Biogeochemistry **32:** 245–263, 1996.

Peat and solution chemistry responses to $CaCO_3$ application in wetlands next to Woods Lake, New York

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Received 28 October 1994; accepted 28 April 1995

Key words: liming, microbial activity, peat, solution chemistry

Abstract. We studied the effect of a calcite ($CaCO_3$) treatment on peat and pore water chemistry in poor fen and conifer swamp wetlands next to Woods Lake and its tributaries to evaluate the role of wetlands in an Experimental Watershed Liming Study (EWLS). Peat was characteristically organic rich and nutrient poor, with exchangeable Ca concentrations of <13 $cmol_c kg^{-1}$. We estimated that between 0.4 to 4 Mg $CaCO_3$ ha^{-1} fell directly on three study sites; however, one year after the treatment the increase in Ca concentration (0–8 cm depth) was equivalent to a $CaCO_3$ dosage of 3 Mg ha^{-1} with an additional 2–4 Mg ha^{-1} of undissolved $CaCO_3$ still present, suggesting the peat retained Ca supplied from uplands. Most aspects of peat chemistry including microbial respiration and SO_4 reduction did not respond to the treatment.

Peat pore water (5 and 20 cm depths) had a mean pH of 4.82 before treatment with high concentrations of dissolved organic carbon (DOC mean of 790 μmol C/l) and low Ca^{2+} concentration (mean of 32 μmol/l). The $CaCO_3$ treatment increased concentrations of Ca^{2+} to a mean of 87 μmol/l and dissolved inorganic carbon (DIC) from 205 to a mean of 411 μmol/l, whereas it decreased monomeric Al concentration from 19 to 10 μmol/l. Otherwise, pore water chemistry showed little response to the treatment, at least within natural spatial and temporal variation of solute concentrations. The results suggest that liming watersheds with the relatively low $CaCO_3$ dosage applied in this study can benefit acidic waters downstream by exporting more Ca and DIC and less monomeric Al, with otherwise little effect on the peat itself.

Introduction

Liming an acidic soil is an established practice to reduce or even neutralize acidity in the soil (Barber 1984). When the lime is calcite ($CaCO_3$), dissolution occurs with H^+, viz. $CaCO_3^+ + H^+ = Ca^{2+} + HCO_3^-$. The benefits of such a reaction are that (i) Ca^{2+} can replace H^+ on soil exchange sites and (ii) CO_3^{2-} consumes H^+ to form the mobile bicarbonate ion (HCO_3^-). Calcite can dissolve in soil with higher pH (>5.5 pH) by reactions with aqueous carbon dioxide ($H_2CO_3^* = [CO2]_{aq} + H_2CO_3^*$) or by hydrolysis ($H_2O = H^+ + OH^-$). Liming a neutral soil can benefit acidic water downstream of that soil upon leaching of the products Ca^{2+} and CO_3^{2-} (Warfvinge & Sverdrup 1988).

How liming affects peaty, organic soil is unclear (cf., Woodin & Skiba 1990), especially, if the peat is intrinsically acidic (e.g., pH values <4.5). For example, peat derived from decomposing *Sphagnum* moss is mostly acidic (Andrus 1986), as the composition of most *Sphagna* is more than 50% uronic acid by mass (Spearing 1972) and partial decomposition of *Sphagnum* produces relatively acidic dissolved organic compounds (McKnight et al. 1985; David & Vance 1991). The H^+ generated in acidic *Sphagnum*-derived peat should enhance $CaCO_3$ dissolution (Nye & Amelko 1987).

Conversely, not all peat is inherently acidic nor is it *Sphagnum*-derived. Peat derived from decomposing *Carex* sedges usually has higher pH values than *Sphagnum*-derived peat (Bohlin et al. 1989) because organic acids are not as prevalent as in *Sphagnum*. Moreover, the high organic matter content of peat bestows a large ion exchange capacity that can bind base cations fed by atmospheric deposition – and by local groundwater, if permitted – effectively neutralizing acidity (Moore & Bellamy 1974). Organic matter also holds water rather tightly, making peat saturated and creating anaerobic conditions. Anaerobic microorganisms can consume H^+ by reduction of either sulfate (SO_4^{2-}), nitrate (NO_3^-), or iron (Fe^{3+}) and manganese (Mn^{4+}), or by production of ammonium (NH_4^+). Such anaerobic reactions are strong enough to prevent acidification in lake sediments even though the overlying water might be acidic (Schiff & Anderson 1986). How these anaerobic reactions neutralize acidity of peat is unclear, apart from the question whether CO_2 produced anaerobically can enhance $CaCO_3$ dissolution (Nye & Amelko 1987).

Another interest in liming peat pertains to hydrologic situations where the wetland occurs in a groundwater recharge area (Siegel 1983); hence liming such areas can bestow benefits to acidic waters downstream (Jenkins et al. 1991).

This study addressed the liming response of small peatlands adjoining Woods Lake, New York, and its tributaries by (i) examining peat chemistry and rates of microbially mediated processes in peat; and (ii) examining pore water chemistry of shallow (5 cm deep) and subsurface (20 cm deep) peat. We anticipated that $CaCO_3$ dissolution would consume acidity and increase the exchangeable pool of Ca for the limed peat. We also expected the treatment to stimulate microbial reduction of SO_4^{2-} and production of NH_4^+ because maximum rates of microbial activity in acidic environments tends to occur at neutral pH (Goodwin et al. 1988). For pore water chemistry, we expected the greatest response at a shallow depth and less response in deeper peat.

Methods

Study sites

The study sites adjoined Woods Lake (42°52′ N, 71°58′ W) and its tributaries. We also established some study sites near Pancake-Hall Creek (15 km from Woods Lake) because we could not find suitable reference areas within the non-limed portions of the Woods Lake watershed. The physiographic settings of the sites at Woods Lake and at Pancake-Hall Creek were quite similar (April & Newton 1985). All of the sites had peat depths >30 cm. All of the sites were open; where trees occurred (red spruce *Picea rubens*), they did not form a closed canopy over the site.

