



# The effects of a whole-watershed calcium addition on the chemistry of stream storm events at the Hubbard Brook Experimental Forest in NH, USA

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## ABSTRACT

Patterns of storm runoff chemistry from a wollastonite (calcium-silicate mineral,  $\text{CaSiO}_3$ ) treated watershed (W1) were compared with a reference watershed (W6) at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (NH), USA to investigate the role of  $\text{Ca}^{2+}$  supply in the acid–base status of stream chemistry. In the summer of 2003, six storm events were studied in W1 and W6 to evaluate the effects of the wollastonite treatment on the episodic acidification of stream waters. Although mean values of  $\text{Ca}^{2+}$  concentrations decreased slightly from 33.8 to 31.7  $\mu\text{mol/L}$  with increasing stream discharge in W1 during the events, the mean value of acid neutralizing capacity (ANC) was positive (1.2  $\mu\text{eq/L}$ ) during storm events, compared to negative values ( $-0.2 \mu\text{eq/L}$ ) in W6. This pattern is presumably due to enhanced  $\text{Ca}^{2+}$  supply in W1 (20.7 to 29.0% of dissolved  $\text{Ca}^{2+}$  derived from the added wollastonite) to stream water as a result of interflow along shallow flowpaths. In addition, the application of wollastonite increased pH and dissolved silica ( $\text{H}_4\text{SiO}_4$ ) concentrations, and decreased the concentration of inorganic monomeric Al ( $\text{Al}_i$ ) in W1 in comparison with W6 during storm events. Despite an increase in  $\text{SO}_4^{2-}$  concentration, likely due to desorption of sulfate from soil after the treatment, the watershed showed an increase in ANC compared to the reference watershed, serving to mitigate episodic acidification.

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## 1. Introduction

Episodic acidification of streams has adverse effects on aquatic ecosystems (Van Sickle et al., 1996; Soulsby, 1995). Acidic episodes occur when the acid neutralizing capacity (ANC) of surface waters decreases below 0  $\mu\text{eq/L}$  primarily from the dilution of base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) and/or increases in concentrations of sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) for short periods. During episodes, stream water hydrogen ion ( $\text{H}^+$ ) and inorganic monomeric aluminum ( $\text{Al}_i$ ) concentrations generally increase, and calcium ( $\text{Ca}^{2+}$ ) concentrations decrease, concurrent with increases in stream discharge (Neal et al., 1992).

The four hydrologic flowpaths from precipitation to the stream channel are: 1) direct precipitation to the stream channel, 2) overland flow, 3) shallow subsurface flow, and 4) groundwater flow (Hornberger et al., 1998). Wigington et al. (1990, 1993) identified two phases in storm hydrographs: 1) a low flow phase where stream water is recharged by groundwater flowing through lower soil horizons enriched in base cations, causing an increase in groundwater stage

until water intersects upper soil horizons with higher hydraulic conductivity; and 2) a high flow condition where streams or lakes experience short-term decreases in ANC, usually during high stream flow associated with large rainstorms or snowmelt. Therefore, streams and lakes experience episodic acidification, including simple dilution caused by an increase of flow from rainfall or snowmelt.

Likens et al. (1998) suggested that long-term depletion of soil exchangeable  $\text{Ca}^{2+}$  from acidic deposition has increased watershed susceptibility to episodic acidification. Watershed addition of base cations has been used to mitigate episodic acidification and improve conditions for aquatic biota impacted by acidic deposition (e.g. Driscoll et al., 1996). This technique was used in watershed 1 (W1) at the HBEF in October of 1999 by the application of a readily-weatherable calcium-silicate mineral, wollastonite ( $\text{CaSiO}_3$ ). This treatment enhanced the supply of  $\text{Ca}^{2+}$  in soil and water, increased pH and ANC and limited the mobilization of Al.

Strontium is a useful isotopic tracer, since Sr isotopes are not fractionated in natural systems and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of dissolved Sr represents only the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the solute source (Hogan and Blum, 2003) without variation in the Sr content of the wollastonite. The wollastonite applied has a distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.70588 and a Ca/Sr ratio of 2870 (mol/mol) allowing the  $\text{Ca}^{2+}$  released by  $\text{CaSiO}_3$  dissolution to be traced by measuring the  $^{87}\text{Sr}/^{86}\text{Sr}$  and Ca/Sr ratios of various components of the forest ecosystem (Dasch et al., 2006). The

