Buffering an Acidic Stream in New Hampshire with a Silicate Mineral

Gene E. Likens,[1,2] Donald C. Buso,[2] Brian K. Dresser,[2,3] Emily S. Bernhardt,[2,4,5]
Robert O. Hall Jr,[6] Kate H. Macneale,[2,4,7] and Scott W. Bailey[8]

Abstract

Ground and pelletized Wollastonite (Wo; $CaSiO_3$) was added to a 50-m reach of an anthropogenically acidified stream within the Hubbard Brook Experimental Forest, New Hampshire, to evaluate its buffering and restoration potential. The Wo was highly effective in raising the pH, acid-neutralizing capacity (ANC), dissolved inorganic carbon (DIC), and Ca^{2+} concentrations of the stream water, but during the short duration of the experiment had no discernable effect on the stream biota. After initial, spike-like fluctuations in pH and concentrations of ANC, DIC, and Ca^{2+}, the relatively slow dissolution rates of the Wo dampened extreme concentrations and contributed to relatively long-lasting (4 months) amelioration of stream-water acidity. Changes in concentrations of Ca^{2+}, dissolved Si, ANC, and DIC were inversely related to streamflow. After several high, stream-discharge events, concentrations quickly and consistently returned to pre-event conditions.

Key words: **acid rain, Hubbard Brook, stream chemistry, stream ecosystems, stream restoration, Wollastonite.**

Introduction

Many lakes and streams throughout eastern North America have been acidified in recent decades from the effects of acid deposition. This anthropogenic acidification has caused numerous adverse biogeochemical changes, including degradation of chemical environments and impoverishment of species assemblages (e.g., Likens et al. 1979; Charles 1991; Driscoll et al. 2001).

Two different approaches are being used in the United States to reverse these adverse changes: (1) the 1990 Clean Air Act Amendments proposed to reduce the major precursors to acid deposition, that is, sulfur dioxide emissions by 10 million mton/year below 1980 values by the year 2000, and nitrogen oxide emissions by lesser amounts, and (2) additions of neutralizing compounds, such as lime, added directly to surface waters and their drainage basins. Both of these approaches have produced limited amelioration so far and, as a result, aquatic ecosystems have recovered very little or slowly from the adverse effects of acid deposition in eastern North America (e.g., Stoddard et al. 1999, 2003; Driscoll et al. 2001; Likens et al. 2001).

Liming is not a new approach for mitigating ecological effects in acidified, aquatic ecosystems. Hasler and colleagues (Hasler et al. 1951; Stross & Hasler 1960) successfully added hydrated lime to naturally acidic lakes in northern Wisconsin some 50 years ago in an attempt to "alkalinize" and clarify the water and to increase the productivity in relatively unproductive, brown-water lakes. Recently, various field studies have examined the effects of $CaCO_3$, $NaHCO_3$, and $CaCl_2$ additions on anthropogenically acidified aquatic ecosystems in the United States (e.g., Burns 1996; Cirmo & Driscoll 1996; Driscoll et al. 1996; Hall et al. 2001; see review by Schreiber 1996). Under extremely acidic conditions, such as acid-mine drainage, even CaO (from fly ash) has been used for reclamation (Czapowski 1976).

At the Hubbard Brook Experimental Forest (HBEF; 43°56′ N, 71°45′ W) in the White Mountains of New Hampshire, recent and large atmospheric inputs of anthropogenic acid anions, SO_4^{2-} and NO_3^-, and reduced atmospheric inputs of Ca^{2+} and Mg^{2+} are correlated with the depletion of base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) within the ecosystem and have resulted in the acidification ($pH < 5$) of headwater streams (Likens 1992; Hedin et al. 1994; Likens & Bormann 1995; Likens et al. 1996, 1998). Long-term biogeochemical studies in these anthropogenically acidified watershed ecosystems of the HBEF suggest that slowly weathering silicate minerals (e.g., plagioclase) are the predominant source of base cations in stream water (Likens et al. 1998), but other sources may be important (Blum et al. 2002; Bailey et al. 2003*a*). It is estimated that some 21,000 mol Ca/ha have been depleted from soils at HBEF from the effects of acid deposition during

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[1] Address correspondence to G. E. Likens, email likensg@ecostudies.org
[2] Institute of Ecosystem Studies, Millbrook, NY, U.S.A.
[3] Present address: NOAA Fisheries, Gloucester, MA, U.S.A.
[4] Cornell University, Ithaca, NY, U.S.A.
[5] Present address: Duke University, Durham, NC, U.S.A.
[6] University of Wyoming, Laramie, WY, U.S.A.
[7] Present address: Northwest Fisheries Science Center, Seattle, WA, U.S.A.
[8] USDA Forest Service, Campton, NH, U.S.A.

1940–1995 (Likens et al. 1998). Headwater streams in the HBEF before the onset of acidic deposition may have had a pH between 5.5 and 6.5 and an acid-neutralizing capacity of 20–50 μeq/L (Likens et al. 1996).

Here, we report on the experimental addition of Wollastonite (Wo), a natural calcium silicate mineral from the Adirondack Mountains, New York, to a 50-m reach of a headwater stream located some 90 m below the gauging weir of Watershed 1 (W1) within the HBEF during June–October 1999. This experimental manipulation was done to test the alkalinization effect of silicate-bonded Ca^{2+} on stream chemistry and on aquatic biota. Subsequently (October 1999), a watershed-scale addition of Wo with a different binder was made to the whole of W1 immediately upstream of this experimental reach (Peters et al. 2004) terminating our experimental study. As far as we know, this is the first attempt to use a natural, calcium silicate mineral as a restoration tool for anthropogenically acidified streams.

