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Biogeochemical responses of two forest streams to a 2-month calcium addition

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SUMMARY

1. Calcium (Ca) has been lost from forest soils at the Hubbard Brook Experimental Forest (HBEF) because of decreased atmospheric input of Ca and high input of acid anions. Through time, this Ca loss has led to low streamwater Ca concentration and this change may affect stream ecosystem processes.
2. To test both the biogeochemical response of streams to increased calcium concentration and the role of streams in retaining calcium lost from soils, we added *c.* 120 μeq Ca L^{-1} as $CaCl_2$ to two second-order streams at HBEF for 2 months. One stream (buffered) also received an equivalent amount of $NaHCO_3$ to simulate the increase in pH and alkalinity if Ca were added with associated HCO_3^- ion. The other stream (unbuffered) received only $CaCl_2$. We collected water samples along a transect above and below the addition site at 11 dates: two before, seven during, and two after the addition.
3. Increase in pH in the buffered stream ranged from 5.6 to about 7.0 in the treated section. There was a net uptake of Ca on all sampling dates during the addition and these uptake rates were positively related to pH. Between 10 and 50% of the added Ca was taken up during the release in the 80-m study reach. In the unbuffered stream, there was net uptake of Ca on only two dates, suggesting lower Ca uptake.
4. Water samples collected after the addition was stopped showed that a small fraction of the added Ca desorbed from sediments; the remainder was apparently in longer-term storage in the sediments. No Ca desorbed from the stream sediments in the unbuffered stream, showing that sorption/desorption may be controlled by a pH-induced increase in the number of exchange sites.
5. These streams appeared to be a significant sink for Ca over a 2-month time scale, and thus, change in streamwater Ca during a year may be due to processing of Ca within the stream channel, as well as to changes in inputs from the catchment.

Keywords: bicarbonate, calcium uptake, Hubbard Brook Experimental Forest, pH, streams

Introduction

Acidic deposition has greatly affected streamwater chemistry and solute budgets for catchments with poorly-buffered soils in many regions of North America (e.g. Charles, 1991). In Hubbard Brook Experimental Forest (HBEF) in New Hampshire (NH) the deposition of acid anions SO_4^{2-} and NO_3^- has caused

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stream water to be acidic, with negative acid-neutralizing capacity (Likens & Bormann, 1995).

One ramification of years of acidic deposition is that storage and export of base cations (e.g. Ca and Mg) from catchments have changed. High deposition of acid anions has leached Ca from the soil that, until 1970, increased Ca concentration in streams. Since 1970, Ca concentration has been dropping in streamwater as exchangeable Ca in forest soils has been exhausted (Likens *et al*., 1998). During the same period, the input of atmospheric base cations has declined, further contributing to a net loss of available base cations in soils and stream water (Hedin *et al*., 1994; Likens, Driscoll & Buso, 1996). This decrease in streamwater Ca has actually coincided with an increase in acid-neutralizing capacity since 1970, because SO_4^{2-} declined at a slightly faster rate than Ca. Current acid-neutralizing capacity at HBEF is considerably lower than presumed pre-industrial values, however (Likens *et al*., 1996).

Increasing and decreasing Ca concentration at HBEF ran counter to our normal expectations in streams. In most studies, Ca concentration is a positive function of acid-neutralizing capacity because studies of lime additions (Burns, 1996; Cirmo & Driscoll, 1996; Schreiber, 1996) and comparisons of geology (Egglishaw, 1968; Krueger & Waters, 1983; Huryn Benke & Ward, 1995) consider Ca and its carbonate anion together. Experimental data show that Ca concentration can interact with pH in determining the survival of fish eggs, which means that Ca itself can be important. (Brown & Sadler, 1989). Conversely, many biological responses to lime addition are attributed to increased pH (e.g. Schreiber, 1996). At HBEF, Ca concentration is negatively related to pH and acid-neutralizing capacity: the highest stream Ca concentration in the streams during the 35-year record was associated with the lowest acid-neutralizing capacity and pH during early 1970s (Likens *et al*., 1996, 1998). Currently, Ca concentrations are decreasing, whereas acid-neutralizing capacity is increasing slightly (Likens *et al*., 1996, 1998). Changes in acid-neutralizing capacity may strongly affect stream processes, such as cation sorption and invertebrate assemblages, as was shown by an experimental addition of sulphuric acid to a HBEF stream (Hall *et al*., 1980).

In this study we address the interaction of Ca and pH in affecting both the biogeochemical response and Ca uptake and storage in the stream channel during experimental Ca additions in two scenarios: (1) with raised acid-neutralizing capacity (i.e. associated with bicarbonate ion) and (2) without bicarbonate and, thus, no change in acid-neutralizing capacity. Streams can control the export of elements from catchments (Fisher *et al*., 1998) and addition of Ca and/or increase in acid-neutralizing capacity may affect how streams transport and store Ca. Hall *et al*. (1980) showed that cations desorbed from sediments when streamwater pH was lowered and, thus, elevated pH may increase base cation sorption. Additionally, any effects of increased Ca may not be apparent during a short-term addition, so we chose to perform a longer-term addition than is typical in stream solute studies. We added calcium to two streams for 7 weeks in summer and measured the response of calcium transport and storage, pH, and aluminium concentration in both treatments.