There are three different wetland types within the Woods Lake watershed (Cronan & DesMeules 1985). One is a poor fen (nomenclature follows Jeglum 1991), located above high water but within 20 m of Woods Lake, dominated by shrubs (*Chamaedaphne calyculata*, *Ledum groenlandicum*, *Myrica gale*), sedges and grasses (*Carex stricta*, *Calamagrostis canadensis*), and *Sphagnum* spp (Mackun et al. 1994). The other two wetlands are poor to transitional conifer swamps dominated by red spruce (*Picea rubens*) and red maple (*Acer rubrum*). One is a riparian swamp, straddling woodland streams, with a nearly complete carpet of *Sphagnum girgensohnii* and lesser amounts of shrubs, sedges and grasses. The other conifer swamp is next to a beaver impoundment and is dominated by sedges and grasses, with lesser amounts of *Sphagnum girgensohnii*; this site was gradually covered by the encroaching impoundment during the study. For each wetland type, we study a limed and a non-limed control.

Hydrologically, the poor fen occurs in a groundwater discharge area because potentiometric head in the area is above the lake surface (Staubitz & Zarriello 1989). We suspected the same was true for the swamp near the beaver pond, as well as for the riparian swamp.

Peat had similar appearance at each site (Table 1). Peat near the surface was fibric, whereas peat below 20 cm was highly decomposed.

Sample collection and analyses

We collected peat samples from each site (n = 3 per sampling date) using an open PVC cylinder (10 cm diameter × 35 cm length) prior to the $CaCO_3$ treatment in October 1989, then again periodically afterward. For each collection, we first made a cylindrical incision through the surface peat with a sharp bread knife, then forced the cylinder through surface vegetation and into the underlying peat. This procedure did not compact the entrained peat within the cylinder. By partial excavation of the peat outside the cylinder, the intact

Table 1. Peat characteristics of three wetland types at Woods Lake prior to $CaCO_3$ application in October 1989. Values are means for three samples per site (± 1 SE).

		Type			
Characteristic	Subcatchment	Poor fen	Riparian swamp	Beaver-pond swamp	Mean
Peat depth (cm)		30	>200	30	
Bulk density (g cm^{-3})					
0–4 cm depth	Reference	0.03	0.08	0.05	0.05
	Treatment	0.03	0.08	0.05	0.05
20–24 cm depth	Reference	0.26	0.20	0.10	0.19
	Treatment	0.27	0.20	0.10	0.19
Organic Matter (%)					
0–4 cm depth	Reference	87	90	87	88
	Treatment	85	90	87	87
20–24 cm depth	Reference	70	81	76	76
	Treatment	70	82	76	76
pH					
0–4 cm depth	Reference	3.85	5.55	5.15	4.30
	Treatment	4.15	4.80	4.50	4.40
20–24 cm depth	Reference	4.05	5.55	5.20	4.48
	Treatment	4.30	5.15	4.75	4.60
Extractable Ca^{2+} ($cmol_c$ kg^{-1})					
0–4 cm depth	Reference	6.3 ± 1.0	3.7 ± 0.6	11.5 ± 1.8	7.2
	Treatment	10.2 ± 1.7	3.5 ± 0.5	6.5 ± 3.5	6.7
20–24 cm depth	Reference	4.1 ± 0.1	1.8 ± 0.1	9.5 ± 1.5	5.1
	Treatment	2.0 ± 0.1	1.9 ± 0.1	14.0 ± 2.0	6.0

peat core was lifted from the site. A rubber cap placed over the bottom of the cylinder and held in place with a hose clamp kept the peat intact.

Analysis of the cores began within 48 h after collection. We extruded the fresh peat from its cylinder and, while it was under a constant stream of O_2-free N_2, cut it into 4-cm thick intervals. We measured pH in water with soil-to-solution ratios of 1:10; the exchangeable pool of Ca in unbuffered 1 M NH_4Cl; and $CaCO_3$ by water displacement of acidified samples.

We also measured microbial respiration and SO_4 reduction on two of the depth intervals per peat core (0–4 and 20–24 cm below the surface) using techniques described by Yavitt & Lang (1990). For microbial respiration, we quantified CO_2 produced by incubated peat samples. For SO_4 reduction we incubated anoxically a fresh peat sample (15 cm^3) along with a 10 μl solution containing 3.7×10^4 Bq of carrier-free ^{35}S-SO_4 for 1 h at 15 °C. The incubated samples were frozen until analyzed for reduced inorganic S (both total and ^{35}S-labeled) and unreacted ^{35}S-SO_4. We determined the concentration of SO_4^{2-} in separate subsamples, so that SO_4 reduction could be calculated as the product of the proportion of added ^{35}S recovered as reduced inorganic S and the initial dissolved SO_4 pool size times 1.06 to account for the microbial discrimination against the heavier ^{35}S isotope.

We also equipped each of the field sites with six zero-tension lysimeters to collect peat pore waters. Three lysimeters collected pore water 5 cm below the peat surface, and the other three collected pore water 20 cm below the peat surface. The lysimeters were similar to those described by Eleuterius (1980). Each lysimeter consisted of a 150 ml bottle with several perforations in its sides, covered by 250-μm-mess plankton netting to exclude peat. We installed all of the lysimeters permanently in July 1988 by inserting each into the peat. The lysimeters collected water under saturated conditions, without any tension applied to the bottle, which we retrieved using a hand pump at approximately monthly intervals from May 1989 to October 1991.

We analyzed pore water samples within 48 h for pH, SO_4^{2-}, NO_3^-, Cl^-, base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+), DIC, DOC, NH_4^+, labile monomeric Al (Al_{tm}) and organic monomeric Al (Al_{om}) using methods described in Driscoll et al. (1996). Unfortunately, the limited sample size did not permit measurement of acid neutralizing capacity (ANC).

