 consumption by microbial decomposition processes. Recent studies also indicate that flooding of stream valleys and wetlands by beaver leads indirectly to higher CH_4 fluxs due to anoxic conditions favoring methanogenic bacteria (Ford & Naiman 1988; Nisbet 1989; Naiman et al. 1991; Yavitt et al. 1990,1992; Roulet & Ash 1992).

As available O_2 is depleted due to aerobic mineralization processes, alternate electron acceptors are used by facultative and obligate anaerobic microbial communities. These alternate electron acceptors include NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-}. Many of these biotically-mediated decomposition processes, along with mineral weathering and cation exchange, involve the uptake of H^+ and the generation or consumption of ANC (Table 1). Acid neutralizing capacity is a useful measure of the sensitivity of surface waters to inputs of acidic atmospheric deposition and watershed drainage. The definition of ANC used here is based on the charge balance approach described in the introductory paper to this series (Driscoll et al. 1996).

Acid neutralizing capacity generation and acid deposition impacts in wetlands

The generation of ANC in anoxic lake and wetland sediments is well documented. The neutralization of atmospheric and drainage inputs of SO_4^{2-} via microbial reduction is an example (Schindler et al. 1980; Kelly et al. 1982; Schindler 1986; Cook et al. 1986; Cirmo & Driscoll 1993). Sulfate reduction has been demonstrated in peatlands receiving high inputs of SO_4^{2-} (Wieder et al. 1987, 1990) as well as in a beaver pond wetland in the Adirondacks (Driscoll et al. 1987; Cirmo & Driscoll 1993). Denitrification and Fe^{3+} reduction have been observed in aquatic systems (Lovley & Phillips 1986; Driscoll et al. 1987), and seasonal variations in NO_3^- retention, NH_4^+ release, and denitrification have been observed to coincide with variations in temperature

Table 1. Acid neutralizing capacity (ANC) generating and consuming reactions. CH_2O is a simplified empirical formula for organic matter.

Process	Equivalents of ANC generated per mole of reactant
Sulfate Reduction:	
$SO_4^{2-} + 2CH_2O + 2H^+ = 2CO_2 + H_2S + H_2O$	+2
Denitrification:	
$NO_3^- + 1.25CH_2O + H^+ = 1.25CO_2 + 0.5N_2 + 1.75H_2O$	+1
Sulfide Oxidation:	
$H_2S + 2O_2 = SO_4^{2-} + 2H^+$	−2
Nitrification:	
$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$	−2
Ammonification:	
$CH_2ONH_3 + O_2 + H^+ = NH_4^+ + CO_2 + H_2O$	+1
Iron Reduction:	
$FeOOH(s) + 0.25CH_2O + 2H^+ = Fe^{2+} + 0.25CO_2 + 1.75H_2O$	+2
Iron Oxidation:	
$Fe^{2+} + 0.25O_2 + 2.5H_2O = Fe(OH)_3(s) + 2H^+$	−2
Cation Exchange:	
$Ca^{2+} + H_2X = CaX + 2H^+$	−2
Anion Exchange:	
$SO_4^{2-} + X(OH)_2 = XSO_4 + 2OH^-$	+2
Aluminum Weathering (e.g.):	
$Al_2O_3{\cdot}3H_2O + 6H^+ = 2Al^{3+} + 6H_2O$	+6

and hydrologic regime in beaver ponds (Naiman & Melillo 1984; Francis et al. 1985; Maret et al. 1987; DeVito et al. 1989; Cirmo & Driscoll 1993).

Relatively few studies of the effects of acidic deposition on wetlands and peatlands have been conducted (Gorham et al. 1984, 1985; Bayley et al. 1987; Wood 1989). The acidity in wetlands is generally attributed to organic acid production, the oxidation of organic or inorganic reduced S, CO_2 production from decomposition, cation exchange processes, or acidic atmospheric inputs of S and N (Gorham et al. 1985; Kerekes et al. 1986; Wood 1989; Hemond 1990). The production of dissolved organic carbon (DOC) from incomplete decomposition processes in wetlands has also been widely reported. Organic solutes contribute to the acidity of drainage waters due to the dissociation of both strong and weak organic acid functional groups (Driscoll et al. 1989b; Hemond 1990, Perdue 1990). Dissolved organic carbon also has an important role in the complexation and transport of trace metals such as Al, Fe, and Hg (Reuter & Perdue 1977; Driscoll et al. 1994). Wetlands and beaver ponds, as sources of DOC and as sinks for strong acid anions (i.e., SO_4^{2-} and NO_3^-) and metals (e.g., Al), warrant study as systems which can contribute to either acidity or ANC.

Cation exchange on mosses, peat, and sediments

The polygalacturonic acid complex found in the cell walls of *Sphagnum* species is known to exchange cations (particularly divalent cations like Ca^{2+} and Mg^{2+}) for H^+ (Clymo 1963; Spearing 1972; Bunzl et al. 1976). *Sphagnum* species are thought to play an active role in the maintenance of acidity in wetland systems (Craigie & Maass 1966; Moore & Bellamy 1974; Andrus 1986). The acidity contributed by *Sphagnum* as well as the measureable 'field' cation exchange capacity of living *Sphagnum* and *Sphagnum* peat, have been the subject of some controversy (Kilham 1982; Andrus 1986). Under similar field and laboratory conditions , base-rich peat seems to release basic cations upon acidification while base-poor peat tends to remove cations from solution (Wood 1989). After $CaCO_3$ treatment the exchange complex on these mosses might act as a Ca^{2+} sink depending on the biological integrity of acidophilic moss species. This biological integrity may be tenuous after a liming since evidence of aquatic macrophyte and moss mortality has been reported subsequent to a lake $CaCO_3$ treatment (Clymo 1973; Bukaveckas 1988). Loss of the exchange complex on these mosses could affect the ecological functioning of wetlands in $CaCO_3$-treated catchments (Curran et al. 1991).

Research questions

We studied the biogeochemistry of two tributary streams of Woods Lake, New York to observe the response of stream water and wetland biogeochemistry to a watershed $CaCO_3$ treatment. This study included an evaluation of the chemical characteristics of both a wetland-impacted and a free-flowing stream, as well as comparisons of the inlet, outlet and water-column biogeochemistry of a beaver pond within a $CaCO_3$-treated catchment. Our goal was to address the following research questions: a) What is the biogeochemical response of headwater streams to a watershed $CaCO_3$- treatment, and what factors control the extent of this response, b) how does a watershed $CaCO_3$ treatment affect the biogeochemistry and generation or consumption of ANC within a beaver pond and associated drainage waters, and c) is the $CaCO_3$ treatment of a wetland or hydrologic source area within a drainage system an effective approach to increasing the supply of base and ANC to downstream waters?

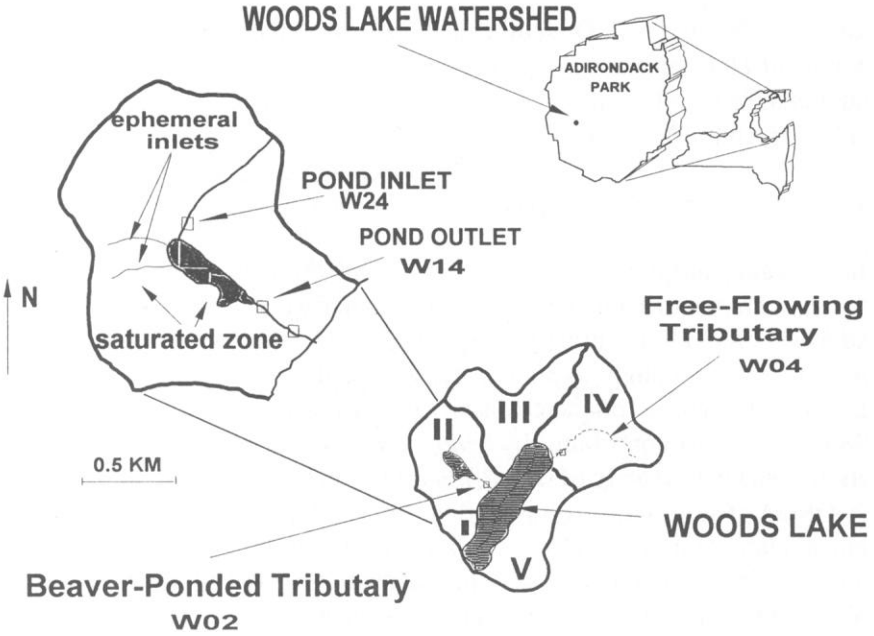

Fig. 1. The Woods Lake watershed and subcatchments including locations of stream sampling sites and the beaver pond within subcatchment II.

Methods

Study site description, hydrology, and $CaCO_3$ application

Woods Lake has two major tributary streams draining subcatchments II and IV of the watershed (Fig. 1). Hydrologic discharge was monitored with United States Geological Survey (U.S.G.S) gauging stations on both streams just upstream of their entrance to Woods Lake. The operation of these gauging stations and a description of the associated stream sampling is described in the introductory paper to this series (Driscoll et al. 1996).

A beaver pond wetland is located at the headwaters of the tributary stream in subcatchment II (Fig. 1). The beaver pond has a volume of 7500 m^3, a surface area of approximately 1.26 ha, and a mean depth (based on winter bathymetry) of 0.59 meters (Fig. 2). The main surface inlet to the pond is a small, nearly perennial first-order stream (sampling site W24). There are also several ephemeral inlets as well as lateral subsurface flow occurring on the west side of the pond in an extensive saturated wetland zone. Total pond surface and surrounding saturated wetland area is estimated as 2.4 ha. Floating logs and standing dead timber dominate the beaver pond area. Edge and

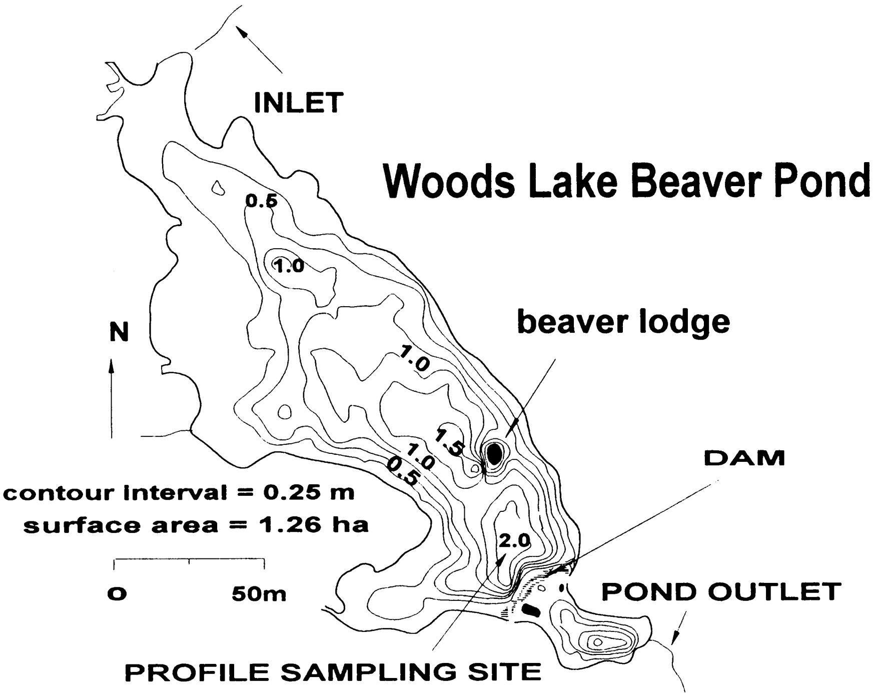

Fig. 2. Bathymetric map of the Woods Lake beaver pond including sampling sites.

shallow zone sediments are predominantly *Sphagnum* covered, and include the species *S. papillosum* Lindb., *S. girgensohnii* Russow, and *S. magellanicum* Brid. Extensive areas of *Polytrichum commune* are also evident. A large coverage of *Utricularia purpurea* Walter is common in the water column during the summer months. Deeper portions of the pond contain highly organic sediments. The pond and surrounding wetland are underlain by glacial till and outwash deposits, topped by peat of from 0.25 to 1.5 meters in depth.