Methods

Study site

The HBEF is located in the White Mountains of New Hampshire, USA (43° 56′N, 75° 45′W). It has a cool, continental climate with about one third of annual precipitation occurring as snow. The basin is forested primarily by American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.) and yellow birch (*Betula alleghaniensis* Brit.). The streams in this study drain south-facing catchments and study reaches were directly below gauging weirs. The study streams have similar slope and aspect and have an extensive biogeochemical record at HBEF (Likens & Bormann, 1995). Streams are poorly buffered because of granitic bedrock, acidic soils and low calcium concentration (Likens *et al*., 1996).

Manipulation

We added calcium to two stream reaches; one received both $CaCl_2$ and $NaHCO_3$ (hereafter the 'buffered stream'). This reach was 50 m below the weir gauging Watershed 3 (W3), the hydrologic reference at HBEF. The second stream reach received only $CaCl_2$ and was located below the confluence of the stream draining Watershed 4 (W4) and Watershed 1 (W1) (hereafter the 'unbuffered stream'). Each stream had a 30-m reference reach upstream of the addition site. The treatment reach was 80 m in the buffered stream and 50 m in the unbuffered stream. The unbuffered stream reach was shorter due to constraints in the overall drainage and road networks. Discharge was continuously gauged with a V-notch weir above the addition site in W3 and in both W4 (50 m above the addition site) and W1 (250 m above the addition site) (Likens & Bormann, 1995).

Solutes were pumped into both streams using Watson–Marlow 504S peristaltic pumps for 7 weeks from 23 June 1997 to 17 August 1997. Target concentration in the stream for all solutes was 120 μeq L^{-1}. In the buffered stream, $CaCl_2$ and $NaHCO_3$ were added from separate carboys using a two-channel pump head since $CaCO_3$ would precipitate in the concentrated stock solution. Flow rate was monitored once or twice daily and adjusted for discharge measured upstream at the weirs. We did not attempt to match the addition rate of solutes to the few large floods that occurred during the study.

Water samples and analysis

We sampled pH and water chemistry twice before, and approximately weekly during, the manipulation. Because we were unable to keep the addition rate high during severe spates, we waited for baseflow conditions for sampling. We always collected samples in the morning after a night of steady stream flow and before we made our daily adjustment to the addition rate, so that concentration within the stream reach would not change with time. It would have been impossible to calculate uptake length of Ca if either discharge or the addition rate had changed within a few hours prior to sampling. According to established protocols, samples were unfiltered and stored in polyethylene bottles and refrigerated until analysis.

At the end of the 57-day release, we collected water samples just before stopping the pump, and at 6 and 24 h afterwards, to examine release of Ca from sediments.

We measured pH in the field using a temperature-corrected combination electrode. Cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were measured using a Dionex ion chromatograph with a CS12 cation column. Anions (NO_3^-, SO_4^{2-} and Cl^-) were also measured using a Dionex ion chromatograph using an AS4A anion column. As part of using an ion chromatograph, samples were immediately filtered by the autosampler (20 μm nominal pore size) to prevent possible damage to the columns. We estimated acid-neutralizing capacity (μeq L^{-1}) as the charge difference between base cations and acid anions. We also measured cations in the stock solutions of $CaCl_2$ and $NaHCO_3$ to estimate contamination from other cations.

Aluminium was measured as total monomeric (Al_{tm}) and as organically bound monomeric (Al_o). Each was measured spectrophotometrically using the pyrocatechol violet method (Driscoll, 1984; McAvoy *et al*., 1992). Inorganic monomeric (Al_m) was estimated by $Al_{tm} - Al_o$. Dissolved organic carbon (DOC) was measured by UV enhanced persulphate oxidation with the resulting CO_2 quantified with an infrared detector.

We measured uptake of Ca in decomposing leaves in the reference and treatment sections of both streams. Air-dried sugar maple leaves collected the previous autumn were put into onion bags (1-cm mesh size) to make 5-g leaf packs. These packs were placed into the stream on day 1 of the Ca addition (23 June 1998) and sampled at days 1, 8, 17, 23 and 31. Leaves in each pack were subsampled for ash-free dry mass. The remaining leaves were dried, weighed and ground finely using a ball mill and subsampled for calcium analysis. Samples of ground leaves (0.1 g) were ashed for 4 h at 500 °C. Two millilitres of 50% nitric acid were added and evaporated on a hot plate, followed by 2 mL of 6 N hydrochloric acid and evaporated again. Finally, we added 2 mL of 6 N hydrochloric acid and 18 mL deionized water to each crucible and stirred to dissolve the remaining ash. We analyzed each of these extracts for Ca using inductively-coupled plasma spectroscopy. Decay rates (d^{-1}) of leaves in each stream were estimated using an exponential decay model (Webster & Benfield, 1986).

Data analysis

We calculated the uptake length of Ca for each sampling day using a linear form of an exponential uptake model:

$$\ln Ca_x = \ln Ca_0 - kx \tag{1}$$

where Ca_x and Ca_0 are calcium concentrations at x m downstream from the addition site (0 m) and k is the per metre uptake rate (Newbold *et al.*, 1981). Uptake length S_c is equal to k^{-1} and is the average distance travelled by a calcium ion before uptake. We corrected Ca^{2+} concentrations for dilution from groundwater inputs using Cl^- concentration from the $CaCl_2$ addition as a conservative tracer (Webster & Ehrman, 1996).