Methods

Study Area

The 50-m experimental reach of this second-order stream had a moderately steep gradient (0.26-m drop/m length) and was a fast-flowing reach with many small waterfalls and shallow riffles. The substrate was a mixture of gravel and coarse sand between numerous boulders and cobbles, with occasional organic debris dams formed by fallen tree boles. Aquatic mosses were common on larger cobbles and boulders but were not abundant. There were at least four small pools in the reach, with water depths up to 0.5 m during periods of moderate flow. Large exposures of bedrock and segments with slow, deep glides were absent from the treated reach. Stream-side vegetation was deciduous, a mixture of sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis* Britt.), and white ash (*Fraxinus americana*). There is no distinct riparian zone along these upland streams in the Hubbard Brook Experimental Forest (HBEF). One obvious area of unchannelized seepage flowed into the stream within the treated reach. There were no fish in this experimental reach and limited periphyton, but typical salamander and invertebrate assemblages were present (Burton 1973; Bernhardt 2001; Macneale 2003).

Experimental Procedures

The 50-m reach was treated with milled and pelletized Wollastonite (Wo) on 18 June 1999 (day of year: d.o.y., 169). Pure Wo ($CaSiO_3$) is 34.5% Ca and 24.2% Si by weight, but typically has impurities of Al_2O_3 and MgO (1.1% each), and Fe (0.2%), Na (<0.1%), and K (<0.1%) (R.T. Vanderbilt Co., Governeur, NY, U.S.A.). The Wo material (Vansil-10) was mined and ground to fine silt-particle size ranging from 4- to 20-μm diameter (median diameter 10 μm) by the manufacturer (R.T. Vanderbilt Co). It then was shipped to a mineral processor for hydraulic compaction and binding (Fuller Company, Catasaqua, PA, U.S.A.) to facilitate handling. The binder was lignin molasses (51.4% organic matter, 5.3% sugars, 2.4% Na, 1.8% Cl, all other inorganic elements <1% by weight; manufacturing specifications from United Molasses Corp., Houston, TX, U.S.A.), which was diluted 1 : 1 with water, and added at 5% to the powdered Wo. This mixture was compacted, granulated, and dried, resulting in a final binder mass in the pelletized Wo of approximately 1.5%. Pellets were subangular "granules" 3 to 7 mm in cross-section.

The Wo granules were spread evenly by hand, using volumetric cups, each holding 350 ± 5 g. Two 1-m long × 4-m wide PVC grids, centered on the stream channel, were used to guide the application. The grids were moved successively downstream during the application. The stream channel varied from about 1.7 to 3.5 m in width in this reach, so some Wo was applied to the adjacent bank on both sides of the stream within the grid areas. Overall, we treated an area of 184 m^2. The area of ambient wetted stream channel treated was 112 m^2 and the bankfull, channel area was 126 m^2, covering the entire 50-m reach.

The mass of Ca^{2+} applied in Wo pellets was roughly 50% greater than the amount of Ca^{2+} depleted from south-facing, headwater watershed ecosystems at HBEF during the previous 50 years (Likens et al. 1998). Correcting for impurities and binder, Wo was applied at about 336 g Wo/m^2 to the experimental reach, or 116 g Ca/m^2 and 81 g Si/m^2. A total of 61.824 kg Wo was added to the experimental reach (37.713 kg directly to the wetted stream channel, 42.164 kg to the bankfull stream area, and 19.660 kg to the adjacent bank area).

Solute Chemistry and Temperature. To establish pretreatment chemical conditions, samples were taken 15 and 8 days before the experimental addition, and then twice each day for 4 days before the addition from sites above, within, and below the experimental reach. Before the experiment, the chemistry of these paired sites was essentially identical and similar to streamwater chemistry in Watershed 1 (W1) above the experimental reach, which had been measured for some 36 years (Likens & Bormann 1995). Samples were taken frequently (15 minutes apart in the treated reach and 1 hour apart in the reference reach) during the first 3 hours of the Wo application: This frequency was reduced to twice a day after that, and once a week after 3 weeks. Several additional samples were taken during high-flow events (spates), both on the rising and falling limb of the W1 hydrograph.

Samples of stream water taken above and below the treated reach were collected in the field in clean 1-L LDPE bottles (Buso et al. 2000) and returned to the laboratory for filtration. After filtration, concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, dissolved Si, pH, and dissolved organic carbon (DOC) were determined. Dissolved inorganic carbon (DIC), dissolved oxygen (DO), acid-neutralizing capacity (ANC), specific electrical conductance (SC), and temperature (° C) were measured on the unfiltered portion of the sample or in situ (see Likens & Bormann 1995 and Buso et al. 2000 for analytical details). We placed recording DO electrodes above and below the study reach to estimate whether short-term respiration changed as a result of the Wo addition. Electrodes were calibrated together and recorded every 10 minutes throughout the day of the addition. We could not calculate actual rates of metabolism because the gas exchange with the atmosphere is unknown, but changes in DO concentration in the downstream probe relative to the upstream probe show whether a change in metabolism occurred. An auto-sampler (N-CON type, N-CON Systems, Inc., New Rochelle, NY, U.S.A.) was used to collect stream samples from the reference (upstream) reach at 1-hr intervals during the day of the application.

Particulate Matter. We used 47-mm diameter Gelman (Pall Gelman Laboratory, Ann Arbor, MI, U.S.A.) polyethersulfonate membrane filters (pore size of 0.45 μm) loaded into clean, nondisposable polycarbonate holders. Collection bottles were shaken (but not constantly agitated), and the contents passed through the filter with a peristaltic pump at a rate of about 200 mL/min. The total volume of water filtered was measured with a graduated cylinder with an error of less than 1%. The average total streamwater volume filtered per sample was 729 and 714 mL from above and below the addition, respectively. Filters were handled with PVC tweezers and stored in 50-mm diameter polystyrene petri dishes. Laboratory-grade, deionized water was filtered to produce analytical blanks.