Statistical analyses

The treatment main effect ($CaCO_3$ application) was replicated in EWLS with two treatment and two reference subcatchments (Driscoll et al. 1996); however, we could not find comparable study sites for each of the three wetland types in treatment subcatchments II and IV and in reference subcatchments I and V. Hence the treatment main effect could not be replicated for each wetland type. We did evaluate the difference in any given characteristic between the reference and treatment prior to liming for each site by Student's t-test, and we used repeated-measures analysis of variance (ANOVA) to analyze peat characteristics following the treatment. Significance level was 0.05.

Results

Peat chemistry

Peat in the Woods Lake watershed is acidic to circumneutral, with an extremely small pool of exchangeable Ca (Table 1). Peat in the poor fen was significantly more acidic than peat in the two conifer swamps. Further, the

Table 2. Rates of microbial respiration and sulfate reduction (both nmol cm^{-3} hr^{-1}) of peat samples per depth in wetlands within Woods Lake watershed, which received $CaCO_3$ in October 1989. Each value is the mean (± 1 SE) of three wetland types per sampling date.

Sampling date	Microbial respiration	Sulfate reduction
October 1988		
0–4cm depth	23 ± 7	2 ± 1
20–24cm depth	73 ± 30	12 ± 5
May 1989		
0–4cm depth	189 ± 81	<1 ± <1
20–24cm depth	507 ± 381	9 ± 6
October 1989		
0–4cm depth	33 ± 7	2 ± 1
20–24cm depth	162 ± 63	11 ± 6

pool of exchangeable Ca was significantly less in peat in the riparian swamp than in the poor fen and the beaver-pond swamp. These data illustrate the natural variation in peat chemistry we met before the $CaCO_3$ application.

One year after the $CaCO_3$ application, peat pH at the 0–4 and 4–8 cm depths had increased significantly relative to pH values at those depths prior to liming – and the increase in peat pH persisted into the second year (Fig. 1). The pH of deeper peat ($>$ 8 cm depth) did not change significantly even two years after the application. Likewise, the pool of exchangeable Ca increased to 24.1 $cmol_c$ kg^{-1} at the 0–4 cm depth and 14.1 $cmol_c$ kg^{-1} at the 4–8 cm depth in the first year after the application, with the higher levels continuing into the second year (Fig. 1). There were slight but no significant increases in Ca concentration of deeper peat ($>$ 8 cm depth) even two years after liming. We also found undissolved $CaCO_3$ in peat samples from the 0–4 and 4–8 cm depths, with higher values in the first year after the application than in the second year (Fig. 1).

Microbial respiration and SO_4 reduction, measured in short-term (i.e., 24 hr) incubations of peat samples, provide important measures of the liming response because they generate CO_2 for $CaCO_3$ dissolution. Microbial respiration (Table 2) measured prior to the calcite application in October 1988 showed statistically similar rates to those measured one year after the application in October 1990. On the other hand, rates of microbial respiration measured in May 1989 were higher than those measured in October. Rates of SO_4 reduction (Table 2) were not affect significantly by liming – and the SO_4 reduction rates measured in May were lower (0–4 cm depth only) than rates measured at the same depth in October.