Water draining the wetland was sampled below the beaver dam (site W14). Pond outlet discharge at this site was estimated as 96% of the discharge measured and recorded at the gauging station downstream at site W02. This percentage was based on an areal pro-rating of the discharge within the subcatchment containing the wetland (LaZerte 1993). Estimates of hydrologic inputs to the wetland and pond were made by areal pro-rating of the discharge of the free-flowing stream in subcatchment IV (at gauging site W04) to the upland area draining into the beaver pond (26.6 ha) and its surrounding wetlands. The free-flowing stream in subcatchment IV drains similar topography and is not intersected by a wetland. Sampling of the water chemistry of both main tributaries to Woods Lake, as well as the beaver pond inlet, outlet and water-column (at site W23), was conducted at three-week intervals from June 1989 to September 1991.

Flux and mass balance calculations were performed based on observed solute concentrations from the beaver pond inlet and outlet streams, in combination with the aforementioned discharge measurements and hydrologic input estimates. Solute concentrations at each three-week sampling period were assumed to be representative of the daily concentrations existing for half the period between previous and subsequent sampling dates. Precipitation totals and chemical wet deposition fluxes were calculated based on data from a nearby precipitation monitoring site (Nick's Lake) operated by the New York State Department of Environmental Conservation (New York State Atmospheric Deposition Monitoring Network 1991). Piezometer and well recovery data indicated that subsurface flow into the wetlands around the beaver pond was lateral and extremely slow, as influenced by the low hydraulic conductivity ($< 10^{-7}$ cm $\sec^{-1}$) of the glacial till underlying the pond. Due to this fact, and since the pond represented a topographic low except for the area around its outlet, subsurface outseepage from the pond was assumed to be negligible. For budget calculations and statistical comparisons, 'summer' was defined as July 1 through September 30, and 'non-summer' as October 1 through June 30.

The mean $CaCO_3$ application rate to the two subcatchments was estimated as 6.89 Mg $CaCO_3$ ha^{-1} (Driscoll et al. 1996). Calcium carbonate was applied to the pond and wetland as part of the treatment of subcatchment II. Floating basket collections on the pond during the $CaCO_3$ application (n=7) revealed that 8.71 ± 1.63 Mg (6.91 ± 1.29 Mg ha^{-1}) of pelletized limestone was applied directly to the ponded waters. Based on 82% $CaCO_3$ content of the limestone (Driscoll et al. 1996), a total application of 7.14 ± 1.34 Mg $CaCO_3$ (5.67 ± 1.06 Mg $CaCO_3$ ha^{-1}) or 143 ± 21.1 Keq Ca^{2+} (114 ± 16.7 keq Ca^{2+} ha^{-1}) was determined for the pond and its associated wetland.

Chemistry and data analysis

Standard chemical methods and quality assurance/quality control (QA/QC) procedures were followed in all analyses, as described in Driscoll et al. (1995). Ferrous iron was determined in the field at the time of sampling using a modified o-phenanthroline method (APHA 1985) with immediate fixation and spectrophotometric readings done using a portable spectrophotometer. Bottles for Fe^{2+} analysis were wrapped in aluminum foil and chilled to 4 °C if analysis could not be immediately conducted. Dissolved oxygen was fixed in the field and titrated within 12 hours using a modified Winkler method (APHA 1985). Temperature and pH were measured in situ or within four hours of collection (for pH) at the laboratory facility in Thendara, New York.

Sediment cores were collected along with living *Sphagnum* from the Woods Lake beaver pond and wetland, as well as from an untreated reference beaver ponded wetland at nearby Pancake-Hall Creek (Cirmo & Driscoll 1993) for determination of exchangeable Ca^{2+}. Standard sediment/soil extraction techniques were followed (Cappo et al. 1987) using NH_4Cl and KCl extractants. A Ca^{2+} exchange study was also conducted using pond water and living *Sphagnum* from both the $CaCO_3$ -treated (Woods Lake) and untreated (Pancake-Hall Creek) beaver ponds.

Inorganic monomeric Al (Al_{im}) was calculated as the difference between measured values of total monomeric Al (Al_{tm}) and organic monomeric Al (Al_{om}) (Driscoll 1984). The chemical thermodynamic equilibrium model ALCHEMI (version 4.0, Schecher & Driscoll 1994) was used to calculate the equivalency of inorganic monomeric Al, or Al^{n+}. The ALCHEMI model allows the thermodynamic calculation of Al speciation and complexation with inorganic and organic ligands, as well as dissolved inorganic carbon (DIC) speciation and solid mineral phase saturation index. Saturation index is defined as:

$$SI = \log (Q_p/K_p),$$

where Q_p is the ion activity product and K_p is the thermodynamic solubility product of the mineral phase of interest. Negative SI values indicate conditions of undersaturation with respect to a given solid phase, whereas positive values suggest oversaturation. Water-column chemistry was evaluated with regard to the solubility of aluminum mineral phase hydroxides ($Al(OH)_3(s)$) including synthetic gibbsite ($\log {}^*K_{so} = 8.11$) and amorphous Al hydroxide ($\log {}^*K_{so} = 10.80$), as well as for $CaCO_3$ ($\log K_{so} = 8.34$). The equivalence of organic acids ($RCOO^-$) used in ANC budget calculations was estimated using a triprotic organic acid analog model (Driscoll et al. 1994). The chemical thermodynamic equilibrium model MINEQL+ (version 2.2, Schecher & McAvoy 1991) was used to estimate saturation with respect to manganite (MnOOH, $\log {}^*K_{so} = 25.27$) and siderite ($FeCO_3$, $\log K_{so} = 10.55$) solubility. Saturation indexes were calculated relative to atmospheric CO_2 ($P_{CO_2} = 10^{-3.5}$) for stream chemistry, and as closed to atmospheric CO_2 for post-treatment beaver-pond chemistry.

Statistical analyses were conducted using PC-SAS version 6.03 (SAS Institute Inc. 1985). Values and statistical comparisons of mean annual and seasonal water quality parameters for the two streams from 1984–1989 (pre-treatment) are presented elsewhere (Cirmo & Driscoll, unpublished) and are used for comparisons in this study. A non-parametric Wilcoxon rank sum test was used for a comparison of before- and after-treatment streamwater chemistry. It was not possible to determine statistically significant differences between pre- and post-treatment chemistry for the beaver pond inlet, outlet and pond waters due to the inadequate number of pre-treatment observations (summer of 1989 only), and the lack of replication of the treatment site. Observations from an untreated beaver pond (Pancake-Hall Creek) were used in qualitative comparisons (Cirmo & Driscoll 1993). Linear regressions were calculated between various chemical parameters in the evaluation of controls on the production of ANC. These regressions were statistically evaluated using F statistics. True replication of treatment sites was not possible, and the use of inferential statistics for comparisons should be interpreted in this light (Hurlburt 1984; Eberhardt & Thomas 1991).

Results and discussion

Stream biogeochemistry after $CaCO_3$ treatment

The catchment $CaCO_3$ application in October of 1989 had significant impacts upon the chemistry of both tributary streams to Woods Lake. Over 90% of the increase in ANC in both streams was associated with increases in Ca^{2+} for up to 18 months after the manipulation, and both streams approached $CaCO_3$ saturation immediately after treatment (Fig. 3). Although both streams showed immediate and significant increases in pH and ANC, as well as in Ca^{2+}, Mg^{2+}, and DIC concentrations, there were subtle differences in the magnitudes of these changes (Figs 3 and 4, Tables 2 and 3). The beaver-ponded stream remained near saturation with respect to $CaCO_3$ throughout the post-treatment period, and also exhibited higher export of Ca^{2+} for a longer period. In comparison to pre-treatment values, concentrations of DOC increased in both streams immediately after treatment (Table 3). Dissolved organic carbon concentration was normally higher in the beaver-ponded stream as compared to the free flowing stream before the treatment, and continued to be higher during the post-treatment period. As expected from the increase in pH, calculated concentrations of organic anion ($RCOO^-$) also increased due to the subsequent deprotonation of acidic functional groups associated with DOC.

Concentrations of Al_{tm} and Al_{im} declined markedly in both streams immediately after the treatment, but returned to near pre-treatment concentrations rapidly (one summer season) only in the free-flowing stream (Fig. 5). Following the $CaCO_3$ application, both streams were oversaturated with respect to the solubility of synthetic gibbsite and approached saturation with respect to

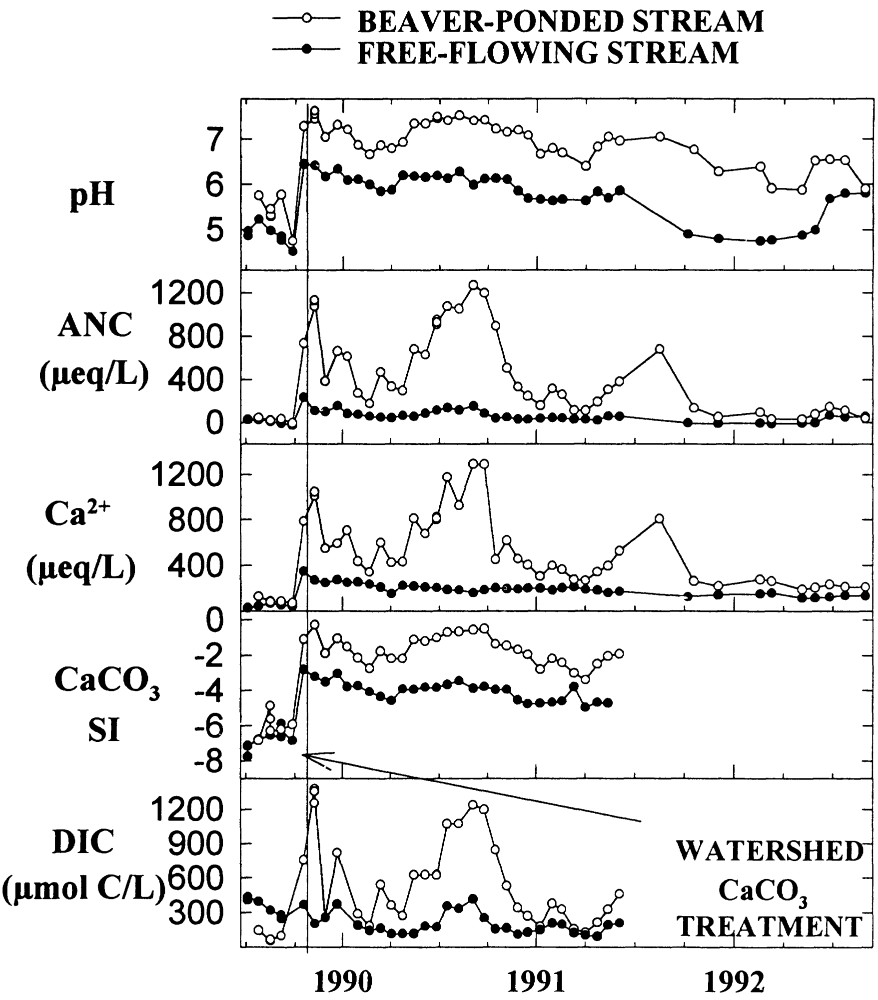

Fig. 3. pH, ANC and Ca^{2+} concentrations (in μequiv L^{-1}), $CaCO_3$ saturation index (SI), and dissolved inorganic carbon concentration (DIC, in μmol C L^{-1}) of the two tributary streams to Woods Lake from 1989–1992.

amorphous Al hydroxide (SI = −1.0 to +0.5, Fig. 5). This phenomenon was also observed after a water column $CaCO_3$ treatment of Woods Lake (Driscoll et al. 1989a). Rapid hydrolysis and precipitation of aluminum hydroxides in the pond could establish a less crystalline solid phase control of Al concentrations in the pond outlet stream. This phenomenon was more immediately evident and of longer duration in the beaver-ponded stream as compared to the free-flowing stream, and reflects a potentially important function for upstream wetlands as potential sinks for Al mobilized in acidified upland soils (Cirmo & Driscoll 1993; Bailey et. al. 1995).