Filters were treated with concentrated HCl to dissolve the Wo. Samples were evaporated to dryness on a hot plate, taken up in 2N HCl, and then diluted to 0.2N HCl. Resulting solutions were analyzed for metal cations on a Varian Vista ICP (Varian, Inc., Palo Alto, CA, U.S.A.). Known amounts of crushed Wo pellets were added to unused filters and analyzed to determine recovery (approximately 91%). Reference samples collected upstream of the treated reach were analyzed for Ca^{2+} in the same way to determine flux of native particulate materials during the experiment.

Hydrology. Streamflow in the treated reach was based on continuous measurements at the gauging weir for W1 (Federer et al. 1990; Bailey et al. 2003*b*) just upstream of the experimental area.

Element Flux. We used the continuously measured discharge from gauged W1 to calculate the dissolved and suspended particulate Ca^{2+} flux into and out of the treated reach on an hourly basis. Calcium concentration values used in these flux calculations were derived from the average of dissolved concentrations measured in water samples and on filters taken at the beginning and end of specified periods as determined by the samples (see Solute Chemistry and Temperature Section). This average Ca^{2+} concentration was multiplied by the total streamflow in liters between sample collections to determine the total Ca^{2+} flux for each of these periods (Buso et al. 2000). Each period was summed, stepwise for 122 days of the experiment to determine a total value for dissolved or particulate matter export above or below the treated reach. We added to this measured discharge an estimate of water inputs from ungauged areas adjacent to the treated reach, but outside of W1, using surveyed areas and area-flow values proportional to gauged W1. The error for dissolved and particulate fluxes in stream water was estimated at approximately 5% (Buso et al. 2000).

Macroinvertebrates. To assess the effect of the Wo addition on stream macroinvertebrates, we collected drift and emergence samples before and after the application at multiple sites upstream and within the treated reach. We collected 24-hr invertebrate drift samples before and for 3 days after the application to assess any immediate effect on invertebrate drift density. One net was positioned approximately 20 m upstream of the treated reach, one in the middle, one at the end, and one approximately 50 m below the treated reach. Drift nets were positioned on the stream substrate so that each filtered between 50 and 85% of the discharge. We found eight Wo pellets in the net positioned within the treated reach on one day, but otherwise there was no significant accumulation of debris in the nets that obstructed flow during the sampling periods. Streamflow was too low during much of the summer to continue drift sampling or to take quantitative benthic samples. Taxa were identified to genus or to family (Merritt & Cummins 1996).

We collected emerging insects before and for 6 weeks after the application to assess any effect of Wo on the density and phenology of emergence. Emerging insects were collected in traps (Macneale et al. 2002) placed at four sites within and four sites above the treated reach, and at five sites within 200 m upstream of the W1 weir. Traps were emptied every 2 to 3 days. Because the densities of emerging stream macroinvertebrates are low in June and July, we limited analyses to an abundant stonefly (Insecta; Plecoptera; *Leuctra ferruginea*), whose emergent period started within days after the application and ended by 19 August 1999 in this stream.

Results

During the treatment, flow at the gauging station above the treated reach varied widely from 0.001 to 300 L/sec; the baseflow averaged approximately 0.9 L/sec for the period preceding Tropical Storm Floyd in September 1999. Before Tropical Storm Floyd, there were four substantial hydrologic events (spates) (Fig. 1G):

(1) On 2 July 1999 (day of year, d.o.y., 183), brief, heavy showers (approximately 15 mm total rainfall) increased streamflow from approximately 0.1 L/sec at 1100 hours EST to

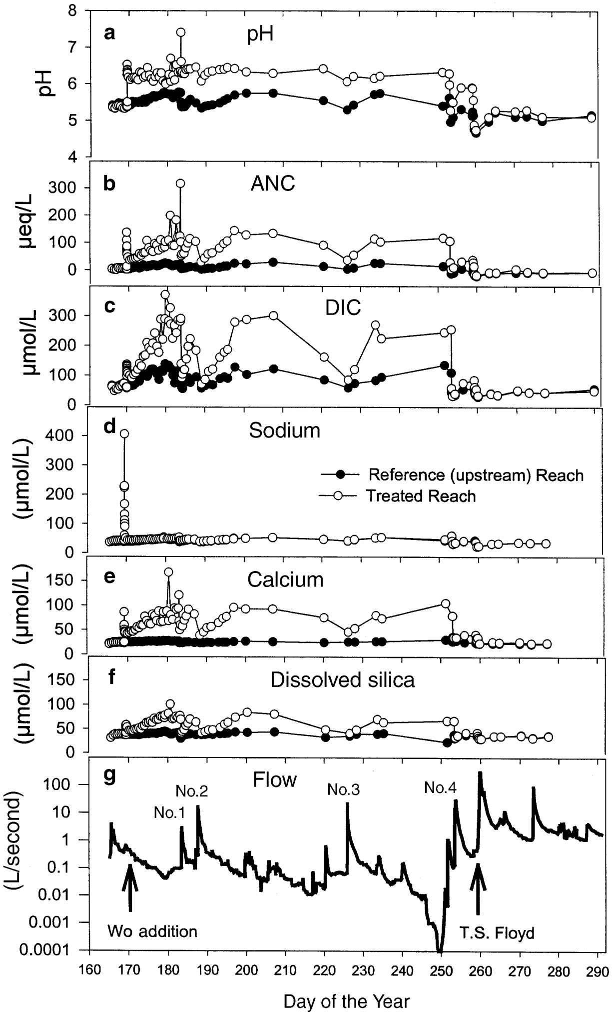

Figure 1. Streamwater chemistry and flow in a treated (○) and upstream reference (●) reach of the stream below the gauging weir in Watershed 1 of the Hubbard Brook Experimental Forest. Wollastonite (Wo) was experimentally added to a 50-m reach (treated reach) on 18 June 1999 (see text for details). Spate no. 4 was caused by rain from Tropical Storm Dennis. ANC, acid-neutralizing capacity; DIC, dissolved inorganic carbon.