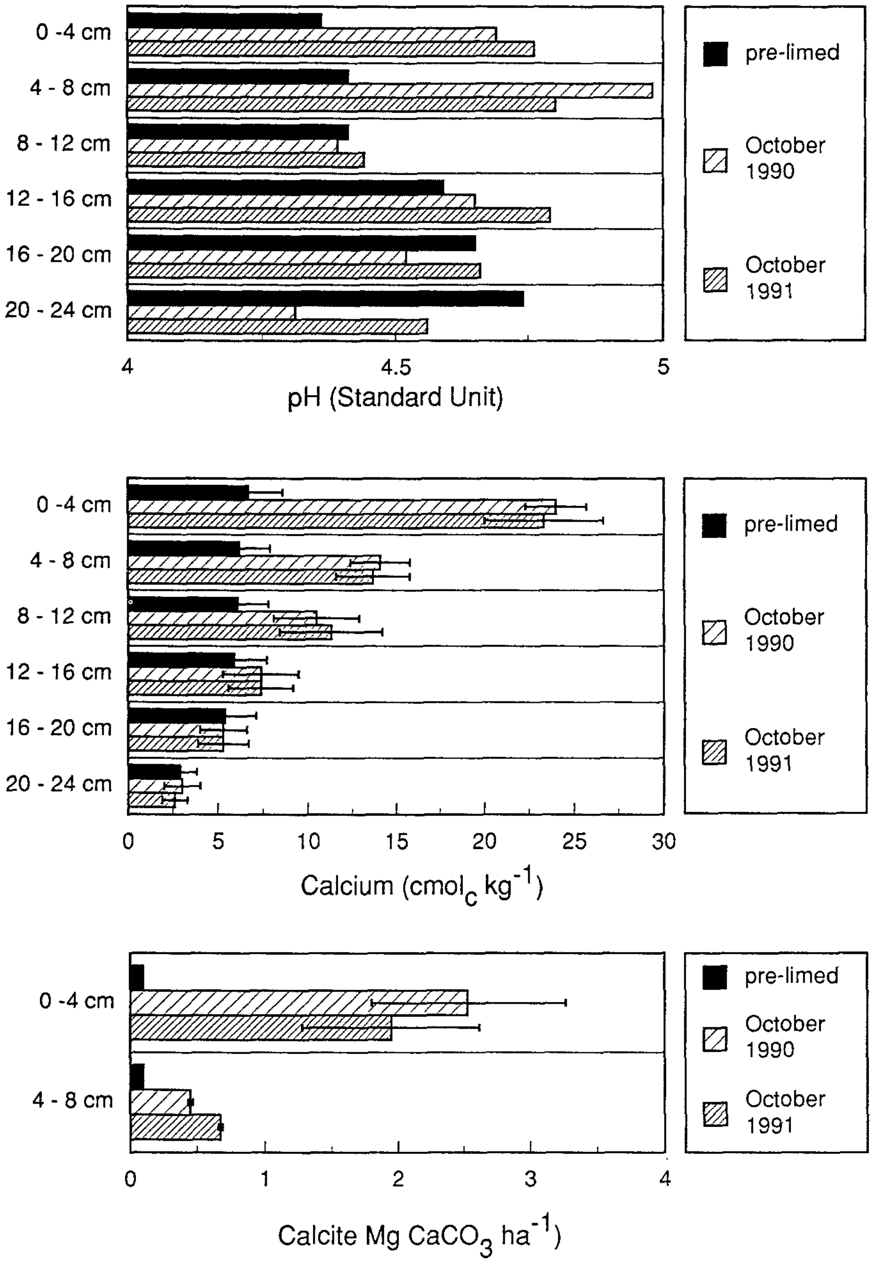

Fig. 1. Comparison of pH, Ca concentration and calcite content of peat within Woods Lake watershed, which received $CaCO_3$ application in October 1989. Each value is the mean of three wetland types, per sampling date and per depth interval.

Table 3. Solute concentrations (μmol/l except standard unit for pH) in peat pore water per wetland site within Woods Lake watershed. Means and range (averaged for 5 and 20 cm depths) are for samples collected in 1989 from reference and treatment subcatchments prior to $CaCO_3$ application in October of that year.

Solute	Subcatchment	Fen		Riparian		Beaver pond	
		Mean	Range	Mean	Range	Mean	Range
pH	Reference	4.67	4.44–5.04	5.11	4.95–5.76	5.72	5.39–6.28
	Treatment	4.53	4.20–4.98	4.96	4.74–5.43	4.70	4.48–5.03
DOC	Reference	585	355–997	1255	525–2825	1031	678–1445
	Treatment	464	358–833	848	500–1418	557	257–982
DIC	Reference	179	67–406	358	75–960	217	60–491
	Treatment	115	24–240	296	64–1117	203	56–714
Cl^-	Reference	8.8	6.3–11.8	12.4	9.1–17.0	8.9	7.2–11.9
	Treatment	7.4	3.9–11.1	10.0	3.7–15.8	10.2	6.2–16.7
SO_4^{2-}	Reference	75.1	68.6–88.9	59.9	13.8–92.7	52.8	37.6–70.5
	Treatment	69.4	63.3–79.0	52.5	11.3–83.0	64.0	36.0–83.9
NO_3^-	Reference	64.4	0.1–144.0	6.4	0.2–29.5	5.3	0.6–27.6
	Treatment	63.0	1.4–96.3	11.7	1.5–40.3	114.5	54.6–212.5
Ca^{2+}	Reference	25.5	21.7–30.2	24.0	12.3–48.2	43.5	16.2–59.6
	Treatment	36.3	23.2–43.2	28.0	18.9–53.6	36.9	26.6–50.5
Mg^{2+}	Reference	7.8	6.2–9.1	7.2	2.2–12.8	10.7	5.3–14.8
	Treatment	8.8	5.8–10.3	8.8	5.4–14.4	10.3	4.5–16.0
K^+	Reference	6.5	3.8–9.7	19.6	8.4–37.4	15.4	2.3–25.9
	Treatment	6.6	4.1–11.0	8.7	5.1–11.3	23.1	8.2–44.0
Na^+	Reference	28.5	17.4–41.0	35.1	27.0–46.5	41.2	20.9–55.7
	Treatment	23.2	20.9–26.2	35.9	29.6–49.6	45.6	30.9–64.5
NH_4^+	Reference	2.9	0.7–8.5	56.3	18.5–97.9	22.9	4.4–52.3
	Treatment	1.1	0.1–1.7	12.9	2.2–27.7	7.5	1.4–23.8
Al_{tm}	Reference	45.6	22.1–69.8	34.0	18.0–64.3	15.6	11.8–23.1
	Treatment	22.8	19.0–29.4	35.1	18.3–56.0	23.4	14.3–49.5
Al_{im}	Reference	30.4	19.9–41.6	20.1	14.4–33.0	8.8	6.1–13.4
	Treatment	19.0	16.6–20.6	18.1	10.4–24.6	18.8	11.1–32.6
Al_{om}	Reference	5.4	4.1–6.8	10.3	5.9–20.0	6.7	4.9–9.9
	Treatment	5.5	5.0–6.4	6.5	5.1–9.2	5.2	2.8–7.5

Solution chemistry

We checked lysimeters for water samples about monthly during snow-free periods. In 1989, we found enough water for chemical analyses during three distinct periods: (i) the spring-snowmelt period (20 March, 3 April, 20 April); (ii) early summer (12 June, 18 July); and (iii) again after plant senescence in autumn (10 October). Otherwise, the lysimeters yielded too little water for chemical analysis (i.e., < 20 ml). We summarize these data in Table 3. In 1990, the lysimeters had only enough water for chemical analysis during the snowmelt period and in autumn, whereas in 1991 we made collections only during the snowmelt period.

In the three wetland types, peat pore water had low to neutral pH values of 4.20 to 6.28 (Table 3). Some solutes showed relatively uniform concentrations among sites (i.e., Cl^-, SO_4^{2-}, Mg^{2+}, Al_{om}), whereas other solutes were more variable in peat pore water (i.e., DOC, DIC, NO_3^-, K^+, Na^+, NH_4^+, Al_{tm}, Al_{im}). The concentration of Ca^{2+} in peat pore water averaged across reference and treatment subcatchments were similar among the three sites. At all three sites, both NO_3^- and NH_4^+ were prevalent in peat pore water, but when NO_3^- dominated (e.g., in the poor fen), then NH_4^+ concentration was low, and vice versus (e.g., in beaver-pond swamp).