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dissolution of  $\text{CaSiO}_3$  supplies  $\text{Ca}^{2+}$ ,  $\text{H}_4\text{SiO}_4$ , and ANC to solution, while consuming  $\text{H}^+$  (Eq. (1)):



The objective of this study was to investigate the effects of the  $\text{Ca}^{2+}$  manipulation on stream chemistry during hydrological events. We hypothesized that  $\text{Ca}^{2+}$  supply to stream water would be enhanced during summer storm events due to the routing of water through shallow flowpaths. We examined the hydrochemical processes that occur during storm events at the HBEF in order to improve understanding of the effects of  $\text{Ca}^{2+}$  application on episodic acidification. This objective was accomplished through a comprehensive suite of major cation and anion measurements of a base-treated watershed (W1) in comparison with a reference watershed (W6) at the HBEF, and statistical analyses of these data.

## 2. Materials and methods

### 2.1. Study site features

A  $\text{Ca}^{2+}$  treated watershed ecosystem (W1) and a reference watershed (W6) at the HBEF in the southern portion of the White Mountain National Forest in central New Hampshire, USA (43°56'N, 71°45'W) were used as experimental sites in this study (Likens and Bormann, 1995; Fig. 1). The bedrock of the HBEF is mostly the Silurian Rangely Formation, consisting of quartz mica schist and quartzite, interbedded with sulfidic schist and calc-silicate granulite (Johnson et al., 2000). The soils at Hubbard Brook are predominately Spodosols (Typic Haplorthods) that were derived from glacial till. The average depths of the forest floor and the mineral soil are 6.9 cm and 50.3 cm, respectively (Johnson et al., 1991a,b). The climate at the HBEF is humid-continental, characterized by long, cold winters and short cool summers (average temperature for January is  $-9^\circ\text{C}$  and for July is  $10^\circ\text{C}$ ). Average annual precipitation is 1395 mm, 25–33% of which falls as snow. Average annual runoff is 870 mm (Federer et al., 1990). About half of annual stream discharge occurs during the months from March to May due to snowmelt and rainfall (Federer et al., 1990).

The chemical manipulation (addition of  $\text{CaSiO}_3$ ) was conducted in W1 in October of 1999. W1 is 11.8 ha and ranges in elevation from 488 m to 747 m; W6 is 13.2 ha and ranges in elevation from 549 m to 792 m. W1 and W6 are considered paired treatment and reference watersheds, respectively, for this study, since both watersheds have

similar aspect, vegetation, and soils. We estimate that 1804  $\text{m}^2$  of W1 and 2006  $\text{m}^2$  of W6 represent the stream channel area of the watersheds (Peters et al., 2004).

### 2.2. Collection of water samples and analysis

Storm water was sampled during six rain events at locations 10 m above each weir of W1 and W6 using ISCO portable automatic water samplers (ISCO-PAWS) from May to August of 2003. These units are equipped with a liquid level actuator (model 1640) which is placed directly above the surface of the stream water and activates the sampler pump to begin collection during increases in stream flow. The automatic samplers were programmed to begin sampling upon activation (hour zero) and continue collecting 1000 ml samples every hour for the first 12 h of the event and then 1000 ml samples every subsequent 3 h for a total of 24 individual samples spanning 47 h. During each event we sampled bulk precipitation at a single rain gauge clearing (RG-1) located 50 m directly to the northeast of the W1 stream gauging station. Soil waters collected from zero-tension lysimeters placed below the organic (average depths of lysimeters in W1 and W6: 5 and 4 cm at O horizons, respectively) and mineral horizons within W1 and W6 (average depths of lysimeters in W1 and W6: 10 and 23 cm at Bh, 20 and 44 cm at Bs horizons, respectively) and stream water was sampled monthly as part of a long-term monitoring program.

For each event, bulk precipitation, soil water, and stream water samples were placed in 500 ml bottles, packed in coolers with ice bags, and sent to Syracuse University for analysis. All water samples were refrigerated and analyzed for pH, ANC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , monomeric aluminum ( $\text{Al}_\text{m}$ ), organic monomeric Al ( $\text{Al}_\text{o}$ ),  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , dissolved silica ( $\text{H}_4\text{SiO}_4$ ), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC), using the methods described in Table 1.  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  were measured by simultaneous ICP-OES at the University of Michigan for purposes of calculating Ca/Sr ratios. Quality Assurance and Quality Control (QA/QC) measures were used for all water sample analyses. To evaluate QA/QC, we used initial calibration (correlation coefficient  $>0.995$ ), initial calibration verification (ICV within  $\pm 10\%$  of expected value), initial calibration blank (ICB), method detection limit (MDL within 75–125% recovery), continuing calibration verification (CCV within  $\pm 10\%$  of expected value), continuing calibration blank (CCB), preparation blank (PB),