2.8 L/sec by 1200 hours; flows returned to less than 0.2 L/sec by 1800 hours. (2) On 6 July 1999 (d.o.y., 187), an intense, brief thundershower (approximately 32 mm of rain) increased flow from approximately 0.3 L/sec at 1500 hours to a peak of approximately 16.3 L/sec at 1545 hours; flows returned to less than 1.0 L/sec within 24 hours. (3) On 13 August 1999 (d.o.y., 225), thundershowers (approximately 25 mm) increased flow from 0.1 L/sec at 1930 hours to 21.9 L/sec at 2200 hours, but returned to less than 1.0 L/sec within 24 hours. It became very dry after this date, and there was no flow in the stream for about 2 weeks. (4) On 10 September 1999 (d.o.y., 253), rain from spent Tropical Storm Dennis (approximately 50 mm of rain) elevated flows from approximately 0.1 L/sec at 0100 hour to a peak of 29.1 L/sec at 1515 hours. Flows returned to less than 1.0 L/sec by d.o.y., 254. (5) On 16 September 1999 (d.o.y., 259), steady, heavy rain from Tropical Storm Floyd increased flow from 0.6 to a peak of 305 L/sec by 2050 hours. These rains continued into midday on 18 September, with a total rainfall of approximately 113.4 mm for the 3 days (47.1 mm on 16 September, 54.2 mm on 17 September, and 12.1 mm on 18 September). Streamflows were greater than 100 L/sec for about 6 hours on 16 September, and stayed above 50 L/sec for most of 17 September. Flows did not drop below 1.0 L/sec for the remainder of the month. On an annual basis, streamflow related to Tropical Storm Floyd represented 11.6% of the total streamflow (973.9 mm) for the 1999–2000 water-year in Watershed 1 (W1), and 55% of the total streamflow during this study. Flow on 16 September 1999 was the fifteenth highest daily flow in W1 since 1956.

After Tropical Storm Floyd, another spate occurred on 30 September 1999 (d.o.y., 273) when approximately 32 mm of rain increased streamflow from approximately 1.3 L/sec at 0600 hours to a peak of 86.3 L/sec by 1200 hours; flows receded more gradually because of reduced transpiration (deciduous leaf fall and cold temperatures), and leveled out at 2.0 L/sec some 6 days later.

Initial Responses

We started the Wollastonite (Wo) application at the top of the experimental reach at 1115 hours ($t = 0$) on 18 June 1999 (d.o.y., 169); it took about 85 minutes to apply the Wo throughout the reach ($t = 85$ minutes). The Wo pellets remained intact on the surface of the stream sediments and on the bank adjacent to the stream, but by $t = 255$ minutes, those in the stream had started to degrade and lose cohesion. Some pellets were still clearly visible in and on the streambed on d.o.y., 266 after the major flushing effect of Tropical Storm Floyd.

This experiment was terminated on 17 October 1999 (d.o.y., 290) because of the aerial application of Wo to the entire W1 area in a separate experiment, upstream of the 50-m treatment area (see Peters et al. 2004 for details of that experiment).

Within 45 minutes of the start, the added Wo impacted the water chemistry at the bottom of the treated reach (Figs. 1 & 2). At $t = 60$ minutes, stream water was slightly cloudy and noticeably tea colored at the bottom of the treated reach. By $t = 255$ minutes, the cloudiness and color were mostly gone from the entire treated reach. Shortly after the addition, the dissolved organic carbon (DOC) concentration rose from 160 ($t = 45$ minutes) to nearly 2,000 µmol/L ($t = 90$ minutes) (evidently from the molasses binder; Fig. 2A), whereas the percent saturation of dissolved oxygen (DO) dropped from 90 to 86% over the same period. The DO in the reference reach remained at approximately 91% saturation for the entire period. The DOC and Na^+ concentrations, both constituents of the binder, declined to pre-treatment concentrations within 24 hours of the application (Figs. 1D & 2A). Subsequent changes in DOC during the remainder of the experiment

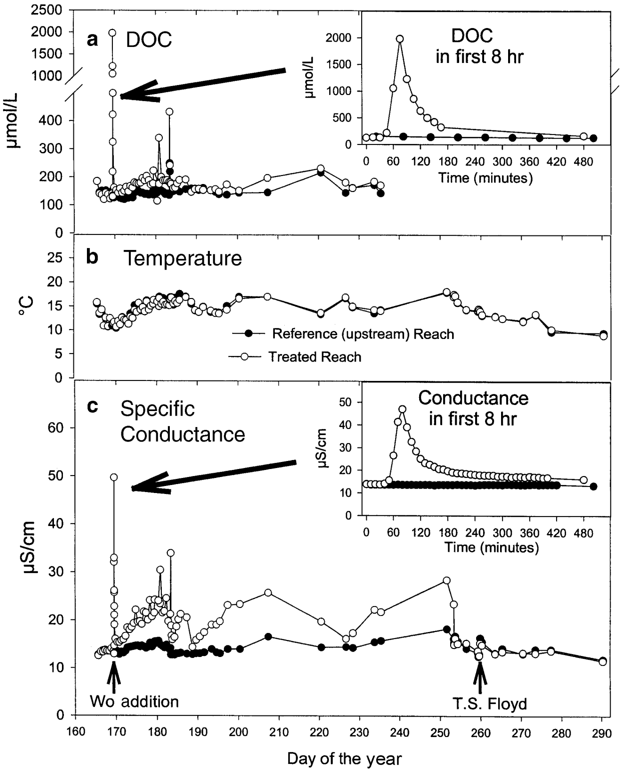

Figure 2. Dissolved organic carbon (DOC), temperature, and specific conductance in a treated (○) and upstream, reference (●) reach (see text and Fig. 1 for additional details). Inserts show response at the initiation of the experiment.

were not associated with changes in Na^+ concentrations, and were concurrent in both treated and untreated sections, suggesting that these were natural shifts in stream chemistry (Figs. 1D & 2A).