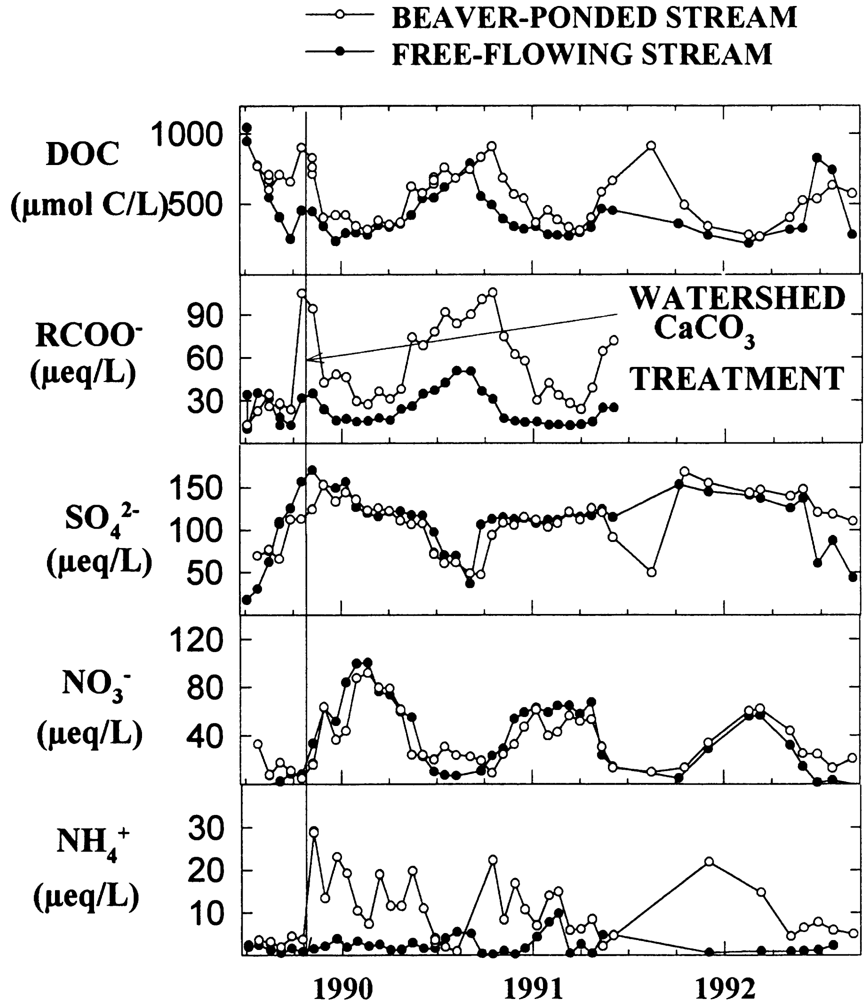

Fig. 4. Dissolved organic carbon (DOC, in μmol C L^{-1}), organic acid anion ($RCOO^-$), SO_4^{2-}, NO_3^-, and NH_4^+ concentrations (all in μequiv L^{-1}) of the two tributary streams to Woods Lake from 1988–1992.

Pre-treatment differences in H_4SiO_4 concentration between the two streams became insignificant after the manipulation (Fig. 5, Tables 2 and 3). Moreover, retention of H_4SiO_4 in the pond was observed during the pre-treatment period, a phenomenon which has also been observed in another Adirondack wetland (Cirmo & Driscoll 1993). In contrast, H_4SiO_4 inputs to the pond were nearly matched by outlet concentrations after the treatment. It is possible that a source of H_4SiO_4 within the pond may have been mobilized, since elevated pH, coupled with high DOC, has been shown to

Table 2. Comparison of mean solute concentrations for the beaver-ponded (P) and free-flowing (F) streams at Woods Lake after $CaCO_3$ treatment, using a Wilcoxon rank sum test. All comparisons made at the $p \leq 0.05$ level, ns = not significant.

Analyte	Annual	Summer	Non-summer
pH	P>F	P>F	P>F
ANC	P>F	P>F	P>F
DOC	P>F	ns	P>F
DIC	P>F	P>F	P>F
SO_4^{2-}	ns	ns	ns
Cl^-	ns	ns	ns
F^-	P>F	P>F	P>F
NO_3^-	ns	P>F	ns
NH_4	P>F	ns	P>F
Na^+	ns	F>P	ns
K^+	P>F	P>F	P>F
Ca^{2+}	P>F	P>F	P>F
Mg^{2+}	P>F	P>F	P>F
Al_{im}	F>P	F>P	F>P
Al_{om}	F>P	F>P	P>F
Fe_{tot}	P>F	ns	ns
Mn_{tot}	P>F	ns	P>F
H_4SiO_4	ns	F>P	ns

accelerate the dissolution of amorphous silica sources, such as opaline silica in diatom frustules or poorly formed mineral silicates in the underlying peat and sediments (Bennett et al. 1991; Hiebert & Bennett 1992). The lack of significant silicate content in the applied pelletized limestone precluded any additional input from the treatment itself. Dissolved silica concentrations in both streams increased significantly from pre-treatment conditions during all seasons.

Nitrate concentrations increased from pre-treatment values in the free-flowing stream in all seasons (Table 3). Soil response to a simulated $CaCO_3$ treatment at this same site (Yavitt & Newton 1990/91; Simmons et al. 1996) revealed an increase in nitrification in O-layer soil horizons in contrast to untreated soils. The lack of a corresponding NO_3^- increase downstream of the beaver pond (except during the summer) could be due to the retention of upland NO_3^- inputs to the beaver pond, a phenomenon observed elsewhere (Cirmo & Driscoll 1993). Mean annual ammonium concentrations downstream of the beaver pond nearly doubled on an annual basis after treatment,

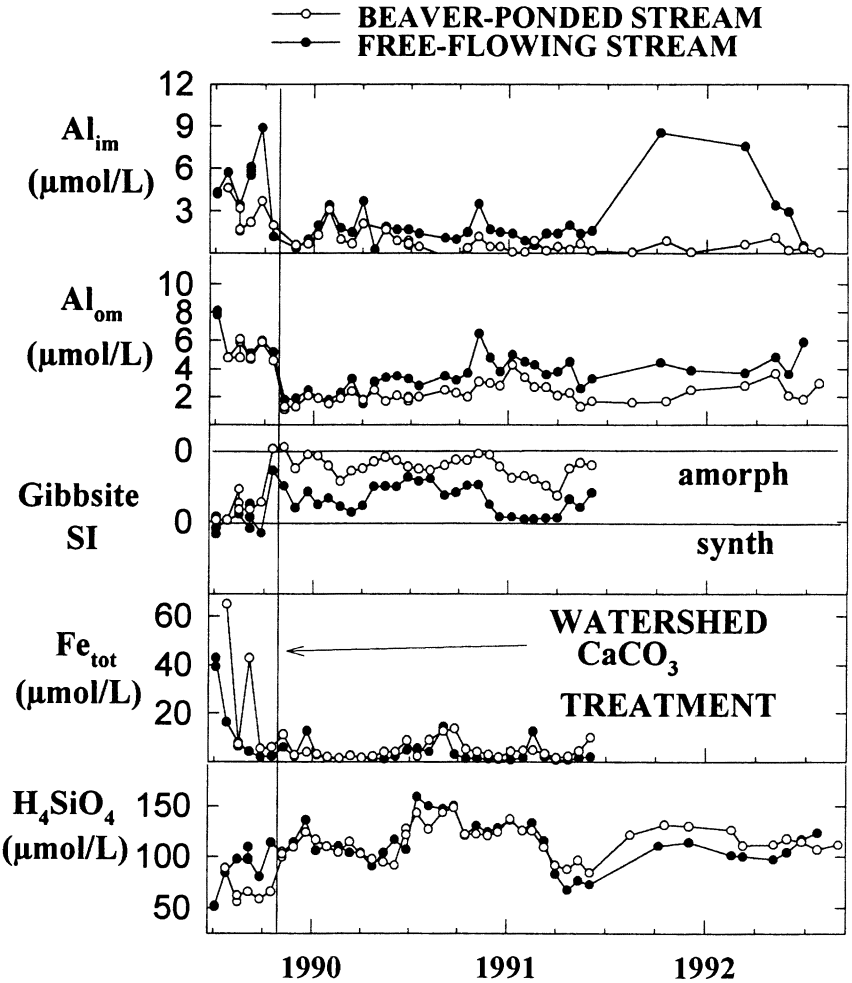

Fig. 5. Inorganic monomeric aluminum (Al_{im}), organic monomeric aluminum (Al_{om}) concentrations, gibbsite saturation index (SI), total iron (Fe_{tot}) and dissolved silica (H_4SiO_4) concentrations (in μmol L^{-1}) of the two tributary streams to Woods Lake from 1988–1992.

but remained unchanged during the summer season. The lack of a significant summer increase in NH_4^+ concentrations downstream of the beaver pond may reflect an increase in the rate of nitrification of wetland produced NH_4^+ in the warmer, higher pH streamwater below the pond. In the free-flowing stream, NH_4^+ concentrations remained low with only a slight increase during the summer. Notably, an increase in streamwater NO_3^- was observed during the snowmelt period of 1990 throughout the region (Driscoll and Van Dreason 1993). It is possible that the observed NO_3^- increases noted in the two streams reflected this trend. The lack of a significant increase in annual NO_3^- con-

Table 3. Comparison of seasonal and annual mean solute concentrations in the beaver-ponded and free-flowing streams before and after watershed $CaCO_3$ treatment. '+' indicates an increase in mean value, '–' a decrease. ns = not significant, * = $p < 0.05$, ** $p < 0.01$.