Following the $CaCO_3$ application, pore water pH and the concentrations of Ca^{2+} and NH_4^+ increased significantly; in contrast, the concentrations of Al_{tm} and Al_{im} decreased significantly with liming (Table 4). The other solutes studied had non significant (all P's $> .05$) treatment effects, although interactions between treatment, wetland type, and depth were significant in some cases (analysis not shown).

In particular, liming caused an immediate (i.e., autumn 1989) and sustained increase in the concentration of Ca^{2+} by more then 100 μmol/l in peat pore water at the 5 cm depth in the poor fen and in the riparian swamp, whereas the increase was delayed (i.e., autumn 1990) in the beaver-pond swamp (Fig. 2). The deeper peat in each site showed a delayed (i.e., autumn 1990 or later) and lower response in Ca^{2+} concentrations.

A more typical response is that for NO_3^-, for example (Fig. 3), with no consistent pattern in the concentration among treatment and reference sites for each wetland type, as well as nothing attributed to the liming.

Discussion

Peat chemistry

Liming and subsequent dissolution of $CaCO_3$ affected peat chemistry mostly by increasing the pool size of exchangeable Ca, whereas it increased pH to a lesser extent. The response in Ca confirms the casual notion that peat retains added Ca, making peat a likely target for liming to increase Ca availability in acidic environments (Jenkins et al. 1991). However, we emphasize that peat in the Woods Lake watershed had an extremely low concentration of Ca before liming, with concentrations typical of those in the most nutrient deficient,

Table 4. Solute concentrations (μmol/l except standard unit for pH) in peat pore water within Woods Lake watershed. Means and range (averaged across wetland site and 5 and 20 cm depths). Pre-treatment samples were collected in 1989, and post-treatment samples were collected in 1990 and 1991.

Solute	Subcatchment	Pre-treatment		Post-treatment	
		Mean	Range	Mean	Range
pH	Reference	4.98	4.44–6.28	4.59	4.27–5.88
	Treatment	4.69	4.20–5.43	4.87	4.40–6.19
DOC	Reference	957	355–2825	1368	322–4081
	Treatment	629	358–1418	1086	389–2210
DIC	Reference	251	60–960	408	93–1280
	Treatment	205	24–1117	414	48–1441
Cl^-	Reference	10.0	6.3–17.0	11.1	1.3–20.9
	Treatment	9.2	3.7–16.7	12.4	0.6–50.2
SO_4^{2-}	Reference	62.6	13.8–92.7	61.1	1.0–115.6
	Treatment	62.0	11.3–83.9	64.7	9.9–123.8
NO_3^-	Reference	25.4	0.1–144.0	51.2	1.6–126.3
	Treatment	63.1	1.4–212.5	45.9	1.6–212.4
Ca^{2+}	Reference	31.0	12.3–59.6	35.2	17.5–57.4
	Treatment	33.7	18.9–53.6	87.2	21.5–227.0
Mg^{2+}	Reference	8.6	2.2–14.8	10.0	6.2–15.2
	Treatment	9.3	4.5–16.0	11.4	5.8–19.3
K^+	Reference	13.8	2.3–37.4	2.0	0.6–5.1
	Treatment	12.8	41.–44.0	10.8	0.6–117.4
Na^+	Reference	34.9	17.4–55.7	29.5	21.8–43.5
	Treatment	34.9	20.9–64.5	34.1	17.4–60.9
NH_4^+	Reference	27.4	0.7–97.9	38.1	0.8–130.6
	Treatment	7.2	0.1–27.7	14.9	0.7–81.7
Al_{tm}	Reference	31.7	11.8–69.8	27.6	8.1–40.9
	Treatment	27.1	14.3–56.0	10.8	3.7–19.2
Al_{im}	Reference	19.8	6.1–41.6	32.3	25.3–39.4
	Treatment	18.6	10.4–32.6	10.1	5.1–18.7
Al_{om}	Reference	7.5	4.1–20.0	8.7	3.6–20.8
	Treatment	5.7	2.8–9.2	5.6	1.4–11.9

ombrotrophic bogs (i.e., < 13 cmol$_c$ kg^{-1}; Stanek & Jeglum 1977), i.e., peatlands that receive solutes in atmospheric deposition alone (Sjors 1952). Soil solutions in the Adirondack Mountain region of New York state have low Ca^{2+} concentrations (Geary & Driscoll 1996) because of the granitic gneiss bedrock (Newton et al. 1987); therefore, any contact with the peat probably supplies little Ca to the peat.