At $t = 45$ minutes, the specific conductance (SC) started to rise from approximately 13 µS/cm to a peak of 48 µS/cm at $t = 75$ minutes. The SC then dropped to a stable level of about 20 ± 5 µS/cm at $t = 90$ minutes (Fig. 2C). Most of the measured solutes followed the same pattern.

From $t = 45$ to $t = 75$ minutes, pH rose from 5.5 to 6.5, then remained at about 6.2–6.3 for 85 days even though there were four spates during this time (Fig. 1A & 1G). The pH of the reference section above the treatment varied (range 5.2–5.7), but averaged about 5.5 during the study (Fig. 1A).

After an almost immediate spike in concentration, acid-neutralizing capacity (ANC) and dissolved inorganic carbon (DIC) then increased in the treated reach, but more slowly than pH (Fig. 1). The ANC rose from about 5 to 137 µeq/L and DIC from approximately 50 to 140 µmol/L from $t = 45$ to $t = 75$ minutes (Fig. 1B & 1C).

Sodium climbed from 50 to 400 µmol/L, dropped precipitously to less than 100 µmol/L at $t = 165$ minutes, and within 24 hours, returned to pre-treatment levels (approximately 50 µmol/L; Fig. 1D). We assume this is the period when the binder decomposed and was washed out of the stream.

Magnesium concentrations (not shown) increased by perhaps 10% in the treated section, but only several days after the initial application—this increase may have been in response to the dissolution of impurities (e.g., 1% diopside) in the Wo or to sediment ion-exchange reactions. Potassium concentrations (not shown) did not respond initially to the treatment, although they appeared to be marginally higher (approximately 5–10%) in the treated section for much of the study. Differences in Mg^{2+} and especially K^+ concentrations are close to the expected error of measurement for these solutes.

Calcium and dissolved Si concentrations responded differently initially (Fig. 1E & 1F). The Ca^{2+} concentration increased more quickly, climbing from 25 to about 85 µmol/L at $t = 75$ minutes, then dropped to approximately 50 µmol/L after $t = 105$ minutes. Dissolved Si concentration lagged behind, rising to about 50 from 40 µmol/L at $t = 75$ minutes, and continued to rise to a stable peak of about 60 µmol/L at $t = 105$ minutes. Thus, the Ca : Si (molar) ratio shifted from 0.6 ($t = 0$ minute) to 1.7 ($t = 75$ minutes) and back to approximately 1.0 ($t = 105$ minutes) during the first 100 minutes (Fig. 3). Much of the initial pulse in Ca^{2+} and dissolved Si concentrations was likely due to the dissolution of finer particles of Wo that were added to the stream with the Wo pellets. Subsequent changes in Ca^{2+} and dissolved Si concentrations in stream water were related to dissolution of the larger Wo pellets.

Stream temperature was not significantly different in the above or treated reach at any time during the experiment (Fig. 2B).

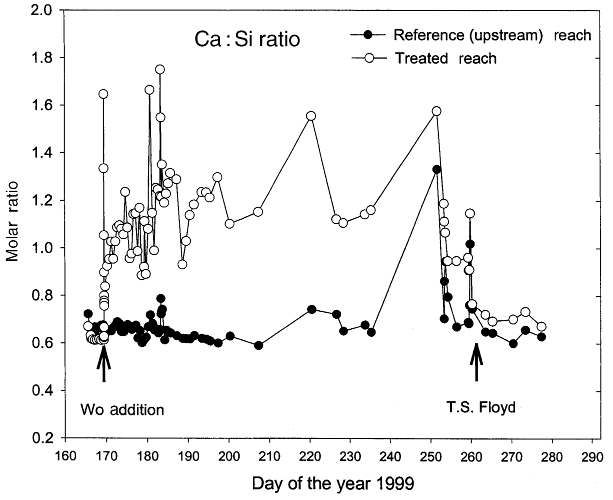

Figure 3. The Ca : Si ratio in a treated (○) and upstream, reference (●) reach (see Fig. 2 for additional details). Wo, Wollastonite.

Longer-Term Responses

After the large, initial changes in streamwater chemistry, subsequent changes were significant, but less dramatic. For example, the DOC concentration in the treated reach returned to near pre-treatment concentrations quickly and were not statistically different than upstream concentrations after 48 hours (Fig. 2A). The SC was significantly higher in the treatment reach (20.4 ± 4.4 μS/cm) than in the reference reach (14.3 ± 1.3 μS/cm) for nearly 3 months (Fig. 2C). The SC declined with increasing flows, indicating dilution, and SC rose as streamflow decreased, paralleling the increase in solute strength at lower flows (Figs. 1 & 2). After spate no. 4 (Tropical Storm Dennis), the SC remained thereafter at reference values (Fig. 2C).

The ANC and DIC concentrations increased more or less steadily to maximum values of 317 and 371 μmol/L, respectively, between d.o.y., 180 and 182, then dropped precipitously on d.o.y., 183 to reference levels in correlation with spate no. 1 (Fig. 1B & 1C). Concentrations rebounded and then declined again with spate no. 2 on d.o.y., 187. This pattern was repeated twice more (spate nos. 3 and 4) before Tropical Storm Floyd. Similar patterns were observed for concentrations of Ca^{2+} and dissolved Si, and more weakly for pH (Fig. 1).