Analyte	Beaver-ponded stream			Free-flowing stream		
	Annual	Summer	Non-Summer	Annual	Summer	Non-Summer
pH	** +	** +	** +	** +	** +	** +
ANC	** +	** +	** +	** +	** +	** +
DOC	ns	ns	** +	ns	ns	* +
DIC	** +	** +	** +	* +	ns	** +
SO_4^{2-}	** –	** –	** –	ns	ns	ns
Cl^-	ns	** –	ns	ns	* –	ns
F^-	** –	ns	** –	** –	ns	** –
NO_3^-	ns	** +	ns	** +	* +	** +
NH_4^+	** +	ns	** +	ns	ns	ns
Na^+	ns	ns	ns	ns	** +	ns
K^+	** +	ns	** +	** +	** +	** +
Ca^{2+}	** +	** +	** +	** +	** +	** +
Mg^{2+}	** +	** +	** +	** +	** +	** +
Al_{im}	** –	** –	** –	** –	** –	** –
Al_{om}	** –	** –	** –	ns	ns	ns
Fe_{tot}	ns	ns	* +	ns	ns	ns
Mn_{tot}	** –	** –	** –	** –	** –	** –
H_4SiO_4	** +	** +	** +	** +	** +	** +

centration in the wetland-impacted stream in comparison to the free-flowing stream (Table 3) would suggest that the beaver-pond wetland may have been a sink for any additional NO_3^- originating in the upland catchment.

Mean SO_4^{2-} concentrations were significantly lower in the beaver-ponded stream after $CaCO_3$ application, but remained unchanged in the free-flowing stream (Fig. 5, Tables 2 and 3). This decline could reflect enhanced SO_4^{2-} reduction in the pond, although Yavitt & Fahey (1996) did not observe an increase in SO_4^{2-} reduction rate in peat sampled from this pond after the $CaCO_3$ treatment. An increase in SO_4^{2-} reduction might be expected since the treatment resulted in elevated pH, a condition more favorable for microbial activity in general. One may hypothesize that SO_4^{2-} concentrations remained the same in the free-flowing tributary since elevated pH has relatively little effect on this conservative solute in upland forest soils of the Northesastern United States. Total Mn (Mn_{tot}) declined at all sites and seasons after the

Table 4. Linear regression analysis between ANC and major ionic solutes in beaver-ponded and free-flowing streams after watershed $CaCO_3$ treatment. r^2 values, $* = p < 0.05$, $** = p < 0.01$.

	Beaver-ponded	Free-flowing
DOC	** 0.68	** 0.23
DIC	** 0.89	ns
SO_4^{2-}	** 0.28	ns
Cl^-	ns	ns
F^-	ns	ns
NO_3^-	** 0.32	* 0.22
NH_4^+	ns	ns
Al^{n+}	** 0.32	** 0.25
Na^+	ns	** 0.55
K^+	** 0.69	ns
Mg^{2+}	** 0.75	ns
Ca^{2+}	** 0.90	** 0.33

manipulation, due likely to precipitation and solid phase control by manganite (MnOOH, SI = −0.07) at elevated pH (Driscoll et al. 1989a). Manganite has been shown to control the solubility of Mn in acidic Adirondack waters (White & Driscoll 1987). The bacterial oxidation of soluble Mn^{2+} released by decomposition from anoxic sites, and the subsequent precipitation of relatively insoluble Mn^{4+}hydroxides, occur more rapidly at elevated pH (Chapnick et al. 1982).

The watershed $CaCO_3$ treatment had a marked effect on the distribution of ionic solutes, particularly during low-flow conditions in the beaver-ponded stream. Linear regressions of major ionic solutes contributing to ANC (Table 4) reveal the chemical controls on ANC production and consumption after manipulation. Post-treatment controls on changes in ANC were largely associated with Ca^{2+}, Mg^{2+} and DIC due to $CaCO_3$ dissolution. There were also significant contributions from DOC, SO_4^{2-}, NO_3^-, and Al presumably due to the influence of wetland processes in the beaver-ponded stream (Driscoll et al. 1987; Cirmo & Driscoll 1993). The free-flowing stream had similar controls on changes in ANC. A major contribution from Na^+ is likely due to the predominant influence of catchment soils and bedrock on this stream (Newton et al. 1987), in contrast to the wetland and beaver pond controls from sediment and microbial processes associated with an aquatic system.

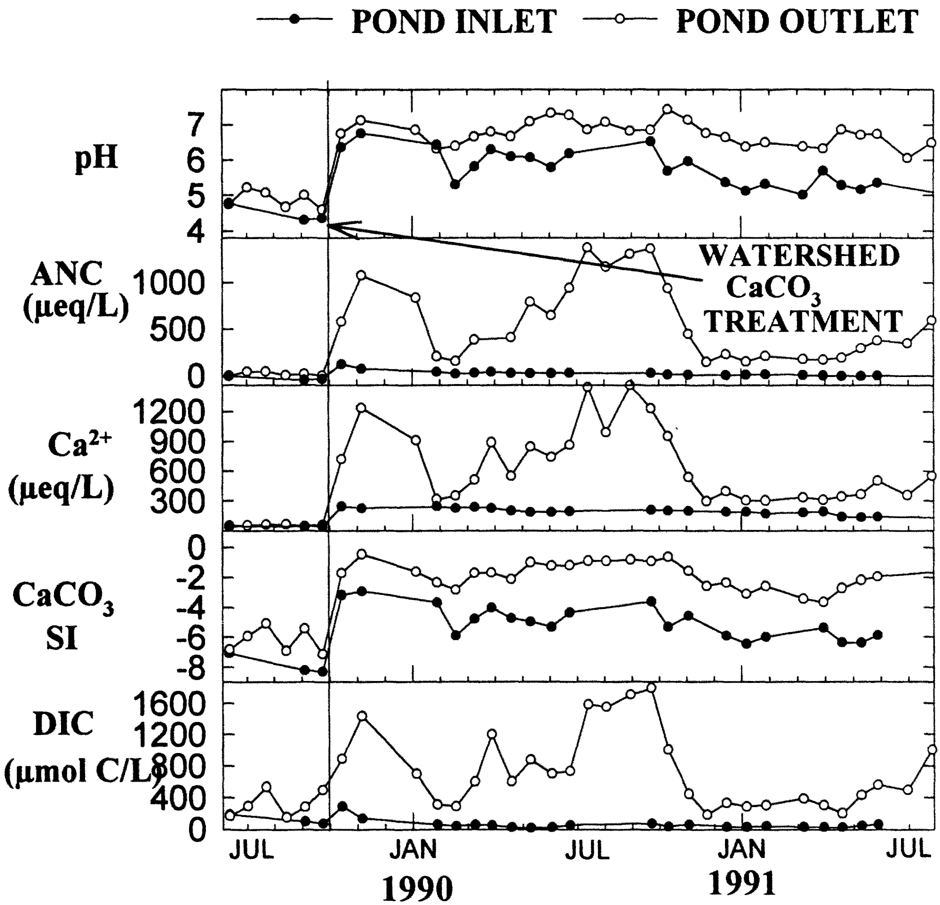

Fig. 6. pH, ANC and Ca^{2+} concentrations (μequiv L^{-1}), $CaCO_3$ saturation index (SI), and dissolved inorganic carbon (DIC) concentration (μmol L^{-1}) in the beaver pond inlet and outlet streams for the pre- and post-treatment period.

Beaver pond biogeochemistry

Beaver Pond Inlet/Outlet Comparison – Beaver pond inlet/outlet data prior to treatment was available for the summer of 1989 only (June through September). Nevertheless, distinct differences in inlet and outlet pond chemistry were evident, and similar to those found during a more extensive study in a nearby beaver pond (Cirmo & Driscoll 1993). During the summer before treatment, ANC and pH rarely exceeded 0.0 μeq/L and 5.00, respectively, in the pond inlet stream, while these parameters were both elevated in the pond outlet stream (Fig. 6). After $CaCO_3$ treatment, increases in pH, ANC and Ca^{2+} concentrations occurred in both the pond inlet and outlet. In contrast to the pond outlet, pond inlet chemistry returned to near pre-treatment values of pH, ANC and Ca^{2+} concentrations within 18 months. This may have been in response to reacidification of soil water draining the upland catchment (Geary & Driscoll 1996). The immediate post-treatment increase in pH for both inlet and outlet water was likely due to rapid dissolution of $CaCO_3$ deposited in the upland stream bed and within the beaver pond and wetland itself. The increase in Ca^{2+}, ANC and DIC concentrations in the pond outlet during low-flow periods in mid-winter and summer was indicative of the dissolution of $CaCO_3$ within the pond (Fig. 6). Most of the release of ANC and DIC was associated with release of Ca^{2+} from the anoxic near-sediment zone (discussed later). Dissolved inorganic carbon concentration and $CaCO_3$ SI values increased between the pond inlet and outlet. Carbon dioxide saturation declined (90% to 50%) in the outlet stream when ice-out occurred in April 1990, and again during water-column mixing in the Fall of 1990. This pattern reflects the reaeration of CO_2-charged water during discharge over the dam and downstream. An accumulation of DIC from microbial respiration and/or $CaCO_3$dissolution was evident under the ice, and in warm, stagnant waters during summer low-flow periods. Calcium carbonate dissolution within the ponded waters was again suggested by the continued high $CaCO_3$ SI noted in the pond outlet (Fig. 6).

An increase in DOC in pond waters occurred during the summer after treatment (Fig. 7) reflecting similar conditions in the nearby reference beaver pond at Pancake-Hall Creek (Cirmo & Driscoll 1993). The beaver pond continued to be important source of DOC to the receiving stream and downstream lake (Driscoll et al. 1996). Sulfate concentrations were substantially lower in the outlet stream compared to the inlet during the summer before treatment due to extensive SO_4^{2-} reduction within the pond. A further decline in outlet SO_4^{2-} concentration during the summer after treatment suggests enhanced microbial reduction at higher pH values, or a decline in O_2 availability due to higher decomposition rates in pond sediments. Tentative findings during the summers after liming indicate that the pond sediments and peat have experienced an increase in O_2 consumption rate subsequent to the manipulation (Cirmo, unpublished). The rapid development of anoxic conditions and low redox potential, along with circumneutral pH, might support higher rates of SO_4^{2-} reduction. Inlet SO_4^{2-} concentrations did not change in response to the treatment, once again reflecting the conservative nature of SO_4^{2-} transport through the upland terrestrial soils.