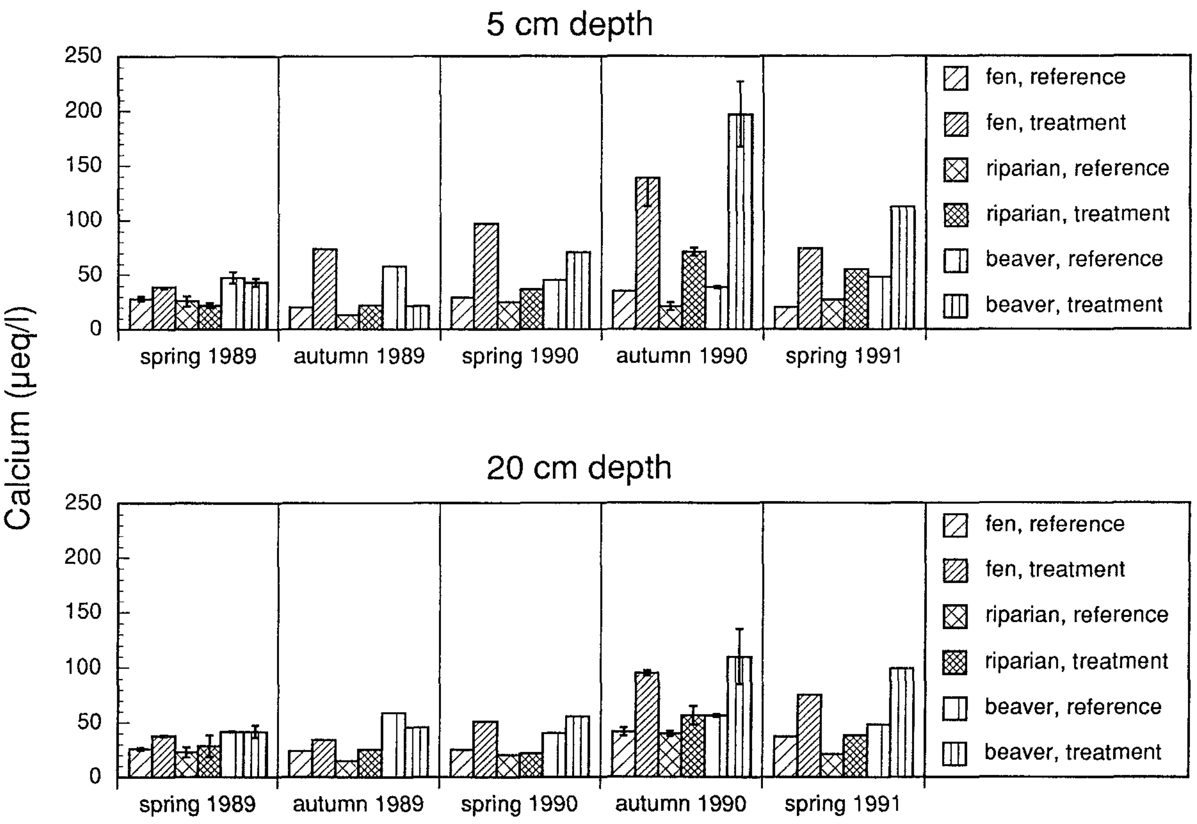

Fig. 2. Comparison of Ca^{2+} concentration in peat pore water at three different sites within Woods Lake watershed, which received $CaCO_3$ application in October 1989. Each value is the mean of three replicates per site and per sampling date, averaged for 5 and 20 cm depths.

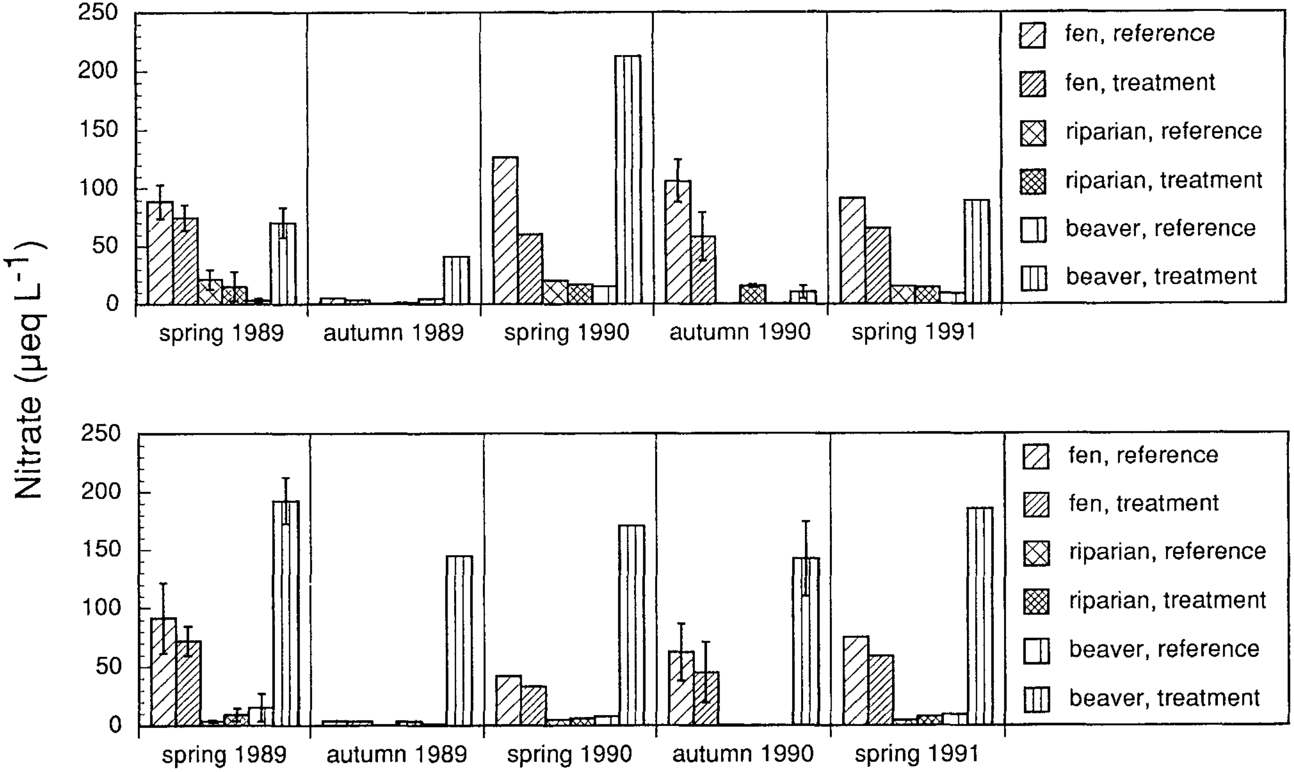

Fig. 3. Comparison of NO_3^- concentration in peat pore water at three different sites within Woods Lake watershed, which received $CaCO_3$ application in October 1989. Each value is the mean of three replicates per site and per sampling date, averaged for 5 and 20 cm depths.