After the first few hours of the experiment, the Ca : Si molar ratio averaged greater than 1.1 in the treated section, although the value was quite variable, and appeared to respond to changes in flow (Fig. 3). Starting some 15 days after the initiation of the treatment, concentrations of Ca^{2+} and dissolved Si were strongly and inversely related to flow during each spate. A Ca : Si ratio greater than 1.4 implies either continued dissolution of Ca^{2+} from Wo at a higher rate than the dissolved Si because the molar ratio in pure Wo is 1.0, or perhaps precipitation of the dissolved Si in some secondary material in the streambed. Other than one sample with a Ca : Si ratio of approximately 1.3 at very low flow (d.o.y., 252), the ambient Ca : Si ratio in the reference reach was quite stable at about 0.6 (Fig. 3). The high ratio (1.3) occurred just as the stream channel became wetted after nearly 2 weeks of essentially zero flow, and was correlated with elevated concentrations of Ca^{2+} and K^{+} (10-fold), unchanged concentrations of Mg^{2+} and Na^{+}, and decreased concentrations of dissolved Si (approximately 50%). The Ca : Si ratio in the treated reach was higher (higher Ca^{2+}) than the reference reach at the end of the experiment, suggesting cation exchange in the sediments or dissolution of residual pellets of Wo.

The pH increased in the treated reach with increasing Ca : Si ratios (Fig. 4). In the reach upstream of the treatment, pH decreased slightly with decreasing Ca : Si ratios, but was highly variable during the experiment (Fig. 4).

Mass Balance Calculations

Based on a mass balance of all inputs to and outputs from the treated reach (Table 1), dissolved Ca^{2+} in stream water was the major mode of loss (87% of total Ca^{2+} input) of Ca^{2+} from the study reach. We estimated that some 12% of the total Ca^{2+} inputs to the reach remained within the sediments of the reach by exchange reactions and/or in incompletely dissolved Wo pellets, and about 0.1% was lost as suspended particulates (Table 1). Based on the amount of Ca^{2+} in Wo applied directly to the bankfull area of the treated reach (14.6 kg), dissolved and suspended particulate outputs and residual represented 312, 4, and 44%, respectively, of this input (Table 1).

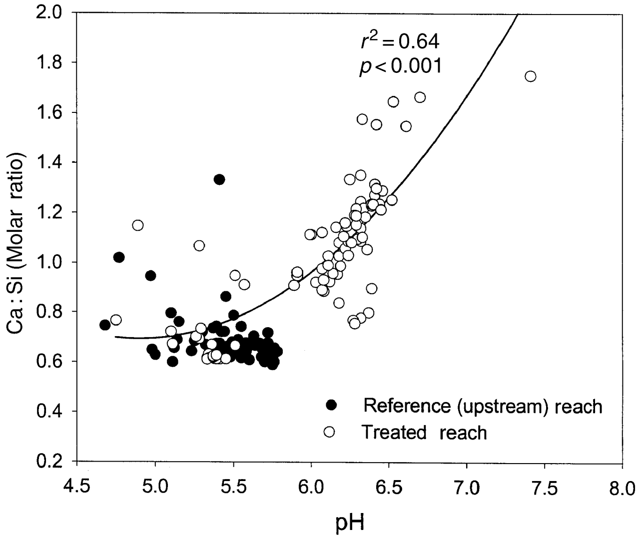

Figure 4. Ca : Si ratios versus pH in a Wollastonite treated (○) and upstream, reference (●) reach (see Fig. 1 for additional details).

The residual, partitioned in Table 1 as exchange, represents an estimate of the net sorption/storage capacity for Ca^{2+} in the sediments of this stream ecosystem. The fine particulate Ca represents suspended particles collected by filtration of water samples. The amount of coarse particulate (pellets?) Ca exported from the treated reach in bedload is quantitatively unknown, but pellets were observed in the stream channel downstream of the treated reach, including in nets used to measure insect drift. Most of the measured suspended fine particulate Ca loss occurred early (first 21 days) in the experiment and was associated with spates nos. 1 and 2. In general, particulate export is exponentially related to discharge in these streams (e.g., Likens & Bormann 1995).

Biological Responses

There was no indication that the Wo application affected the larval macroinvertebrate drift behavior or the density or phenology of emergence of an abundant stonefly (*Leuctra ferruginea*) in the stream ecosystem. Individuals from over 25 aquatic taxa were collected along with some terrestrial adults in drift samples, but there were no significant differences in the taxonomic composition of the drift after the Wo application. Drift densities were low at all sites, Chironomidae: 102 ± 54 (SE) per 100 m^3; all other aquatic taxa

Table 1. Mass balance of calcium after 122 days after Wollastonite (Wo) addition to a 50-m experimental reach below Watershed 1 within the Hubbard Brook Experimental Forest (HBEF), New Hampshire.

	kg	*Estimated Error*	*%*
Calcium inputs to experimental reach[a]			
Applied with Wo to bankfull stream area (126 m^2)	14.6	±1.5	27.8
Dissolved from upstream	37.7	±1.9	71.7
Suspended particulates from upstream	0.3	<0.1	0.5
Total inputs	52.6	±3.4	100.0
Calcium outputs from the experimental reach			
Dissolved in stream water	45.6	±2.3	86.7
Suspended particulates in stream water	0.6	<0.1	0.1
Balance (residual)	6.4	±2.3	12.2
Residual partitioned (estimated)			
Exchanged on stream sediments	3.8	1.3–6.3[b]	7.2
Stored or exported as "pellets"	2.6[c]	5.1–0.1	4.9

[a] Applied to entire experimental area (184 m^2): the values were 21.3 kg and 100.0%. Retained in adjacent bank area, assuming none was lost in dissolved or particulate form in stream water during the study (see Peters et al. 2004): the values were 6.7 kg and 31.5%.