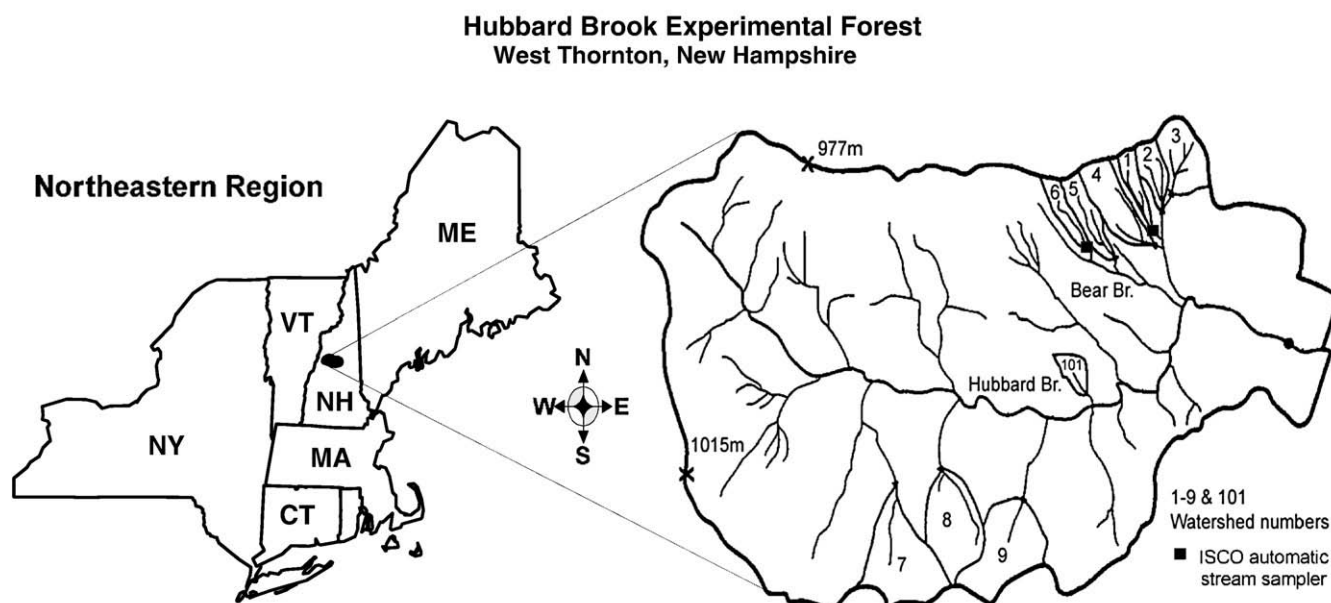


Fig. 1. A map of watersheds at the HBEF in New Hampshire, showing sampling locations of storm water.

**Table 1**

Chemical analytical methods of precipitation, soil water, and stream water samples.

Analyte	Method	Reference
Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> NH <sub>4</sub> <sup>+</sup>	Atomic absorption spectroscopy (AAS), flame atomic emission Automated phenate method	Slavin (1968) Cappo et al. (1987) APHA (1992)
SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , F <sup>-</sup> Total monomeric Al (Al <sub>m</sub> ) Organic monomeric Al (Al <sub>o</sub> ) Inorganic monomeric Al (Al <sub>m</sub> )	Ion chromatography (IC) Pyrocatechol violet (PCV), automated analysis	Tabatabai and Dick (1983) McAvoy et al. (1992)
Dissolved H <sub>4</sub> SiO <sub>4</sub> pH	Al <sub>m</sub> -Al <sub>o</sub> Molybdenum blue colorimetry, automated analysis Potentiometric	Driscoll (1984) APHA (1992)
Acid neutralizing capacity (ANC)	Strong acid titration, Gran plot analysis	Gran (1952)
Dissolved inorganic carbon (DIC)	Acid purge, infrared (IR) CO <sub>2</sub> detection	Dohrman (1984)
Dissolved organic carbon (DOC)	UV enhanced persulfate oxidation, infrared (IR) CO <sub>2</sub> detection	Dohrman (1984)
Ca/Sr	ICP-OES	Peters et al. (2004)

laboratory control sample (LCS within  $\pm 10\%$  of expected value), matrix spike/matrix spike duplicate sample (MS/MSD within  $\pm 15\%$  and relative percent difference  $< 10\%$ ), and duplicate sample (DS within relative percent difference  $< 10\%$ ). All laboratory analyses were reanalyzed when QA/QC criteria were not met.