Even after liming, peat still had a relatively small pool of exchangeable Ca, with values typical of those in relatively nutrient-deficient, poor fens (i.e., 10 to 40 $\text{cmol}_c\ \text{kg}^{-1}$; Vitt & Chee 1990). For example, peat from nutrient-rich fens can have Ca concentrations as high as 400 $\text{cmol}_c\ \text{kg}^{-1}$ (Vitt & Chee 1990). Consequently, liming did not appear to saturate exchange sites with Ca.

We estimated 3 Mg $CaCO_3$ ha^{-1} had to dissolve to account for the observed increase in exchangeable Ca concentration of the peat at each site. Moreover, the amount of undissolved $CaCO_3$ recovered in peat samples one year later (Fig. 1) accounted for an additional 2.0 to 4.4 Mg $CaCO_3$ ha^{-1}, depending on the site, resulting in an 'apparent' $CaCO_3$ application of 5 to 7.4 Mg $CaCO_3$ ha^{-1}. On the other hand, we estimated the amount of lime added during the application period (Driscoll et al. 1996) was only 0.72 Mg $CaCO_3$ ha^{-1} in the poor fen, 3.35 Mg $CaCO_3$ ha^{-1} in the riparian swamp, and 4.74 Mg $CaCO_3$ ha^{-1} in the beaver-pond swamp. The largest discrepancy occurred in the poor fen where the application was particularly small. At the other extreme, the $CaCO_3$ budget nearly balanced in the beaver-pond swamp. Some reasons for the discrepancy include (i) additional $CaCO_3$ deposited in throughfall or by erosion from uplands that bypassed the collectors and (ii) groundwater discharge of Ca^{2+} from surrounding uplands, combined with Ca adsorption by peat. The second reason confirms the notion our study sites were hydrologically connected to local groundwater and not domed peatlands in areas of groundwater recharge (cf., Siegel 1983).

As opposed to the Ca response, other aspects of peat chemistry showed little change following liming. The increase in peat pH, for example, was not at all dramatic, except in the poor fen, which was fitting given the low pH prior to liming. Notwithstanding, peat pH was relatively high for the Ca status (Moore & Bellamy 1974), suggesting some factor other than base cation concentration must buffer these peats and limit the pH response following liming.

Microbial activity under anaerobic conditions can supply acid neutralizing capacity (Schiff & Anderson 1986) by consuming H^+. The rates of microbial respiration reported here (Table 2) were higher than findings for other peat studied accordingly (i.e., anaerobic, *in vitro* incubations). For example, Bridgham & Richardson (1992) measured microbial respiration rates of only 4 to 20 nmol cm^{-3} hr^{-1} for peat from pocosin peatlands in North Carolina, and Magnusson (1993) reported rates of about 1 to 20 nmol cm^{-3} hr^{-1} for peat from forested poor fens in Sweden. In contrast, Yavitt & Lang (1990) measured microbial respiration rates of 20 to 153 nmol cm^{-3} hr^{-1} for peat from poor fens in West Virginia. The magnitude of acid neutralizing capacity generated by this level of microbial activity is unclear without knowing the pathways involved (cf., Mattson & Likens 1992), but it is likely large.

Sulfate reduction is one such pathway of anaerobic microbial respiration. The SO_4 reduction rates reported here were typical of rates for other freshwater environments, even though they were sustained by quite lower SO_4^{2-} concentration. For example, the rates shown in Table 2 are greater than maximum rates of about 1 nmol cm^{-3} hr^{-1} for sediments of shallow soft water lakes in the Netherlands (Schuurkes & Kok 1988) and about equal to rates of 30 nmol cm^{-3} hr^{-1} for sediments of Lake Constance in Germany (Bak & Pfennig 1991) and 7 nmol cm^{-3} hr^{-1} for *Sphagnum*-derived peat in poor fens West Virginia (Wieder & Lang 1988). Notwithstanding, SO_4^{2-} concentrations measured in each of those studies were >150 μmol/l versus concentrations <100 μmol/l measured in our study. In our study, SO_4 reduction would consume the entire dissolved pool of SO_4^{2-} in less than one day. Obviously there is either a high, continuous rate of SO_4^{2-} supply to the peat or oxidation of reduced sulfide resupplies SO_4^{2-}.

Another indication of the magnitude of SO_4 reduction in the peat is the comparison with SO_4 reduction in Woods Lake sediments. Rudd et al. (1986) estimated SO_4 reduction rates on a depth-integrated basis of 7.5 μmol m^{-2} d^{-1} for lake sediments compared to our depth-integrated estimate of 1950 μmol m^{-2} d^{-1} in October and 1430 μmol m^{-2} d^{-1} in May. Unfortunately we can not ascertain the amount of acid neutralizing capacity produced by these SO_4 reduction rates without knowing the fate of reduced products from SO_4 reduction (Anderson & Schiff 1987), but the magnitude must be large.

Both microbial respiration rates and rates of SO_4 reduction were unaffected by liming. There is a general notion in the literature, however, that liming increases microbial respiration rates (cf., Haynes 1984). Other studies have reported such a response following liming (cf., Zelles et al. 1987); however, the response is usually not dramatic. A large response of microbial respiration to liming generally occurs where there is sufficient labile organic matter to fuel the additional microbial activity, regardless of the improvement in pH conditions. For example, Condron et al. (1993) showed a modest (about 50%) increase in microbial respiration following liming with $Ca(OH)_2$, but adding fresh organic matter along with the lime resulted in a more than a 10-fold rate increase. It is also possible that some of the CO_2 produced by microbial activity went towards $CaCO_3$ dissolution rather than accumulating in the incubation vessel.

Pore water chemistry

Our results for solute concentrations in peat pore waters agree with findings for other nutrient-deficient peatlands in which H^+ and Ca^{2+} are the dominant cations and SO_4^{2-} or DOC are the dominant anions (Gorham et al. 1985). In our study, concentrations of Ca^{2+} in peat pore waters were more typical of ombrotrophic bogs (Gorham et al. 1985) than more nutrient-poor fens (Vitt & Chee 1990). Indeed $CaCO_3$ treated peat had concentrations of Ca^{2+} similar to those in moderately rich fens and much lower than concentrations of 1,000 to 2,000 μmol/l in extremely rich fens (Vitt & Chee 1990).