Nitrate concentrations in the beaver-pond inlet and outlet generally reflected seasonal biological activity within the watershed (Fig. 7). Concentrations were low in both pond inlet and outlet waters during the growing season (May–September), while concentrations were below detection limits

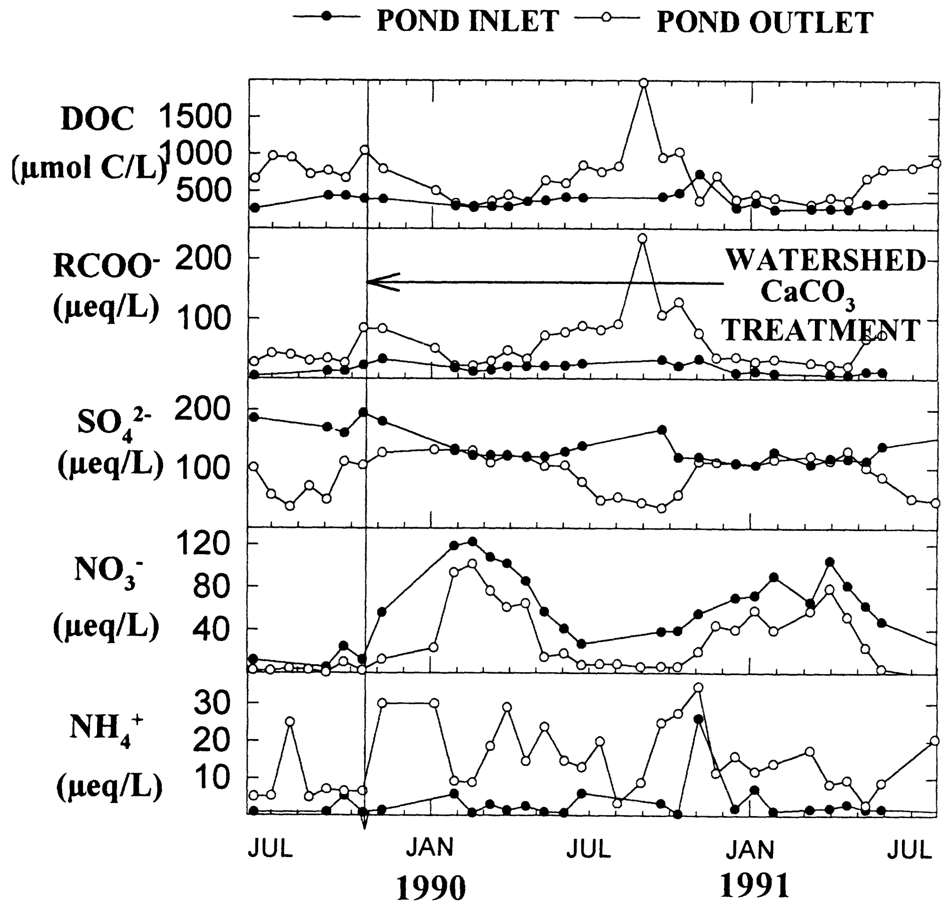

Fig. 7. Dissolved organic carbon (DOC, in μmol C L^{-1}), organic anion ($RCOO^-$), SO_4^{2-}, NO_3^-, and NH_4^+ (all in μequiv L^{-1}) of the beaver pond inlet and outlet streams for the pre- and post-treatment period.

in the pond outlet at mid-summer low flow, both before and after the $CaCO_3$ application. Ammonium was released in an irregular fashion for most of the year (Fig. 7) and beaver-pond outlet NH_4^+ concentrations exceeded inlet concentrations throughout the summer. Ferrous iron concentrations were consistently higher in the pond outlet in comparison to the inlet, with highest concentrations occurring during low-flow conditions in late summer (Fig. 8). Similar patterns in Fe^{2+} concentrations were observed during summer low-flow periods in the outlet of the reference pond at Pancake-Hall Creek (Cirmo & Driscoll 1993). Ferrous iron concentrations in this $CaCO_3$-treated system could be controlled by siderite ($FeCO_3$) solubility, although these waters remained undersaturated with respect to $FeCO_3$ during the observation period

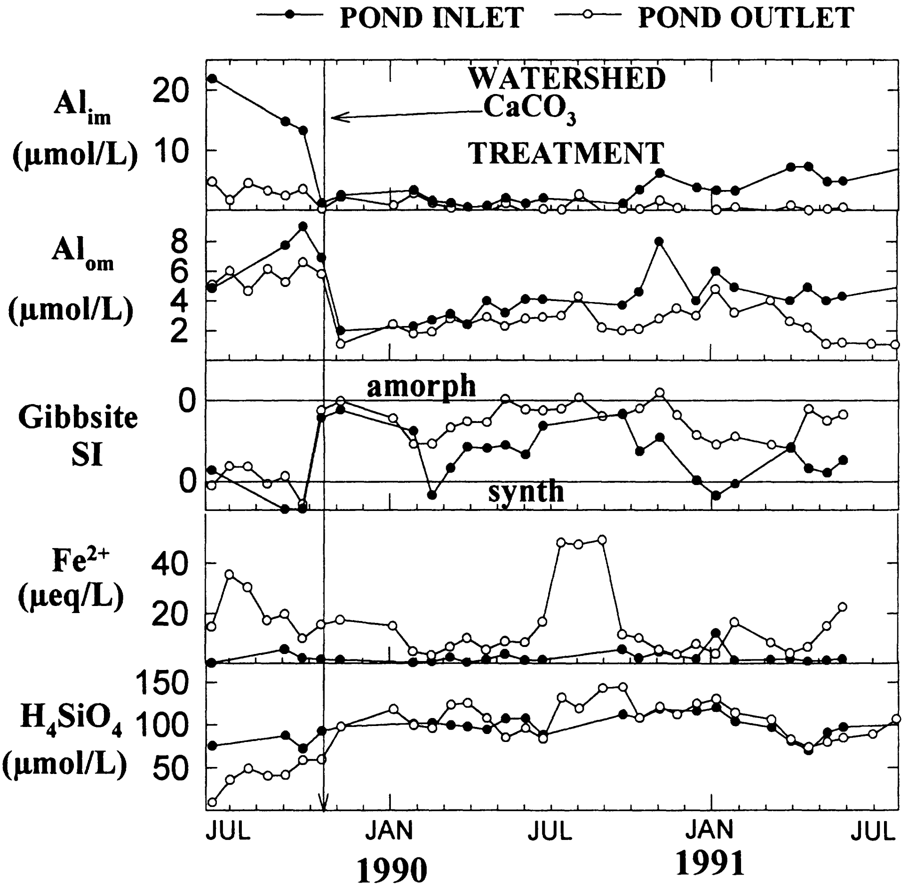

Fig. 8. Inorganic monomeric aluminum (Al_{im}), organic monomeric aluminum (Al_{om}) concentrations, gibbsite saturation index (SI), total iron (Fe_{tot}) and dissolved silica (H_4SiO_4) concentrations (in μmol L^{-1}) of the beaver pond inlet and outlet streams for the pre- and post-treatment period.

(SI = -1.0 to -2.0). The oxidation rate of Fe^{2+} (to relatively insoluble Fe^{3+} oxyhydroxides) is greater in circumneutral waters (Stumm & Morgan 1981). A rapid reoxidation of Fe^{2+} released from anoxic zones in the pond could lead to lower 'observed' in-pond concentrations, regardless of the rate of generation of Fe^{2+} within the pond sediments and waters.

Concentrations of Al_{im} were lower in the pond outlet compared to inlet waters during the summer before treatment (Fig. 8). This phenomenon has also been observed in the reference beaver pond (Cirmo & Driscoll 1993) and in a headwater pond in New Hampshire (Bailey et al. 1995). Pond water was near saturation with respect to the solubility of synthetic gibbsite during this period, while after treatment (up to 18 months) the beaver-pond outlet was closer to saturation with amorphous Al hydroxide. Pond inlet SI values also approached the solubility of amorphous Al hydroxide, but were closer to synthetic gibbsite solubility control during the subsequent winter and spring snowmelt. Pond inlet concentrations of all forms of Al began to increase again within one year of $CaCO_3$ treatment, while Al concentrations in the outlet stream remained extremely low. In-pond retention of Al became an increasingly important phenomenon as the upland drainage water reacidified, with subsequent mobilization and transport of Al to the circumneutral pond and wetland water.

Retention of H_4SiO_4 in the beaver pond (evident during the growing season prior to treatment) was not evident in the two subsequent seasons (Fig. 8). An increase in H_4SiO_4 concentration was also noted at both tributary stream sampling sites after treatment (see previous section). Concentrations of H_4SiO_4 in the beaver-pond outlet were greater throughout the post-treatment period, again suggesting the mobilization of a source of H_4SiO_4 in the pond (dissolution of silicates or diatom frustules at the higher pH and DOC concentrations). Laboratory analysis of the applied limestone revealed that silicates in the limestone matrix were not soluble in the conditions present in the pond (Driscoll et al. 1996).

Beaver Pond Water-Column Chemistry – Pond surface temperatures of up to 24.1 °C were attained during the summer, and the pond developed a weak clinograde thermal stratification during this period, with effective isolation of near-sediment waters from surface waters, except during large storms and hydrologic events. A reverse thermal stratification developed under thick ice cover (up to 0.5m) in winter and resulted in isolation of deeper pond water during mid-winter. Near anoxic conditions (<20 μmol/L O_2) developed near the sediments during these times. These seasonal anoxic periods corresponded with an accumulation of ANC (Fig. 9) in the near-sediment zone during the summer pre-treatment period and the initial winter after treatment. The near-sediment accumulation of ANC was predominantly associated with Ca^{2+}. This was likely due to enhanced microbial activity induced by the circumneutral pH, or to the decomposition of organic or Fe coatings surrounding the $CaCO_3$ particles. High P_{CO_2} near the sediments would also facilitate $CaCO_3$ dissolution during these periods (DePinto et al. 1989; Nye & Amelko 1987). Through the succeeding summer and winter stratification periods, patterns of Ca^{2+}-associated ANC accumulation and dissipation occurred. The accumulation of Fe^{2+} and NH_4^+ in the near-sediment zone (Fig. 9) was also indicative of microbial anaerobic decomposition associated with Fe^{3+} reduction and organic-N mineralization, respectively. An initially large Fe^{2+} release in the winter and summer following treatment declined by the summer of 1991, indicating either a depleted source of readily soluble Fe, or possible siderite

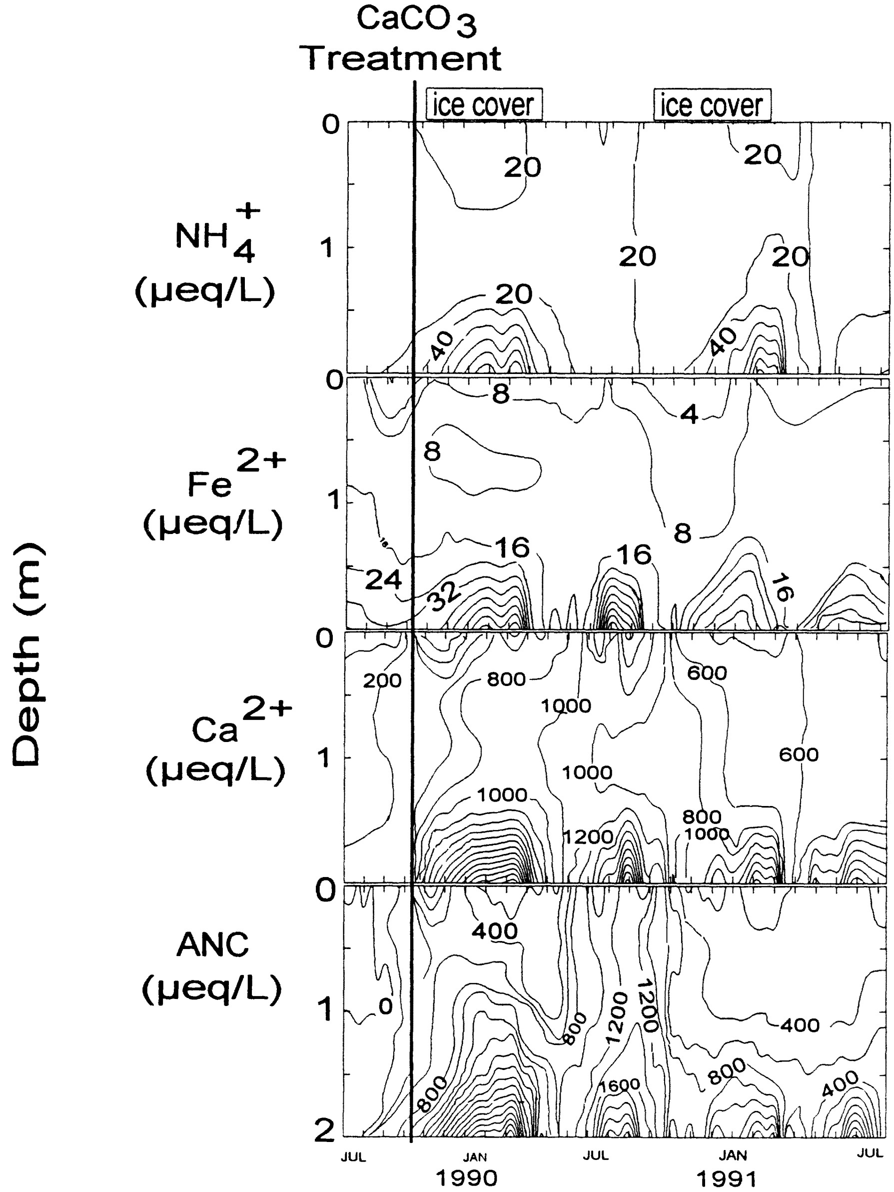

Fig. 9. Isopleths of acid neutralizing capacity (ANC), Ca^{2+}, Fe^{2+}, and NH_4^+, in μequiv/L, at the deepwater site over time in the Woods Lake beaver pond.