The fraction of Ca<sup>2+</sup> derived from wollastonite dissolution in stream water during episodic events was calculated, using a Ca–Sr mixing calculation. The CaSiO<sub>3</sub> added has a much higher Ca/Sr ratio than pre-application stream values (Peters et al., 2004). Consequently, changes in the Ca/Sr ratios indicate changes in the sources of Ca<sup>2+</sup> in stream water. In this study, the fraction (%) of Ca<sup>2+</sup> from wollastonite was determined for each stream water sample using a Ca–Sr mixing calculation, based on the Ca/Sr (mol) ratios of the wollastonite pellets applied (2870 (mol/mol); Dasch et al., 2006) to the watershed and the pre-application stream water chemical composition (306 (mol/mol); Peters et al., 2004). Based on the mixing calculations and mixing diagram (Peters et al., 2004), the Ca/Sr ratio was used to quantify the proportion of Ca in each stream water sample that was derived from the CaSiO<sub>3</sub> added to the watershed.

The chemical mechanisms responsible for changes in ANC during episodic events were evaluated by examining changes in the concentrations of major ionic solutes. ANC can be calculated based on the composition of major ions in solution (Eq. (2); Stumm and Morgan, 1981).

$$\text{ANC} = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-] - [\text{F}^-] \quad (2)$$

where ion concentrations are expressed in  $\mu\text{mol/L}$  and the units of ANC are  $\mu\text{eq/L}$ .

### 2.3. Statistical methods

In this study, MINITAB (version 14; statistical software) was used to calculate the range between the largest and smallest flow values, and the interquartile range (IQR) that is a measure of the variability in the flow distribution between the 75th and the 25th percentiles. MINITAB was also used to compute the confidence level which was 95% for all tests and for hypothesis testing which was focused on decision making. In order to test hypotheses by comparing means or medians of two populations, two diametrically opposed hypotheses were considered: 1) the null hypothesis ( $H_0$ ) in which the observation is random variation; and 2) the alternative hypothesis ( $H_a$ ) in which a meaningful pattern is observed. The criterion for evaluating which hypothesis is true was based on the significance level ( $p$ -value) of the test, which is denoted by  $\alpha = 0.05$ .

In the parametric approach, independent samples were evaluated with a separate variance  $t$ -test (also called the two independent sample  $t$ -test), and paired samples with a paired  $t$ -test. In a non-parametric approach, two independent samples were evaluated with the Mann–Whitney test, and for paired data the Wilcoxon test was used. The paired  $t$ -test and two sample  $t$ -test were used to determine relationships between storm events and stream water Ca<sup>2+</sup>, Ca/Sr ratio, and %Ca<sup>2+</sup> derived from wollastonite in W1, using the statistical significance by  $p$ -values based on an  $\alpha$ -value = 0.05 and a 95% confidence interval. Analyses of paired  $t$ -tests and two sample  $t$ -tests were also conducted to evaluate the role of the cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup>) and anions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and F<sup>-</sup>; Eq. (2)) that are responsible for changes in ANC during the storm events studied. The watersheds are assumed to be paired in concentrations of major ions except Ca<sup>2+</sup>. It is also assumed that the treated watershed has higher Ca<sup>2+</sup> concentrations (two sample  $t$ -test) simply due to the addition of wollastonite. The objective of this analysis was to

**Table 2**

Characteristics of six storm events monitored at watershed 1 (W1) and watershed 6 (W6) in the Hubbard Brook Experimental Forest (HBEF).

Date of storm events	Precipitation (mm)	Discharge (m <sup>3</sup> /s)		Range <sup>b</sup>		Interquartile range (IQR) <sup>c</sup>		Ranking <sup>d</sup>	
		Max flow <sup>a</sup>							
		W1	W6	W1	W6	W1	W6	W1	W6
24–26 May 2003	32.3	0.0430	0.0660	0.0022	0.0047	0.0005	0.0013	4	4
5–7 June 2003	19.0	0.0475	0.2124	0.0016	0.0032	0.0011	0.0022	3	3
9–11 June 2003	6.4	0.0209	0.0691	0.0005	0.0013	0.0004	0.0009	1	1
16–18 July 2003	32.0	0.0104	0.0371	0.0007	0.0031	0.0005	0.0015	2	2
22–24 July 2003	35.7	0.0249	0.0703	0.0014	0.0047	0.0011	0.0012	5	5
3–6 August 2003	36.8	0.2075	0.3996	0.0076	0.0153	0.0022	0.0073	6	6

<sup>a</sup> Max discharge during each storm period.