Using uptake length, we calculated the uptake rate of Ca (U_c μeq m^{-2} h^{-1}) as:

$$U_c = \frac{(Q \times Ca_0)}{(S_c w)} \tag{2}$$

where Q is stream discharge (m^3 h^{-1}) and w is stream width (m) (Newbold *et al.*, 1981). We also calculated uptake velocity (UV m h^{-1}) for Ca uptake, which is the same as the mass-transfer coefficient (Stream Solute Workshop, 1990). It is calculated as:

$$UV = \frac{Q}{(S_c w)} \tag{3}$$

Uptake velocity allows comparison of uptake that is corrected for differences in depth and velocity, which are primary determinants of solute uptake length in HBEF streams (R.O. Hall & E.S. Bernhardt, unpublished).

Changes in chemical composition downstream of the addition site were compared to the upstream reference site using *t*-tests to determine differences. We recognize that, with our unreplicated design, differences cannot strictly be ascribed statistically to our manipulation.

Results

Daily calcium concentration downstream of the addition site was estimated by dividing Ca addition rate by daily discharge. Calculated added Ca concentration ranged from 100 to 200 μeq L^{-1} during baseflow conditions downstream of the addition site (Fig. 1). Measured Ca concentration above background was higher than our target value of 120 μeq L^{-1} (Table 1), because we always sampled before making our daily adjustment of the Ca addition rate and we always sampled when precipitation had not increased discharge the previous night. Spates caused the concentration of Ca added to decrease greatly (Fig. 1). The event of 15 July was the highest of 1997 at HBEF (Hall & Likens, in press). It was impossible to add Ca during that spate since we would have drained the 50-L carboys in 20 min to match the high discharge.

The addition of bicarbonate increased pH in the buffered stream by 1–1.4 pH units from *c.* pH 5.6 to 7.0 downstream of the addition site (Table 1). Background pH was higher in the unbuffered stream (average 6.3) and decreased by 0.1 pH unit downstream of the addition site (Table 1).

In addition to the large increases in Ca, Cl and Na as added solutes, we did see some chemical changes in streamwater downstream of the addition sites (Table 1). Potassium and magnesium were significantly higher downstream in both treatments. This increase was not caused by exchange of Ca, but rather the $CaCl_2$ we used contained small amounts of K and Mg as contaminants. The $NaHCO_3$ contained no detectable cations besides Na. We saw no change in the acid anions SO_4^{2-} and NO_3^- downstream of the addition sites. There was no change in DOC concentration downstream of the addition site in either stream.

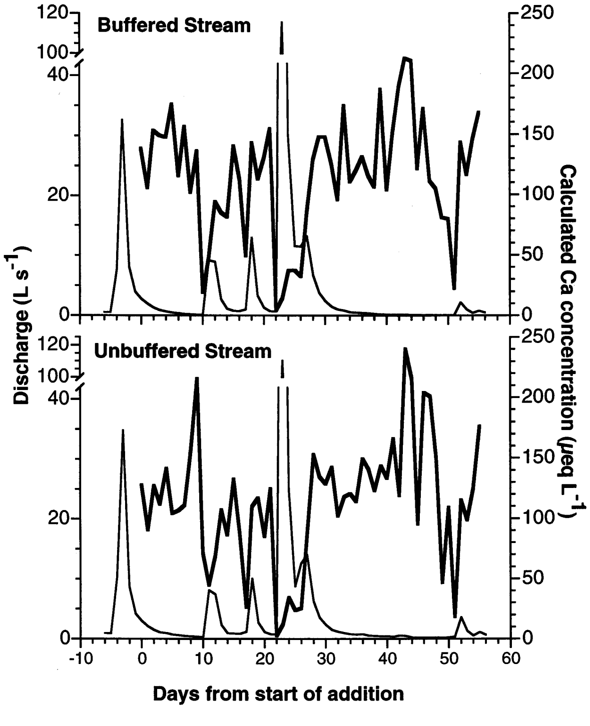

Fig. 1 Daily averaged discharge (thin line) and calculated increase in Ca concentration (thick line) during the 7-week Ca addition in both the buffered and unbuffered stream. Note the axis break on the discharge axis.