[b] Based on bankfull area of 126 m^2 and a sorption capacity of 10–50 g Ca^{2+}/m^2 during 2 months after an experimental addition of $CaCl_2$ and $NaHCO_3$ to a nearby stream in the HBEF (Hall et al. 2001).

[c] By difference.

combined were 124 ± 39 per $100\,m^3$, but there were no significant differences among sites. In addition, there were no significant differences in the density or in the timing of emergence of *L. ferruginea*. The emergence densities, summed over the entire emergence period, were variable among traps ($284 \pm 69\,m^2$), but there were no significant differences correlated with the Wo application.

Similar to the experimental addition of Ca^{2+} for 2 months in another stream ecosystem at Hubbard Brook Experimental Forest, there were no observable effects on algal biomass, algal accural rates, or community composition (species richness and relative dominance) (Hall et al. 2001; E. S. Bernhardt, unpublished observation; http://www.hubbardbrook.org/currentresearch/streams).

Discussion

Initially, chemical changes in stream water were large after the addition of Wollastonite (Wo) but were predictable based on the ambient concentrations in the stream, the composition of the mineral and binder, and hydrologic events. The pH, acid-neutralizing capacity (ANC), Ca^{2+}, and dissolved Si increased quickly in stream water, reaching steady-state values after a few hours, then generally decreased over the following weeks.

During the course of the experimental manipulation, there were four significant spates before Tropical Storm Floyd with flows ranging from about 1 to about 30 L/sec. These spates quickly reduced dissolved inorganic carbon (DIC), dissolved Si, Ca^{2+}, and ANC concentrations to "ambient" (reference reach) or near-ambient concentrations. The response pattern for pH was similar during these spates, but not as marked relative to returning to baseline levels during the first three spates.

The recovery rate for ANC after spates nos. 2, 3, and 4 was remarkably similar (slopes of 10–12 $\mu eq\,L^{-1}\,day^{-1}$; $r^2 = 0.98$–0.99). Concentrations returned to a new steady-state value of $120 \pm 10\,\mu eq/L$ in about 5 days after spate nos. 2 and 3. The rate of recovery after spate no. 1 was approximately three times faster, and, although the recovery rate for spate no. 4 was similar (slope of 10 $\mu eq\,L^{-1}\,day^{-1}$), the new steady-state value was four times less than that for the previous post-spate periods. Eventually (d.o.y., 261), extremely high flows from Tropical Storm Floyd apparently depleted and/or exported most of the available Wo from the streambed and returned the treated reach to near pre-treatment conditions. There was no recovery of ANC after Tropical Storm Floyd. Moreover, the high flows associated with Tropical Storm Floyd appeared to deplete the buffering capacity of the reference reach as well. The pH levels in both treated and reference reaches were similar in magnitude and response after Tropical Storm Floyd.

Increased flow during major spates diluted concentrations of Ca^{2+}, dissolved Si, DIC, and ANC, but the concentrations rebounded rapidly and consistently after a spate. There were two exceptions to this pattern: (1) concentrations of Ca^{2+} increased markedly and almost instantaneously when the Wo was added to the stream, and (2) Ca^{2+} concentrations did not increase after the major flushing effects of Tropical Storm Floyd. It is probable that the initial dissolution of Wo was enhanced because of broken bonds on mineral surfaces, created during the grinding process. After an initial period of faster release, weathering would be expected to be slower, more in line with long-term weathering rates (e.g., Brantley & Chen 1995).

Overall, however, concentrations changed relatively little (<2 orders of magnitude) compared with large changes (>6 orders of magnitude) in streamflow during the experiment, showing that the buffering capacity of Wo and combined sediment sorption can act except during the highest flow events. Thus, sediment sorption/desorption provides a mechanism to buffer the pH in the water column during high flows, and thereby reduce acidification pulses.

Changes in Ca^{2+} and dissolved Si concentrations were relatively insensitive to changes in flow in the reference reach. Interestingly, however, the stream-chemistry pattern after spates in the reference reach was similar to that in the treated reach as described above, although the magnitude of response was much dampened. This similar pattern would suggest that the Wo acts, regarding dissolution and exchange, similarly to the native Ca minerals in terms of dissolution and stoichiometry in these streams, and is dissimilar to $CaCO_3$ or $Ca(OH)_2$. The ANC and Ca^{2+} components were analogs in both reference and treated reaches of the stream: Y (difference between $[Ca^{2+}]$ reference and treated reach) = 1.01 X (difference in ANC values between reference and treated) + 10.1, in μeq/L.

Calcite ($CaCO_3$) has been used to ameliorate the impact of acid rain in various locations (e.g., Driscoll et al. 1996). Laboratory studies of mineral dissolution suggest that calcite weathers several orders of magnitude faster than Wo: 10^{-8} mol mineral $cm^{-2}\,sec^{-1}$ for calcite (Morse 1983) versus 10^{-12} mol mineral $cm^{-2}\,sec^{-1}$ for Wo (Brantley & Chen 1995). In response to hydrologic events, we expect this contrast in weathering rates to affect a stream addition of calcite compared with Wo as follows: calcite addition would result in a (1) steeper slope in the recovery rate of ANC and dissolved Ca^{2+}, (2) higher steady-state pH, ANC, and Ca^{2+} levels, and (3) calcite would be depleted faster. Also, the undissolved material in the Wo pellets tended to settle in pools at low flows and during the recession limb of the hydrograph after a spate. Because of a slower rate of dissolution, Wo may remain in the stream ecosystem longer than the same weight of $CaCO_3$ and thus could provide longer buffering action for acidified streams. Therefore, there is relatively greater potential for adding Wo versus calcite in management applications, for example, fisheries recovery from acidification, because the Wo application might maintain a more stable chemical environment, with less extreme changes, and possibly for a longer period. The Wo pellets that were spread on the streambank apparently did not migrate overland and were still observed on the banks in early 2002. This finding agrees with Peters et al. (2004) in the subsequent Watershed 1 (W1) experiment. As such, these pellets potentially could buffer the system over an even longer period, once they dissolve and enter water pathways.