($FeCO_3$) precipitation and/or coating of $CaCO_3$ particles. Increased H_4SiO_4 concentrations in the near-sediment zone immediately after the $CaCO_3$ application (not shown) indicated the enhanced dissolution of an 'in-place' source

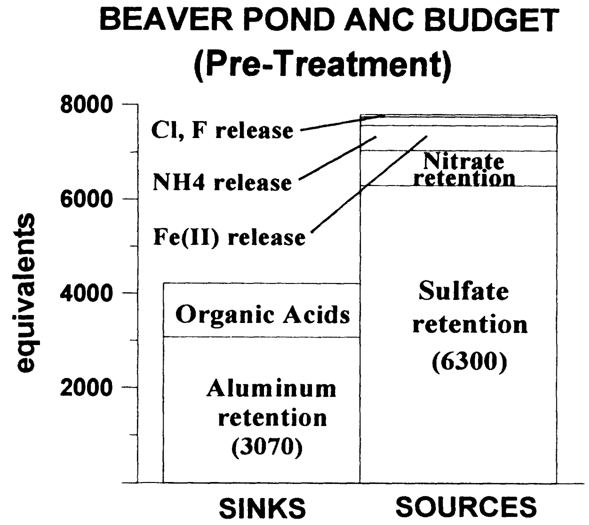

Fig. 10. Acid neutralizing capacity budget (sources and sinks) for the Woods Lake beaver pond in the pre-treatment period.

of H_4SiO_4, perhaps diatomacous detritus deposited during the previous summer season. This dissolution of a H_4SiO_4 source in the sediments is reflected in the downstream observations previously discussed. These profiles reveal that near-sediment processes during relatively anoxic periods were important to the control of beaver-pond outlet stream chemistry, and may have enhanced the dissolution of $CaCO_3$ particles which reached the pond sediments.

Acid neutralizing capacity and Ca^{2+} budgets

The determination of element mass balances and ANC budgets for the beaver pond and wetland during the pre- and post-watershed manipulation periods allowed identification of the biogeochemical processes most important in the production and consumption of ANC within this wetland complex (Figs 10 and 11, Table 5). During the pre-treatment period (summer of 1989) Al^{n+} retention (3070 equiv) and $RCOO^-$ release (1150 equiv) were the major ANC sinks, while SO_4^{2-} and NO_3^- retention (6300 and 747 equiv, respectively) and Fe^{2+} release (525 equiv) were the major ANC sources in the pond (Fig. 10). The ANC production rate of 822 mequiv m^{-2} yr^{-1} is high in comparison to other aquatic systems (Schindler 1986). Aluminum retention was consistent with hydrolysis of Al_{im} inputs from the headwater stream, and the pond was an important sink for Al mobilized in the watershed during the post-treatment period.

Table 5. Inputs, outputs and retention/release of major solutes from the Woods Lake beaver pond. DOC, DIC, Al_{tm} and H_4SiO_4 in moles x 10^3. All others in equivalents × 10^3. '−' = retention, '+' = release.

	Pre-treatment July 1, 1989–September 30, 1989			Post-treatment October 1, 1989–September 30, 1990		
Constituent	IN	OUT	+/−	IN	OUT	+/−
DOC	25.4	34.2	+8.80	93.4	147	+53.6
$RCOO^-$	1.92	3.07	+1.15	10.4	17.5	+7.10
Cl^-	0.49	0.32	−0.16	4.27	2.62	+1.65
NO_3^-	1.06	0.31	−0.75	22.8	12.2	−10.6
F^-	0.13	0.11	−0.02	0.36	0.53	+0.17
SO_4^{2-}	10.7	4.40	−6.30	38.1	30.4	−7.7
NH_4^+	0.20	0.25	+0.04	0.55	4.76	+4.21
Na^+	1.60	1.23	−0.37	6.60	7.76	+1.16
K^+	0.73	0.75	+.02	2.63	3.93	+1.30
Ca^{2+}	2.89	3.12	+0.23	62.1	185	+123
Mg^{2+}	8.02	8.17	+0.15	5.86	11.1	+5.24
Al_{tm}	1.49	0.44	−1.05	1.35	0.88	−0.48
Al^{n+}	4.18	1.11	−3.07	2.36	0.61	−1.75
Fe^{2+}	0.17	0.70	+0.53	0.46	3.15	+2.69
H_4SiO_4	4.29	2.33	−2.59	27.5	28.5	+1.00

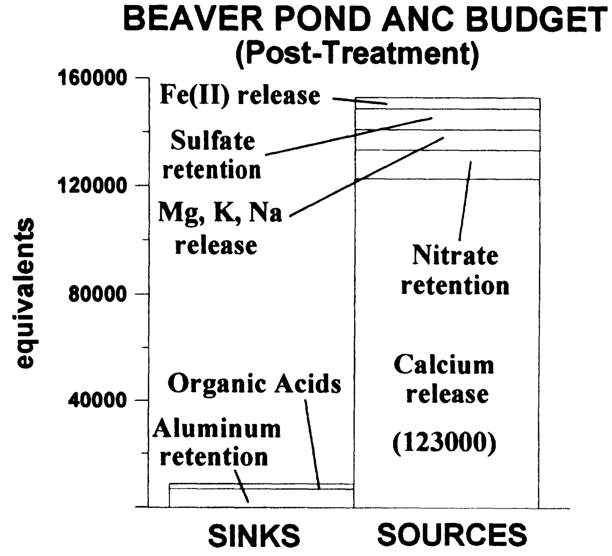

Fig. 11. Acid neutralizing capacity budget (sources and sinks) for the Woods Lake beaver pond in the post-treatment period.

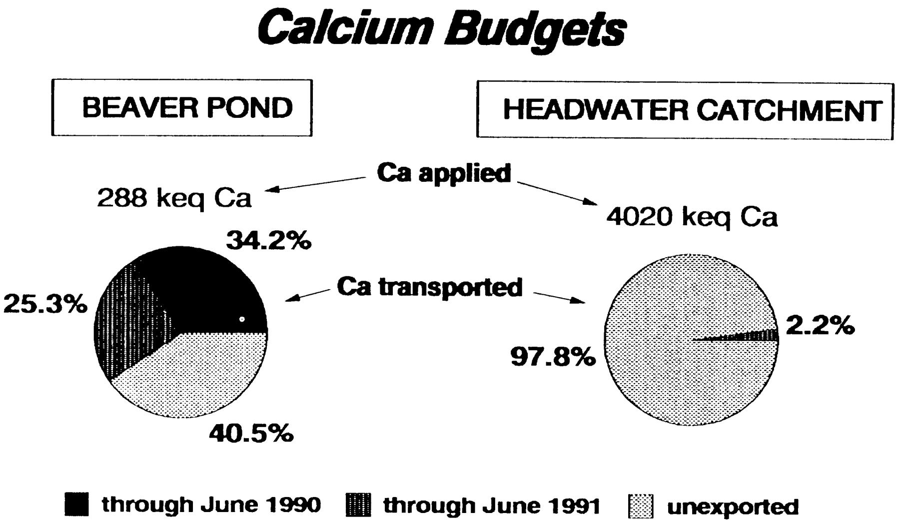

Fig. 12. Mass balance of Ca^{2+} from the beaver pond and wetland compared to that from the upland headwater catchment above the beaver pond.

During the first year after treatment a large release of Ca^{2+} was observed. The pond contributed 123000 equiv of Ca^{2+} downstream (12100 mequiv m^{-2} yr^{-1}), or 78% of total ANC generation (Fig. 11). An increase in NO_3^- retention also contributed to ANC production. This increased retention could be due to increased microbial activity within the pond. The increased input of NO_3^- from the upland catchment after treatment (Simmons et al. 1995; Driscoll et al. 1995) most likely contributed to this increase in observed retention. Increased NO_3^- concentration in the free-flowing tributary stream (Fig. 3, Table 3), supports the hypothesis of increased nitrification in $CaCO_3$ amended catchment soils (Yavitt & Newton 1990/91; Geary & Driscoll 1996; Simmons et al. 1996). Net ANC generation in the pond began to decline in the second year after treatment as the supply of $CaCO_3$ became depleted or inactivated.

A Ca^{2+} budget was constructed to determine the percentage of applied Ca^{2+} which was transported both from the contributing catchment surrounding the beaver pond (26.6 ha), and from the Ca^{2+} applied to the beaver pond and surrounding wetland itself (2.4 ha). Discharge-concentration relations for Ca^{2+} were determined for the pond inlet and outlet streams during the pre-treatment period, and predicted base-flow Ca^{2+} concentration was subtracted from actual post-treatment Ca^{2+} concentration to determine the flux due to $CaCO_3$ dissolution within the pond. By June of 1990, only 1.2% of the 4020 keq of Ca^{2+} applied to the upland portion of subcatchment II had been transported downstream into the beaver-pond (Fig. 12). By June of 1991, only an additional 1.0% had been transported into the pond. In contrast, of the 288 keq of Ca^{2+} applied directly to the combined pond/wetland area, 34.2% was exported downstream by June of 1990, and a total of 59.5% by June 1991. It is evident that processes in the pond and wetland area, or simply the percentage of wetted surface in the hydrologic source area, enhanced the dissolution of $CaCO_3$.

Exchangeable Ca^{2+} on beaver pond sediments and Sphagnum

Sediments and mosses in the Woods Lake beaver pond contained elevated concentrations of exchangeable Ca^{2+} compared to those in the nearby untreated beaver pond at Pancake- Hall Creek. The organic sediment located near the beaver dam contained nearly ten times the exchangeable Ca^{2+} as the untreated reference site (Table 6). Elevated concentrations of exchangeable Ca^{2+} were largely restricted to the upper 10 cm of sediment with concentrations decreasing markedly with depth in cores. This pattern may reflect the potential importance of cation exchange between sediments and the dissolved $CaCO_3$ in the overlying water. Undissolved $CaCO_3$ was not detected in the treated-pond sediments or *Sphagnum*. A mean of 10.8 ± 4.5 mg Ca^{2+} g^{-1} dry weight (n=12, total exchangeable Ca) was determined for the surficial sediments of the treated beaver pond at Woods Lake, while a mean of 1.25 ± 0.76 mg Ca^{2+} g^{-1} dry weight was determined for the reference pond.