Table 1 Change in concentration of major ions below the addition site before and after start of calcium addition

	Buffered stream			Unbuffered stream		
	Mean upstream concentration (μeq L^{-1})	Trt.-ref. pre-treatment (μeq L^{-1})	Trt.-ref. during treatment (μeq L^{-1})	Mean upstream concentration (μeq L^{-1})	Trt.-ref. pre-treatment (μeq L^{-1})	Trt.-ref. during treatment (μeq L^{-1})
Ca^{2+}	66.8	−0.7 (3.7)	179.8 (19.4)	103.2	′−9.1 (2.0)	133.9 (18.2)
Na^{+}	64.4	0.0 (3.9)	181.4 (19.4)	62.5	−3.0 (1.6)	−1.8 (0.9)
Mg^{2+}	27.0	0.0 (1.8)	2.88 (1.41)	32.1	−2.0 (0.2)	−3.2 (0.8)
K^{+}	6.1	0.2 (0.2)	3.7 (0.8)	7.8	−1.4 (0.1)	1.66 (0.9)
Cl^{-}	15.6	−0.2 (0.6)	193.5 (22.9)	14.8	−0.1 (0.3)	158.6 (19.6)
SO_4^{2-}	103.0	−2.0 (5.2)	−1.3 (1.5)	100.9	−0.96 (0.6)	−4.2 (2.3)
NO_3^{-}	3.5	−0.1 (0.2)	−0.4 (0.2)	8.3	−2.4 (0.8)	−2.0 (0.5)
Alkalinity	41.4	1.8 (4.0)	169.0 (13.8)	81.4	−12.0 (4.0)	−17.0 (3.7)
DOC*	178	4.6 (11.5)	−11.1 (3.0)	148	−5.3 (2.2)	−8.6 (3.5)
Al inorganic	2.23	0.15 (0.39)	−1.36 (0.33)	0.73	0.22 (0.12)	0.38 (0.18)
Al organic	5.62	−0.17 (0.23)	−1.68 (0.28)	3.70	0.33 (0.14)	0.11 (0.04)
pH†	5.63	0.08 (0.03)	1.10 (0.09)	6.28	−0.05	−0.1 (0.02)

Each entry represents the mean difference in concentration across sampling dates. Numbers in parentheses are standard errors ($n = 2$ for pre-treatment, $n = 7$ during treatment) Al is reported in both organic and inorganic monomeric forms.

* Units for DOC are μmol L^{-1}.

† pH is unitless.

Aluminium concentration in these streams was low, although both Al_m and Al_o decreased downstream of the addition site in the buffered stream (Table 1). Decreasing Al_{tm} concentration corresponded to increasing pH, as there was a negative relationship between pH and both Al_m and Al_o concentrations when all samples from both streams are considered (Fig. 2). The Al_m was probably converted to particulate Al downstream of the addition site in the buffered stream and deposited on the streambed. Pre-treatment concentration of Al_m was low in both streams, with the buffered stream having a slightly higher pre-treatment concentration because of lower pH. There was little change in Al_{tm} concentration in the unbuffered stream downstream of the addition site. We found no relationship between organic monomeric Al and DOC, when combining all samples from all streams.

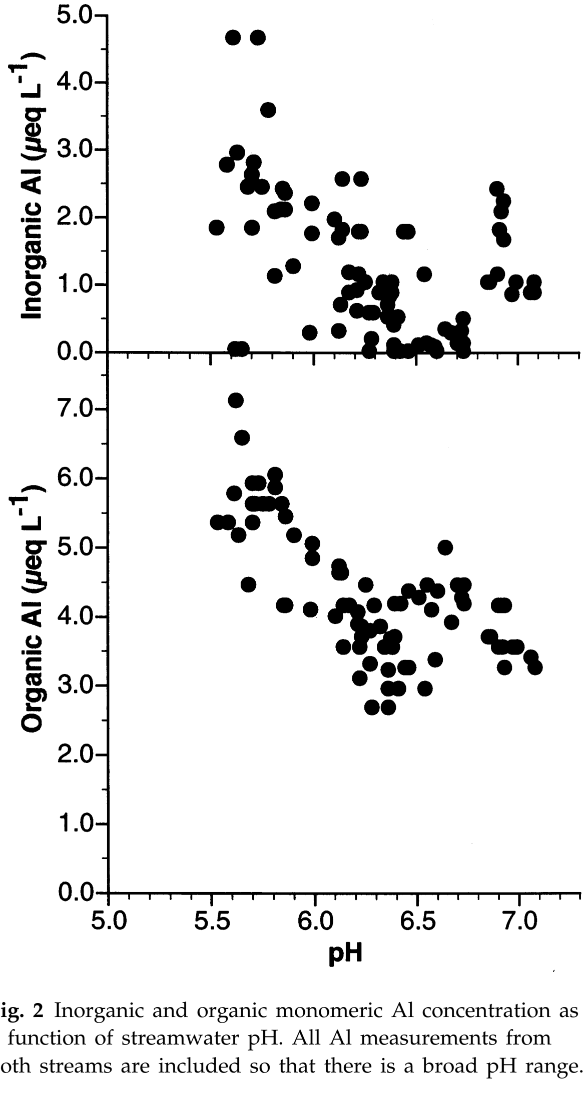

Fig. 2 Inorganic and organic monomeric Al concentration as a function of streamwater pH. All Al measurements from both streams are included so that there is a broad pH range.

There was net Ca removal from the water column each day it was measured in the buffered stream (Table 2). Uptake rate of Ca ranged from 313 to 3300 μeq m^{-2} h^{-1}. In the 80-m reach, 10–50% of the Ca was removed from the water column. Average uptake length for the period was 356 m and showed no tendency to increase or decrease with time. Given that 10–50% of the added Ca disappeared in the 80-m reach, and that we added 700 eq of Ca during the whole period, total Ca retention was probably between 70 and 350 eq/reach (0.9–4.4 kg of Ca). Reach area was 139 m^2; hence, the amount retained on an areal basis ranged from 0.5 to 2.5 eq m^{-2}. Uptake velocity in the buffered stream was positively related to pH (Fig. 3). We estimated the solubility of $CaCO_3$ to ensure that loss of Ca was not caused by precipitation; concentrations of Ca and HCO_3^- were 0.14% of $CaCO_3$ saturation, so precipitation was probably not significant.