We expected liming and dissolution of $CaCO_3$ to cause a sharp increase in DIC. Without $CaCO_3$, DIC concentrations can increase only if CO_2 produced by microbial respiration accumulates in the system rather than emitted to the atmosphere (cf., Mattson & Likens 1993). When $CaCO_3$ is present, however, CO_2 from the dissolution of $CaCO_3$ tends to swamp that produced microbially, causing a sharp increase in DIC concentrations (Cirmo & Driscoll 1996). In our studies, concentrations of DIC in peat pore water were typical of other peatlands in the region (Blancher & McNicol 1987) – and the slight increase in DIC following liming suggests little $CaCO_3$ actually dissolved in the peat or, possibly, the CO_2 produced from $CaCO_3$ dissolution was leached as DIC to downstream water. Further, we did not detect an increase in CO_2 emission into the atmosphere above the peat surface following liming (Yavitt & Newton 1990). The additional CO_2 could have primed microbial activity, especially autotrophic bacteria that consumed CO_2.

However, any change in microbial activity also should have produced or consumed DOC and changed the DOC concentration accordingly. We did find the highest DOC concentrations in peat pore water of the treatment subcatchments (Table 4), suggesting a change in microbial activity following liming; however, the increase was within the variation in DOC concentrations observed before liming (Table 4) and similar to findings in other peatlands with an active population of anaerobic microorganisms (Yavitt & Lang 1990). Moreover, the lack of a large DOC response is consistent with our inability to measure changes in microbial respiration rates by incubated peat samples (Table 2). Cronan et al. (1992) also found that liming with dolomitic limestone did not affect DOC concentrations significantly in a red pine forest floor.

Liming had little effect on concentrations of inorganic N (NH_4^+, NO_3^-), which contrasts sharply the large NO_3^- increase in both the forest floor (Simmons et al. 1996) and in forest soil solutions (Geary & Driscoll 1996) and the anticipated increase in microbially produced NH_4^+ under anaerobic conditions (cf., Buresh & Patrick 1978). In contrast, NO_3^- concentration also did not increase within the beaver-pond at Woods Lake following liming (Cirmo & Driscoll 1996). A combination of the following factors probably limited accumulation of NO_3^- in peat pore water in both reference and treatment subcatchments: (i) relatively low pH values that inhibit autotrophic nitrifying bacteria (Belser 1979); (ii) poorly aerated conditions; and (iii) not enough

N cycling to flow through the nitrification pathway. Total N concentrations $<2.0\%$ in peat in our study area (0.87 to 1.3%, J.B. Yavitt, unpublished data) are too low to support substantial N transformations (cf., Williams & Sparling 1988); hence, the slight increase in pH following liming apparently could not overcome the aeration and N limitation of nitrification. Indeed the highest concentrations of NO_3^- occurred in peat pore water in the beaver-pond swamp following liming, and then only at the 20 cm depth. However, the lysimeter at this site was in basal peat, suggesting it received NO_3^- in groundwater discharge beneath the peat deposit.

On the other hand, NH_4^+ concentrations in peat pore water prior to liming were much higher than typical concentrations even in nutrient-rich fens (Vitt & Chee 1990). In both years following liming, however, our study sites experienced quite dry conditions that may have limited the establishment of intense anaerobic conditions necessary to support anaerobic production of NH_4^+ (Buresh & Patrick 1978).

Liming was strong enough to decrease concentrations of Al_{im} by 50%. Such a decrease represents a substantial improvement in water quality, given the toxicity of Al_{im} in aquatic environments (Driscoll et al. 1980). Concentrations of Al_{tm} were within the concentration range of 0.7 to 74 μmol/l found in several North American peatlands studied by Helmer et al. (1990). However, Helmer et al. (1990) found that Al_{tm} was mostly bound organically versus our finding predominantly Al_{im} rather than Al_{om}. We also had lower DOC concentrations compared to the peatlands studied by Helmer et al. (1990), suggesting that the DOC was relatively saturated by Al. Some evidence for this is the higher Al_{om}:DOC ratio of 0.43 μmol mg^{-1} in our studies compared to the ratio of 0.23 μmol mg^{-1} reported by Helmer's et al. (1990). Nonetheless, reducing Al_{im} represents another benefit of liming peatlands.

Conclusions

The results illustrate the relatively small $CaCO_3$ dosage applied in our study improved water quality, especially Ca^{2+} and Al_{im}. Other aspects of peat and pore water chemistry did not change or were not perceptible within the natural spatial and temporal variability that characterizes peatlands in the study region. A larger dosage of $CaCO_3$ might have had a more profound effect on peat and pore water chemistry. For example, Stoner & Donald (1991) recommend liming a peatland with 20 Mg limestone per ha to affect surface water quality. It is important to remember that microbial processes largely govern peat chemistry, and liming alone might not influence such processes without additional labile carbon to fuel any enhanced activity.

Apart from chemical considerations, specific information on hydrology also is necessary to predict how peatland liming affects the entire watershed. Peatlands occur in groundwater recharge, as well as groundwater discharge, areas. However, leaching from peatlands might be more variable and less frequent than expected. Because peat can retain 10-times its own mass in water, even seemingly saturated peat may not become a source of surface water. For example, our sites did not contribute to surface water throughout most of the summertime; hence, it might be prudent to invoke riparian wetlands in watershed liming strategies only during the spring snowmelt period and possibly in late autumn after seasonal plant senescence.

Acknowledgments

Research supported by grants from Living Lakes Inc., the Electric Power Research Institute, Empire State Electric Energy Research Corporation, and the US Fish and Wildlife Service. We thank Chad Gubala and Charley Driscoll for advice concerning chemical analyses.

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