In an exchange experiment, live *Sphagnum* samples (n=4) from the untreated reference beaver pond were exposed to pond surface water from the $CaCO_3$-treated beaver pond. A reciprocal treatment of *Sphagnum* samples (n=7) taken from the $CaCO_3$-treated beaver pond was performed with pond water from the untreated beaver pond. A mean of 1.25 mg $Ca^{2+}g^{-1}$ dry weight of *Sphagnum* (± 0.32 mg $Ca^{2+}g^{-1}$ dry weight) was exchanged onto the mosses from the $CaCO_3$-treated water. In the reciprocal experiment, a mean of 0.65 mg $Ca^{2+}g^{-1}$ dry weight (± 0.17 mg $Ca^{2+}g^{-1}$ dry weight) was released into untreated pond water. These results are highly suggestive of an active Ca^{2+} exchange complex associated with the*Sphagnum*. The potential for continued release of Ca^{2+} from beaver pond water to reacidifying upland inlet drainage is likely, although its continued importance would be controlled by the viability of the mosses and the exchange complex at higher pH conditions due to the liming (Bukaveckas 1988; Curran et al. 1991).

A dry weight areal estimate of *Sphagnum* coverage within the Woods Lake beaver pond was made based on 10 cm effective depth of living *Sphagnum* (approximate), resulting in an estimate of 0.79 ha of *Sphagnum* coverage within the Woods Lake beaver pond (mid-summer observation). A mean of 11.3 ± 4.7 Keq of Ca^{2+} was estimated to occupy exchange sites on pond *Sphagnum*. This value represents 7.9% of the $CaCO_3$ originally applied to

Table 6. Sediment and *Sphagnum* exchangeable Ca^{2+} (mg Ca^{2+}/g dry weight) in Woods Lake beaver pond ($CaCO_3$ treated) and Pancake Hall Creek beaver pond (untreated).

		n	Mean	Range	Std. dev.
$CaCO_3$-Treated Beaver Pond					
Deep Sediment (organic muck)		8	9.20	13.6–5.80	2.52
Sphagnum		12	10.8	22.3–6.70	4.50
Sediment/Peat Cores:	0–2cm	4	12.7	14.7–7.00	3.30
	2–10cm	4	2.90	4.72–1.55	1.14
	10–20cm	6	1.62	2.62–0.13	0.92
	>20cm	7	0.77	2.07–0.15	0.83
Untreated Beaver Pond					
Deep Sediment (organic muck)		2	1.31	1.36–1.25	-
Sphagnum		7	1.27	1.79–0.25	0.76
Sediment/Peat Cores:	0–2cm	2	2.67	2.94–2.39	-
	>20cm	4	1.33	3.05–0.76	1.00

the pond itself (143 Keq Ca^{2+}). Assuming that the surface sediments and peat in the other portions of the pond contained comparable Ca^{2+} pools, it is likely that the beaver pond acted as an effective sink for the directly applied Ca^{2+}, and that this pool of Ca^{2+} should be available for continued release and neutralization of reacidified beaver-pond inlet waters.

Significance and conclusions

Headwater wetlands and beaver-ponded streams are normally hydrologic source areas and potential discharge zones. In this study, it has been shown that such areas may be important in enhancing the treatment effects and efficiency of dissolution of the acid neutralizing agent $CaCO_3$. The major findings of this study are summarized below.

1. A comparison of beaver-ponded and free flowing streams in different $CaCO_3$-treated subcatchments within the same watershed revealed the importance of saturated conditions and the extent of wetted area in enhancing the dissolution of $CaCO_3$. The beaver-ponded stream responded more quickly, and supplied ANC to downstream waters over a longer period, than the free-flowing upland stream. The beaver pond and its surrounding wetlands were more important than the uplands in facilitating the dissolution and transport

of $CaCO_3$ to acidic drainage waters, with over 50% of the $CaCO_3$ applied to the ponded wetland being mobilized to the stream within two years. In the uplands portions of the subcatchment, only 2.2% of the applied $CaCO_3$ was mobilized. This demonstrates the importance of hydrologic source areas and wetlands as effective zones for the application of acid neutralization materials, and may indicate that the economic efficiency of watershed liming may be enhanced by concentrating applications of base to hydrologic source areas, wetlands and near-stream zones. The long-term efficiency of this method is largely unknown at this time.

2. The abundant *Sphagnum* and peat within the beaver pond acted as a cation exchange sink for applied Ca^{2+}. Moreover, the potential for release of Ca^{2+} upon reacidification of the sediments was demonstrated. Therefore, cation exchange sites associated with *Sphagnum*, peat and wetland sediments are important buffers of added ANC, delaying reacidification of drainage waters. This effect would depend on the viability of emergent and submergent vegetation, including *Sphagnum*, after a $CaCO_3$ treatment. The effects of elevated pH on acid tolerant species, and on the exchange complex of sediments and vegetation, may have unforeseen effects on the effectiveness of this potential Ca^{2+} sink.

3. The application of $CaCO_3$ resulted in an increased release of NO_3^- from upland drainage, while retention of NO_3^- by ponded waters increased. The production of NH_4^+ from decomposition reactions in the pond also increased. There was evidence for an increase in nitrification rate of the NH_4^+ released from the pond due to higher pH after the manipulation. Wetlands and ponds intersecting headwater drainages could offset increased NO_3^- inputs due to possible enhanced nitrification in forest soils from a $CaCO_3$ treatment. This retention of NO_3^- is important because the release of NO_3^- supplies acidity, counteracting the production of ANC from $CaCO_3$ application. Retention of NO_3^- retention could also have implications for the role of wetlands as sinks for increased NO_3^- concentrations in drainage waters due to observations suggesting that the Adirondacks have reached a stage of 'nitrogen saturation' (Aber et al. 1989, Stoddard 1994) or from elevated N deposition in the eastern United States (Driscoll & van Dreason 1993).

4. The beaver pond was an important sink for uplands mobilized Al, before and after the $CaCO_3$ treatment, and assumed a larger role in Al retention after a fairly rapid reacidification of the upland drainage inlet to the pond. The accumulation of hydrolyzed and precipitated Al solid phases within the beaver pond has implications for its potential remobilization if the beaver pond returns to more acidic conditions, or collapses in the usual pond construction-collapse cycle. The fraction of Al_{om}/Al_{tm} was higher in the ponded stream and outlet waters in comparison to inlet waters, indicating the role of wetlands

and beaver ponds as not only sinks for Al, but also in the supply of organic ligands which complex $\mathrm{Al_{im}}$ and mitigate its biotic toxicity.

Acknowledgements

Funding for this project was provided by the Electric Power Research Institute, the Empire State Electric Energy Research Corporation, the United States Fish and Wildlife Service, and Living Lakes, Inc. We thank the Woods Lake Club, B. Aulenbach, R. Geary, D. Burns, R. Newton, K. Bowes, C. Gubala, J. Blaisdell and W. Wang for assistance in the field and laboratory. This manuscript is contribution number 153 of the Upstate Freshwater Institute.

References

Aber JD, Nadelhoffer KJ, Stuedler P & Melillo JM (1989) Nitrogen saturation in northern forest ecosystems. Bioscience 39: 378–386

Aller RC (1980) Diagenetic processes near the sediemnt-water interface on Long Island Sound I. Decomposition and nutrient element geochemistry (S,N,P). Advances in Geophysics 22: 237–350

Andrus RE (1986) Some aspects of *Sphagnum* ecology. Can. J. Bot. 64: 416–426

American Public Health Association (1985) Standard Methods for the Examination of Water and Wastewater. American Public Health Association, New York, NY

Apple LL (1985) Riparian habitat restoration and beaver. In: Riparian Ecosystems and Their Management: Reconciling Conflicting Uses. General Technical Report RM-120 (pp 489–490). Rocky Mountain Forest and Range Experiment Station, USDA Forest Service, Tucson AZ

Bailey SW, Driscoll CT & Hornbeck JW (1995) Acid-base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire. Biogeochemistry 28: 69–91

Bayley SE, Vitt DH, Newbury RW, Beaty KG, Behr R & Miller C (1987) Experimental acidification of a *Sphagnum* dominated peatland: first year results. Can. J. Fish. Aquat. Sci. 44: 194–205

Bennett PC, Siegel DI, Hill BM & Glaser PH (1991) Fate of silicate minerals in a peat bog. Geology 19: 328–331

Berner RA (1980) Early Diagenesis. Princeton University Press, Princeton, NJ

BukaveckasP (1988) Effects of calcite treatment on primary producers in acidified Adirondack lakes – response of macrophyte communities. Lake Reserv. Manage. 4: 107–113

Bunzl K, Schmidt W & Sansoni B (1976) Kinetics of ion exchange in soil organic matter. IV. Adsorption and desorption of $\mathrm{Pb^{+2}}$, $\mathrm{Cu^{+2}}$, $\mathrm{Cd^{+2}}$, $\mathrm{Zn^{+2}}$ and $\mathrm{Ca^{+2}}$ by peat. J. Soil Sci. 27: 32–41

Cappo KA, Blume LJ, Raab GA, Bartz JK & Engels JL (1987) Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey, EPA 600/8–87/020. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV

Chapnick SD, Moore WS & Nealson KH (1982) Microbially mediated manganese oxidation in a freshwater lake. Limnol. Oceanogr. 27: 1004–1014

Cirmo CP & Driscoll CT (1993) Beaver pond biogeochemistry: acid neutralizing capacity generation in a headwater wetland. Wetlands 13: 277–292

Clymo RS (1963) Ion exchange in *Sphagnum* and its relation to bog ecology. Ann. Bot. (N.S.) 27: 309–324

→ Clymo RS (1973) The growth of *Sphagnum*: some effects of environment. J. Ecol. 61: 849–869

→ Cook RB, Kelly CA, Schindler DW & Turner DA (1986). Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. Limnol. Oceanogr. 31: 134–148

Craigie JS & Maass WSG (1966) The cation exchanger in *Sphagnum* spp. Ann. Bot. (London, N.S.) 30: 153–154

Curran RP, Spada DM & Roy KM (1991) Wetland impacts from lake liming. Nat. Wetlands Newsletter 13: 12–13

Dahm CN, Trotter EH, & Sedell JR (1987) Role of anerobic zones and processes in stream ecosystem productivity. In: Averett RC & McKnight DM (Eds) Chemical Quality of Water and the Hydrolgic Cycle (pp 157–178). Lewis Publishers, Inc., Chelsea, MI

Davis JE & Goldstein RA (1988) Simulated response of an acidic Adirondack lake watershed to various liming mitigation strategies. Water Resour. Res. 24: 525–532

DePinto JV, Scheffe RD, Booty WG & Young TC (1989) Predicting reacidification of calcite treated acid lakes. Can. J. Fish. Aquat. Sci. 46: 323–332

DeVito KJ, Dillon PJ & LaZerte BD (1989) Phosphorus and nitrogen retention in five Precambrian shield wetlands. Biogeochemistry 8: 185–204

Driscoll CT (1984) A procedure for the fractionation of aqueoius aluminum in dilute acidic waters. Int. J. Env. Anal. Chem. 16: 267–284

Driscoll CT, Cirmo CP, Fahey TJ, Blette VL, Burns DJ, Gubala CP, Newton RM, Raynal DJ, Schofield CL, Yavitt JB & Porcella DB (1996) The Experimental Watershed Liming Study (EWLS): Comparison of lake/watershed base neutralization strategies. Biogeochemistry 32: 143–174 (this volume)

Driscoll CT, Fordham GF, Ayling WA & Oliver LM (1989a) Short term changes in the chemistry of trace metals following calcium carbonate treatment of acidic lakes. Can. J. Fish. Aquat. Sci. 46: 249–257