There was less Ca retention in the unbuffered stream. Only two of the seven dates had significant relationships between dilution-corrected Ca concentrations and distance downstream. Uptake rates on these two dates averaged 830 μeq m^{-2} h^{-1}, which was within the range observed in the buffered stream.

Leaf packs placed into both reaches of both streams gained in their relative Ca content for the first 1–2 weeks and then lost this Ca later during the decomposition process (Fig. 4). Decay rates were fast. Decay rates in buffered stream reference and treatment sections were 0.029 d^{-1} and 0.017 d^{-1}. Decay rates in unbuffered stream reference and treatment sections were 0.035 d^{-1} and 0.026 d^{-1}. Because of these fast decay rates, there was net loss of Ca in some leaf packs despite the concentration actually increasing with time during the first three weeks. Leaves in the treatment reach of the buffered stream maintained higher Ca than the reference reach throughout the experiment. There was no significant difference after 1 week, even though Ca concentration was increasing in the leaf packs in both reaches. On day 16 and day 23 there was 50 and 100% more Ca on a percentage basis in leaves from the treatment reach relative to the reference reach (Fig. 4); these values were significantly different (t-test $P < 0.05$). Contrary to the buffered stream, there was no evidence that leaves in

Table 2 Uptake of Ca in both streams measured throughout the experiment

Date	Ca uptake length (m)	Measured discharge (L s^{-1})	Ca concentration (μeq L^{-1})	Uptake rate (μeq m^{-2} h^{-1})	% Ca removed at 80 m*
Buffered stream					
25 June	211	1.04	302	3094	32
11 July	704	3.89	288	3299	11
23 July	758	1.51	220	909	10
30 July	234	0.23	208	424	29
5 August	210	0.16	198	313	32
13 August	114	0.09	234	382	50
17 August	261	0.45	296	1058	26
Unbuffered stream					
5 August	316	0.50	246	803	22
13 August	296	0.40	310	862	24

Regressions used to calculate Ca uptake were significant ($P < 0.05$) on every sampling date in the buffered stream, but were only significant for two dates in the unbuffered stream.

* %Ca removed at 80 m is reported for the unbuffered stream to facilitate comparison with the buffered stream. Reach length on the unbuffered stream was 50 m.

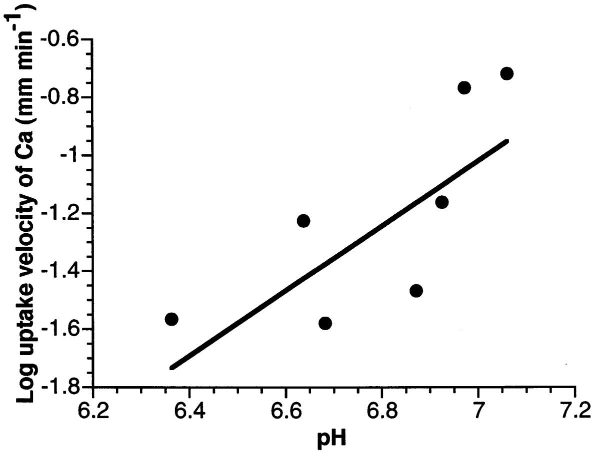

Fig. 3 Relationship between uptake of Ca and pH below the addition site in the buffered stream. Ca uptake is reported as an uptake velocity. Line was fit with least-squares linear regression. Equation is $y = 1.13x - 8.86$ ($r^2 = 0.58$, $P = 0.048$).

the treatment reach of the unbuffered stream contained more Ca than the reference (Fig. 4) (t-test $P > 0.05$).

At the end of the addition period, we observed the generation of Ca in the buffered stream (Fig. 5). Just before shutting off the addition, Ca concentration was slightly higher than Cl concentration downstream of the addition site. Six and 24 h later, much of the Cl had washed out of the reach, yet Ca concentration was still well above background and higher than Cl concentration, suggesting that Ca was being desorbed from sediments. This pattern was not observed for the unbuffered stream, as Cl concentration was consistently higher than Ca concentration 6 and 24 h after the addition, suggesting that no Ca was being released (Fig. 5).

We estimated how much Ca was desorbed in both streams after the Ca addition by comparing actual flux (meq Ca d^{-1}) of Ca through a specific point downstream (e.g. 20 m) with an estimated flux if Ca were only being diluted and not desorbing from sediments (dilution-only) (Fig. 6). Actual flux was computed based on Ca fluxes ($Ca_x * Q$) at 0, 6 and 24 h after the addition was shut off. Dilution-only Ca flux was estimated by multiplying Ca concentration at 0 h after shutoff by the fraction of Cl remaining in the water at each of the three times. By subtracting the dilution-only flux from the actual flux, we estimated total Ca released between that point in the stream and the addition site. Dividing daily flux by area of the stream reach between the addition site and measured flux site gives a release rate (meq m^{-2} d^{-1}). This estimate was made for three sampling sites in each stream (Table 3).