Molar ratios of dissolved Ca^{2+} and dissolved Si in stream water suggest that the Ca^{2+} component of the $CaSiO_3$ was elevated in the water column, possibly because of differential dissolution (Bailey & Reesman 1971; Casey et al. 1993) or because the Si is precipitated as a secondary mineral. The Ca : Si ratio increases at the beginning of a rising hydrograph probably as a result of physical abrasion of pellets, and possibly from relatively greater desorption of Ca from soils in the watershed from this stream and/or from stream sediment exchange sites. Much of the variability in the Ca : Si ratios was correlated with three high-flow events when dissolved Si concentrations decreased much more than Ca^{2+} concentrations. The pH of stream water in the treated reach was strongly correlated with the Ca : Si ratio. Higher pH values were correlated with higher Ca : Si ratios, indicating greater buffering.

The average Ca^{2+} concentration during the first 85 days after experimental addition of Wo was roughly equivalent to the mean Ca^{2+} concentration of 180 μeq/L after addition of 120 μeq Ca/L as $CaCl_2$ in a nearby Hubbard Brook Experimental Forest (HBEF) stream (W3) (Hall et al. 2001). Hall et al. (2001) calculated that 10–50% of the added Ca^{2+} was sorbed to the streambed during the $CaCl_2$ addition because of an increase in pH. The pH increase observed here may also have increased base sorption capacity of the sediments.

The binder had a minimal impact on the stream ecosystem, consisting mainly of temporary (<24 hr) increases in Na^+, Cl^-, and dissolved organic carbon (DOC) concentrations. The DOC was only weakly labile, contributing only a small amount to the charge balance, but it was correlated with a slight decrease in stream dissolved oxygen (DO), suggesting a small, but rapid enhancement in microbial respiration rates. The DO response was almost instantaneous (<10 minutes), but not sustained. That is, there was a short-term response in microbe respiration to the labile dissolved organic matter released from the binder during the first few hours after application of the Wo pellets.

A key question for remediation of acidified streams is: When floods cause pulses of low pH in stream water, will the biota respond to the mean condition or to the acute condition? Bradley and Ormerod (2002) found that after 10 years of liming, very few acid-sensitive taxa were found to persist in treated Welsh watersheds, and that acidic pulses during spates (rather than a lack of dispersal to these streams) may have been responsible for the loss of species. LaCroix (1996) found that when using $CaCO_3$ to protect fisheries in Canadian streams, the pH increased to 6.5, but this did not prevent detrimental excursions to pHs as low as 4.5 during snowmelt runoff. We found no short-term (days to months) effect of the Wo application on the macroinvertebrate taxa present during the experiment. These results are not surprising, because unlike an acid addition, the observed increases in pH and cation concentration are not likely to have presented physiologically stressful conditions. Also, because of the relatively short duration of this experiment, we did not expect to be able to detect the colonization and establishment of acid-sensitive taxa as a result of the treatment.

Is it realistic to attempt an amelioration of stream reaches rather than entire watersheds or whole stream corridors? The stream acted temporarily as a net sink for experimentally added Ca^{2+} through cation exchange in the sediments. If 4 kg Ca^{2+} were taken up by sediment exchange in the 50-m segment, then 62 kg might be taken up in the full stream of W1 (770 m long), which is about 63% of average annual Ca^{2+} export (Likens et al. 1998) from that watershed in stream water. Large storms can dilute the output and reacidify the stream. Medium spates reduced Ca^{2+} concentrations less than would be predicted based on dilution, suggesting that the release rates of dissolved Ca^{2+} from sediments is higher at high flows. This result could be due to physical abrasion of residual pellets; however, it could suggest that biogeochemical processes within the stream may, in part, control the watershed-level pattern of Ca^{2+} export (e.g., Bernhardt et al. 2003).

For managers of aquatic ecosystems, the result of this experiment represents a conservative scenario because the Wo was added to a relatively short, 50-m reach, with some 860 m of untreated stream upstream. Thus, we treated only 5.5% of the entire stream, yet the treatment effect lasted 100 days. It is likely that Wo treatment of the entire stream (910 m) would have lasted much longer. At HBEF, streams are steep and extremely flashy, and Wo would probably persist longer in lower gradient streams.

The Wo costs about 10 times more than lime, but this higher cost may be offset by a 1,000 times longer reaction within an anthropogenically acidified aquatic ecosystem. There are many possible ecological and biogeochemical implications of using Wo as a restoration tool, for example, potential effects of the increased dissolved Si, in reducing the toxicity of dissolved Al and on biotic productivity (diatoms), but further research is warranted.

Conclusions

A one-time application of a natural, calcium-rich mineral (Wollastonite [Wo]) produced a 100-day shift (amelioration) in streamwater pH and acid-neutralizing capacity (ANC) of an anthropogenically acidified stream. Concentrations of Ca^{2+} and dissolved Si, ANC, and dissolved inorganic carbon were inversely related to flow in the treated reach. Rain events diluted the streamwater concentrations temporarily and increased acidity, although the stream pH returned consistently to more alkaline conditions within a few hours. Wollastonite might be useful for management applications in anthropogenically acidified streams by restoring buffering capacity. Although Wo pellets may be washed out of a stream rather quickly, especially when streamflow is very high, it may be longer lasting and produce less extremes in water chemistry than applications of calcite.

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