Driscoll CT, Fuller RD &Schecher WD (1989b) The role of organic acids in the acidification of surface waters in the eastern United States. Water Air Soil Pollut. 43: 21–40

Driscoll CT, Lehtinen MD & Sullivan TJ (1994) Modeling the acid-base chemistry of organic solutes in Adirondack, NY lakes. Water Resour. Res. 30: 297–306

Driscoll CT & van Dreason R (1993) Seasonal and long-term temporal patterns in the chemistry of Adirondack Lakes. Water Air Soil Pollut. 67: 319–344

Driscoll CT, Wyskowski BJ, Cosentini CC & Smith ME (1987) Processes regulating temporal and longitudinal variations in the chemistry of a low-order stream in the Adirondack region of New York. Biogeochemistry 3: 225–241

Eberhardt LL & Thomas JM (1991) Designing environmental field studies. Ecol. Monogr. 61: 53–73

Ford TE & Naiman RJ (1988) Alteration of carbon cycling by beaver: methane evasion rates from boreal forest streams and rivers. Can. J. Zool. 66: 529–533

Francis MM, Naiman RJ and Melillo JM (1985) Nitrogen fixation in subarctic streams influenced by beaver (*Castor canadensis*). Hydrobiol. 121: 193–202

→ Geary R and Driscoll CT (1996) Forest soil solutions: acid/base chemistry and response to calcite treatment. Biogeochemistry 32: 195–220 (this volume)

Gorham E, Bayley SE & Schindler DW (1984) Ecological effects of acid deposition on peatlands: a neglected field of acid rain research. Can. J. Fish. Aquat. Sci. 41: 1256–1268

Gorham E, Eisenreich SJ, Ford J & Santelmann MV (1985) The chemistry of bog waters. In: Stumm W (Ed) Chemical Processes in Lakes (pp 339–363). John Wiley & Sons, Inc., New York

Grieve IC (1990) Effects of catchment liming and afforestation on the concentration and fractional composition of aluminium in the Loch Fleet catchment, SW Scotland. J. Hydrol. 115: 385–396

Gubala CP & Driscoll CT (1991) The chemical responses of acidic Woods Lake, NY, to two different treatments with calcium carbonate. Water Air Soil Pollut. 59: 7–22

Hemond HF (1990) Acid neutralizing capacity, alkalinity and acid-base status of natural waters containing organic acids. Environ. Sci. Technol. 24: 1486–1489

Hiebert FK & Bennett PC (1992) Microbial control of silicate weathering in organic-rich ground water. Science 258: 278–281

Hurlbert SH (1984) Pseudoreplication and the design of ecological field experiments. Ecol. Monogr. 54:187–211

Ivarson KC (1977) Changes in decomposition rate, microbial population and carbohydrate content of an acid peat bog after liming and reclamation. Can. J. Soil Sci. 57: 129–137

Jenkins A, Waters D & Donald A (1991) An assessment of terrestrial liming strategies in upland Wales. J. Hydrol. 124: 243–261

→ Johnston CA & Naiman RJ (1990) Aquatic patch creation in relation to beaver population trends. Ecology 71: 1617–1621

→ Kelly CA, Rudd JWM, Cook RB & Schindler DW (1982) The potential importance of bacterial processes in regulating rate of lake acidification. Limnol. Oceanogr. 27: 868–882

Kerekes J, Beauchamp S, Torden R & Pollock T (1986) Sources of sulphate and acidity in wetlands and lakes of Nova Scotia. Water Air Soil Pollut. 31: 207–214

Kilham P (1982) Biochemistry of bog ecosystems and chemical ecology of *Sphagnum*. Mich. Bot. 21: 159–168

LaZerte B (1993) The impact of drought and acidification on the chemical exports from a minerotrophic coniifer swamp. Biogeochemistry 18: 153–175

Lovley DR & Phillips EJP (1986) Organic matter mineralization with reduction of ferric iron in anaerobic sediments. App. Environ. Microbiol. 51: 683–689

Maret JJ, Parker M & Fanny TE (1987) The effect of beaver ponds on the non-point source water quality of a stream in southwestern Wyoming. Water Res. 21: 263–268

Matzner E, Khanna PK, Meiwas KJ & Ulrich B (1983) Effects of fertilization on the fluxes of chemical elements through different forest ecosystems. Plant and Soil 74: 343–358

Moore PD & Bellamy DJ (1974) Peatlands. Springer-Verlag, Inc., New York, NY

Naiman RJ, Johnston CA & Kelley JC (1988) Alteration of North American streams by beaver. BioScience 38: 753–762

→ Naiman RJ, Manning T & Johnston CA (1991) Beaver population fluctuations and tropospheric methane emissions in boreal wetlands. Biogeochemistry 12: 1–15

Naiman RJ & Melillo JM (1984) Nitrogen budget of a subarctic stream altered by beaver (Castor canadensis). Oecologia 62: 150–155

→ Newton RM, Weintraub J & April R (1987) The relationship between suface water chemistry and geology in the North Branch of the Moose River. Biogeochemistry 3: 21–35

New York State Atmospheric Deposition Monitoring Network (1991) Wet Deposition, Nick's Lake, 1991. New York State Department of Environmental Conservation, Division of Air Resources, Albany, NY

Nisbet EG (1989) Some northern sources of atmospheric methane: production, history and future implications. Can. J. Earth Sci. 26: 1603–1611

Nye PH & Amelko AY (1987) Predicting the rate of dissolution of lime in soil. J. Soil Sci. 38: 641–649

Parker M (1986) Beaver, water quality, and riparian systems. In: Proceedings: Wyoming Water and Streamside Zone Conference (pp 88–94). Wyoming Water Research Center, University of Wyoming, Laramie, WY

Parker M., Wood FJ Jr., Smith BH & Elder RG (1985) Erosional downcutting in lower order riparian ecosystems: Have historical changes been caused by removal of beaver? In: Riparian Ecosystems and Their Management: Reconciling Conflicting Uses (pp 35–38). General Technical Report RM-120, Rocky Mountain Range and Forest Experiment Station, USDA Forest Service, Tucson, AZ

Perdue EM (1990) Modeling the acid-base chemistry of organic acids in laboratory experiments and fresh waters. In: Perdue EM & Gjessing ET (Eds) Organic acids in aquatic ecosystems, Life Sciences Research Report 48, Dahlem Konferenzen, Berlin

Persson T, Lundkvist H, Wirén A, Hyvönen R & Wessén B (1989) Effects of acidification and liming on carbon and nitrogen mineralization and soil organisms in mor humus. Water Air Soil Pollut. 45: 77–96

Plummer LN, Parkhurst DL & Wigley TML (1979) Critical review of kinetics of calcite dissolution and precipitation. In: Jenne EA (Ed) Chemical Modeling in Aqueous Systems, ACS Symposium Series No. 93 (pp 537–573). American Chemical Society, Washington DC

Raddum GG, Brettum P, Matzow D, Nilssen JP, Skov A, Sveälv T & Wright RF (1986) Liming the acid Lake Hovvatn, Norway: A whole ecosystem study. Water Air Soil Pollut. 31: 721–763

Reuter JH & Perdue EM (1977) Importance of heavy metal-organic matter interactions in natural waters. Geochim. Cosmochim. Acta 41: 325–334

Roulet NT & Ash R (1992) Low boreal wetlands as a source of atmospheric methane. J. Geophys. Res. 97: 3739–3749

SAS Institute Inc. (1985) SAS Procedures Guide for Personal Computers, Version 6 Edition. Cary, NC

Schecher WD & Driscoll CT (1995) ALCHEMI: A chemical equilibrium model to assess the acid-base chemistry and speciation of aluminum in dilute solutions. In: Loeppert R, Schwab AP & Goldberg S (Eds) Chemical Equilibrium and Reaction Models (pp 325–356). Soil Science Society of America, Madison, WI

Schecher WD & McAvoy DC (1991) MINEQL+ version 2.2: A Chemical Equilibrium Program for Personal Computers, User's Manual. Proctor and Gamble Co., Cincinnati, OH

Schindler DW (1986) The significance of in-lake production of alkalinity. Water Air Soil Pollut. 30: 931–944

Schindler DW, Wagemann R, Cook RB, Ruszczyunski T & Prokopowich J (1980) Experimental acidification of Lake 223, Experimental Lakes Area: Background data and the first three years of acidification. Can. J.Fish. Aquat. Sci. 37: 342–354

→ Simmons JA, Yavitt JB & Fahey TJ (1996) Response of forest floor nitrogen dynamics to liming. Biogeochemistry 32: 221–244 (this volume)

Spearing AM (1972) Cation exchange capacity and galacturonic acid content of several species of Sphagnum in Sand Ridge bog, central New York State. Bryologist 75: 154–158

Stoddard JL (1994) Long-Term Changes in Watershed Retention of Nitrogen: Its Causes and Aquatic Consequences. In: Baker LA (Ed) Environmental Chemistry of Lakes and Reservoirs, Advances in Chemistry Series No. 237, American Chemical Society, Washington, DC

Stumm W & Morgan JJ (1981) Aquatic Chemistry (2nd.ed.). John Wiley and Sons, Inc., New York, NY

Sverdrup H., Rasmussen R & Bjerle I (1984) A simple model for the reacidification of limed lakes taking into account the simultaneous deactivation and dissolution of calcite in the sediments into account. Chemica Scripta 24: 53–66

Szaro RC & DeBano LF (1985) The effect of streamflow modification on the development of a riparian ecosystem. In: Riparian Ecosystems and Their Management: Reconciling Conflicting Uses (pp 211–215). General Technical Report RM-120, Rocky Mountain Range and Forest Experiment Station, USDA Forest Service, Tucson, AZ

White JR & Driscoll CT (1987) Manganese cycling in an acidic Adirondack lake. Biogeochemistry 3: 87–103

Wieder RK, Lang GE & Granus VA (1987) Sulphur transformations in *Sphagnum*-derived peat during incubation. Soil Biol. Biochem. 19: 101–106

→ Wieder RK, Yavitt JB & Lang GE (1990) Methane production and sulfate reduction in two Appalachian peatlands. Biogeochemistry 10: 81–104

Woo MK & Waddington JM (1990) Effects of beaver dams on sub-arctic wetland hydrology. Arctic 43: 223–230

Wood JA (1989) Peatland acidity budgets and the effects of acid deposition. Discussion Paper No. 5, Ecological Applications Research Division, Environment Canada, Ottawa, Ontario, Canada

Yavitt JB, Angell L, Fahey TJ, Cirmo CP & Driscoll CT (1992) Methane fluxes, concentrations and production in two Adirondack beaver impoundments. Limnol. Oceanogr. 37: 1057–1066

Yavitt JB & Fahey TJ (1996) Peatland porewater chemical responses to $CaCO_3$ applications in wetlands next to Woods Lake, New York Biogeochemistry 32: 245–263 (this volume)

Yavitt JB, Lang GE & Sexstone AJ (1990) Methane fluxes in wetland forest and soils, beaver ponds, and low-order streams of a temperate forest ecosystem. J. Geophys. Res. (Oceans) 95: 22463–22474

Yavitt JB & Newton RM (1990/91) Liming effects on some chemical and biological parameters of soil (Spodosols and Histosols) in a hardwood forest watershed. Water Air Soil Pollut. 54: 529–544

Young TC, DePinto JV, Rhea JR & Scheffe RD (1989) Calcite dose selection, treatment, efficiency and residual calcite fate after whole-lake neutralization. Can. J. Fish. Aquat. Sci. 46: 315–322