The amount of Ca released in the buffered stream during the 24 h after the addition stopped was about the same or less than the average of the daily uptake of Ca (32 meq m^{-2} d^{-1}), suggesting that little of the total sorbed Ca was released immediately following the addition (Table 3). In the unbuffered stream, we observed no net release, indicating that any immobilized Ca was being stored there.

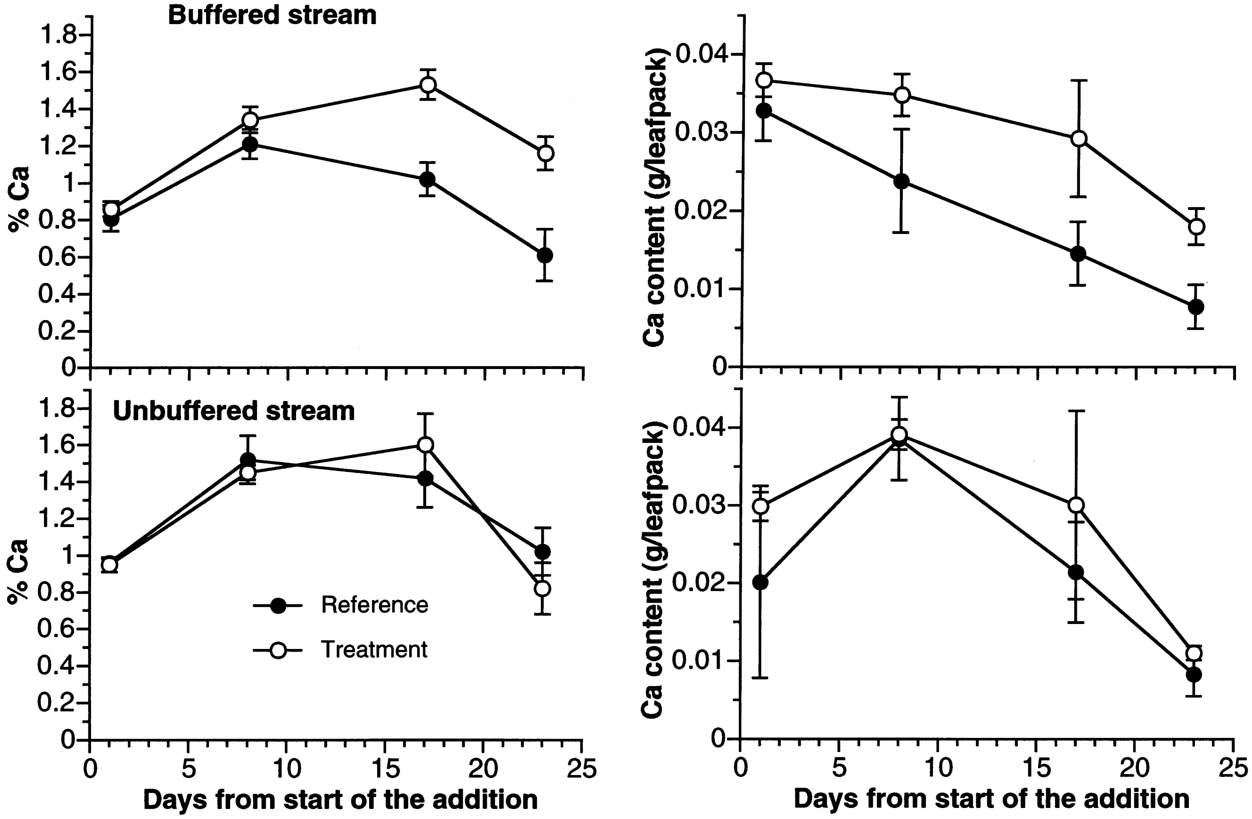

Fig. 4 Concentration of Ca in decaying leaves as a function of time in both catchments. Filled circles are points from upstream reference reach and hollow circles are for treated downstream reach. Ca concentration is reported as % of leaf dry mass.

Discussion

Addition of Ca with a bicarbonate buffer affected stream biogeochemistry more than an unbuffered Ca addition. The pH increased in the buffered stream as expected, and it decreased slightly in the unbuffered stream. We did not see changes in other cations or anions, except for Al_{tm}. Slight increases in K and Mg occurred because of contamination from added $CaCl_2$. When acid was added to a HBEF stream, the concentration of base cations increased, presumably because of replacement by H^+ (Hall *et al.*, 1980). Base cation concentration did not increase in this study (besides Ca); in the unbuffered stream, however, the small decrease in pH downstream could have been caused by displacement of H^+ by Ca.

Both Al_o and Al_m decreased below the addition site in the buffered stream because of increasing pH. The upstream concentration of Al_{tm} was low in both streams because the background pH was high relative to other HBEF streams. The biogeochemical reference stream at HBEF, W6, can have pH near 4.5, particularly during early spring runoff and, thus, has a higher Al_{tm} concentration. Other studies also found decreased Al following lime additions. In a limed Welsh stream, Al declined from about 22 μeq L^{-1} to about 11 μeq L^{-1} (Rundle, Weatherly & Ormerod, 1995). In the drainage stream of Woods Lake in the Adirondack Mountains, Al_m decreased following catchment liming (Burns, 1996). The pH-dependence of Al_m was apparent in this study, but this empirical relationship was not as strong as has been shown in other studies, which could be attributed to the small pH range found in this study (5.4–7.1). Another possibility is that pre-treatment Al_m concentration was already low in proportion to the percentage of particulate Al. With base addition, and thus increasing pH, Al_m can shift to particulate Al. Increased pH probably caused hydrolysis of Al_m and direct precipitation of particulate mineral phases and deposition of particulate Al on the stream bed. Concentrations of DOC did not change in either Ca addition treatment. Increased acid-neutralizing capacity can lower (Hasler, Brynild-son & Helm, 1951) or increase DOC concentrations (Driscoll *et al.*, 1996).

DOC concentration was low in these streams, thus any increase or decrease caused by Ca or bicarbonate addition may be too small to observe.

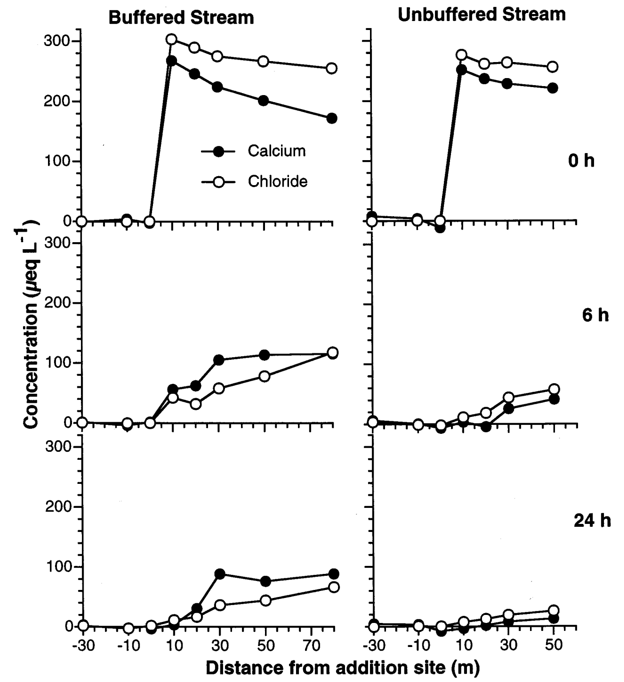

Fig. 5 Ca (filled circle) and Cl (hollow circle) concentrations above background with distance downstream in both streams just before stopping the addition (0 h), and 6 and 24 h after the addition was stopped. Ca concentrations above background were calculated by subtracting the average Ca concentrations in the reference reach at each time.

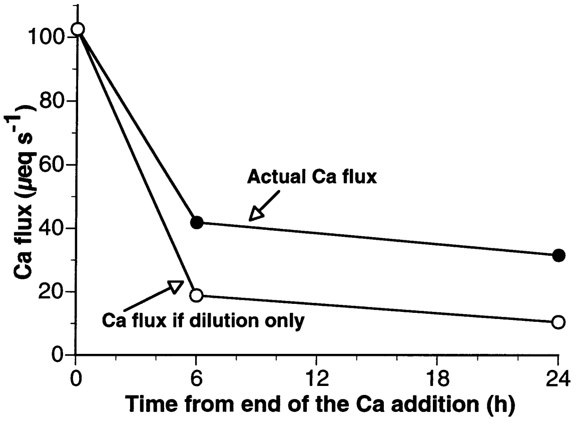

Fig. 6 Ca flux in the buffered stream at 20 m downstream of the addition at 0, 6 and 24 h after stopping the Ca addition. Actual Ca flux (filled circle) is concentration times discharge at each time, while hollow circles represent the calculated Ca flux if there were no desorption of Ca from sediments, and its concentrations were determined strictly by dilution (see text for details).

Table 3 Amount of Ca released from sediments following termination of the Ca addition in each of the two streams. The calculation (see text for details) was made for each of three sites downstream of the addition site in the two streams

	Ca release rate (meq m^{-2} d^{-1})	
Site	Buffered stream	Unbuffered stream
20 m	23	−14
30 m	32	−8
50 m	17	−4

Calcium continued to be immobilized in the buffered stream throughout the study and Ca uptake rate showed no signs of declining with time, which would have suggested that the benthic (mineral sediment or organic matter) exchange sites were becoming saturated with Ca. We hypothesize that there is a large cation exchange capacity in these streams. In a stream draining a limed lake in the Adirondack mountains, Ca was removed continually from the water column for 1 year following treatment (Burns, 1996). This decrease in Ca was associated with increased Ca on exchange sites relative to untreated streams (Burns, 1996). In the buffered stream at HBEF, only small amounts of Ca were released in the day following the end of the Ca addition, roughly equivalent of only 1 day's Ca uptake. Stream discharge was quite low at this time, about 0.5 L s^{-1}, thus it took a long time for Cl to wash out of the reach. Despite the long turnover time of water in the 80-m reach, it was clear that some of the Ca was desorbing from the benthic exchange sites. Release of Ca measured on the 1 day following the addition appeared to have similar kinetics to uptake, in that the amount of Ca released in 1 day was roughly the same as the amount taken up in 1 day. Because of this slow adsorption and desorption in the buffered stream channel, it seems that immobilization of Ca to the point of saturation would take months.

Most Ca sorption was apparently via abiotic exchange and not biotic uptake by microorganisms or mosses. At the level of the whole stream, 10–50 g Ca m^{-2} (5–2.5 eq m^{-2}) was taken up during the release. If fungal biomass were 4% (Paul & Meyer, 1996) of leaf litter standing crop (80 g m^{-2} in Bear Brook, another HBEF stream [Hall & Likens, in press]) then fungal standing stock was *c.* 3.2 g m^{-2}. Moss standing stock was probably close to 3.1 g m^{-2} (Fisher & Likens, 1973). Hence, the amount of adsorbed Ca was much larger than the combined biomass of fungi and moss; uptake was not likely to be biotic. We do note that fungi can make large quantities of calcium oxalate (Graustien, Cromack & Sollins, 1977) and it is possible that the increase in the percentage of Ca in leaves was through formation of this compound.

Uptake of Ca in these streams appears to be mediated by pH. There was high adsorption capacity for Ca in the buffered stream relative to the unbuffered stream, which explains why we saw Ca uptake each time it was measured throughout the 7-week study. Within the buffered stream, uptake velocity of Ca was positively related to pH, showing that about half of the variation in Ca uptake was caused by temporal pH variation in the stream reach. The most probable mechanism by which pH would increase uptake is by increasing negative exchange sites on surfaces. A positive relationship between pH and negative exchange sites has been noted for many minerals (Stumm & Morgan, 1996; Drever, 1997). High pH may have caused a higher sorption capacity for Ca by increasing the quantity of negatively charged exchange sites in the stream channel. When pH was experimentally lowered in another HBEF stream, base cations desorbed from the sediments (Hall *et al.*, 1980), further suggesting that as pH decreases cation sorption capacity of the sediments decreases.

It is possible that differences in stream hydrology or transient storage are responsible for differences in uptake between the two streams (Mulholland *et al.*, 1997; R.O. Hall & E.S. Bernhardt, unpublished) or that the short reach length (50 m) in the unbuffered stream was insufficient to observe uptake. We suggest that the observed differences were not caused by these factors but, for two reasons, by an increase in negative exchange sites caused by the high pH in the buffered stream: 1) because of the relationship between Ca uptake and pH observed in the buffered stream and 2) because Ca concentration was higher in leaf packs in the buffered stream relative to the unbuffered stream. If the relationship between pH and Ca uptake velocity (Fig. 3) were true for the unbuffered stream, Ca uptake in the unbuffered stream would be 226 μeq m^{-2} h^{-1}, compared with an average of 1354 μeq m^{-2} h^{-1} in the buffered stream. This calculation suggests that, based on pH alone, we would predict a five-fold higher uptake in the buffered stream than in the unbuffered stream. Calcium concentration in leaves was nearly twice as high in the treatment reach relative to the reference reach in the buffered stream.

In order not to alter dynamics of solute uptake by a prolonged addition at high concentrations, most studies of solute dynamics in streams have been short-term additions of only a few hours (Newbold *et al.*, 1981; Mulholland, Steinman & Elwood, 1990; D'Angelo & Webster, 1991). By using a longer-term addition with higher concentration, we observed that these streams can be long-term sinks for Ca, which would not have been seen using a short-term addition. Because increased solute concentration can alter the uptake rate (Mulholland *et al.*, 1990), it is fundamentally important to observe how stream ecosystems will alter solute processing under scenarios of increasing or decreasing solute concentration over a long period, e.g. Ca in this study and increased phosphorus loading in others (Elwood *et al.*, 1981; Peterson *et al.*, 1993; Harvey *et al.*, 1998).

An implication of this study relates to the role of streams as part of the larger catchment ecosystem, since streams can exert strong control over the timing and delivery of materials from catchments (e.g. Fisher *et al.*, 1998). Because of the large capacity for Ca uptake in the stream channel that can occur for at least 2 months, both stream channel processes and upland forest processes are important in determining the temporal variation in calcium concentrations measured in streamwater at HBEF. Even though all Ca is ultimately lost from a catchment via its stream, the stream may exert strong control over the timing and delivery of calcium. By the nature of this 2-month experiment, we cannot predict the degree to which stream channels will affect Ca export; however, during our experiment the sorption capacity of Ca by the stream channel was a large fraction of the total Ca export during the same period. Export of Ca from W3 during the experiment was about 340 eq Ca; 70–350 eq of Ca were adsorbed within an 80-m reach during the same time. Because of the pH-driven sorption capability of stream sediments, as pH gradually increases over the next several years in HBEF streams (Likens *et al.*, 1996), the sorption capacity of the streams may increase because of an increase in negative exchange sites (Stumm & Morgan, 1996). This increased Ca sorption may alter the degree to which stream channel processes can alter patterns of Ca export from catchments. We predict that increasing acid-neutralizing capacity in HBEF streams will increase the stream storage of Ca, despite a lower concentration of Ca in streams, because Ca uptake is a positive function of pH.

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