<sup>b</sup> The difference between the largest and smallest flow data values during the sampling period.

<sup>c</sup> A measure of the variability (or spread) in the flow distribution between the 75th and 25th percentiles.

<sup>d</sup> A relative ranking of each storm event based on precipitation, flow range, and IQR from lowest (1) to highest flow (6).

determine which ions play an important role in regulating the variation in ANC between the treated and the reference watershed during storm events.

### 3. Results and discussion

#### 3.1. General characteristics of six storm events

The summer of 2003 was characterized by generally dry conditions interspersed by precipitation events. The average precipitation from May to August of 2003 (140 mm) was somewhat greater than the long-term average (from 1993 to 2002: 111 mm; [www.hubbardbrook.org/research/data/atmos/pwd/pwdi.htm](http://www.hubbardbrook.org/research/data/atmos/pwd/pwdi.htm)). Six storm water events were sampled at W1 and W6 of the HBEF on the sampling dates of May 24–26, June 5–7 and 9–11, July 16–18 and 22–24, and August 3–6 in 2003. The storm events generally provided sufficient streambed flow for water sampling. The July 16–18 event involved sampling up to 32-h following initiation of the storm but there was insufficient water in the channel for sampling after that period. During the July 22–24 event, samples were also not collected between the seventh hour and the fifteenth hour in W1 due to insufficient channel flow.

The general characteristics of the storm events monitored at W1 and W6 are presented in Table 2. To investigate the role of the  $\text{Ca}^{2+}$  supply from the wollastonite application on stream water following a range of summer precipitation events, four metrics were used to rank the hydrologic response of the events studied. The rain events of June 9–11 and the August 3–6 showed the lowest and the highest flow, respectively, in both W1 and W6 based on the ranking of the metrics. The relative ranking was made by precipitation quantity (low amount of 6.4 mm, high amount of 36.8 mm), discharge amounts (low flow in W1 and W6: 0.0104 and 0.0371  $\text{m}^3/\text{s}$ ; high flow in W1 and W6:

0.2075 and 0.3996  $\text{m}^3/\text{s}$ ), range (low flow in W1 and W6: 0.0005 and 0.0013  $\text{m}^3/\text{s}$ ; high flow in W1 and W6: 0.0076 and 0.0153  $\text{m}^3/\text{s}$ ) of discharge, and IQR (low flow in W1 and W6: 0.0004 and 0.0009  $\text{m}^3/\text{s}$ ; high flow in W1 and W6: 0.0022 and 0.0073  $\text{m}^3/\text{s}$ ). This approach was used to aid in the presentation of data and to demonstrate the patterns of relative change in solute concentrations with storm discharge.

#### 3.2. Solute chemistry during storm period

The arithmetic mean concentrations of bulk precipitation, storm water, stream water, and soil water of organic and mineral horizons from May to August of 2003 are shown in Table 3. Precipitation at the HBEF is generally acidic, with a mean pH of 4.39 and a mean ANC of  $-49 \mu\text{eq}/\text{L}$ . The most common weather systems involve prevailing winds from the west which transport acidifying compounds (i.e.,  $\text{SO}_2$ ,  $\text{NO}_x$ ) associated with the atmospheric source area (Driscoll et al., 2001). The base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ),  $\text{H}_4\text{SiO}_4$ ,  $\text{Al}_i$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  were considerably lower in precipitation than in stream and storm water. Sulfate concentrations were lower in precipitation compared with stream water due to dry sulfur deposition and watershed supply of previously deposited sulfur (Likens et al., 1998). Ammonium,  $\text{NO}_3^-$ , and DIC, were elevated in precipitation in comparison to stream water during base flow and storm events.

Soil solution chemistry is fundamental to understanding the hydro-biogeochemical control of stream chemistry. In this study, soil water samples of organic and mineral horizons were used to examine biogeochemical relationships between base flow and storm stream water chemistry. pH values were low in soil water of both watersheds compared to stream water collected during the routine sampling and during storm flow. The low pH of soil water reflects high concentrations of DOC and associated naturally occurring organic acids and  $\text{NO}_3^-$

**Table 3**

Arithmetic mean, standard deviation, and statistical test results of bulk precipitation, storm water, stream water, and soil water of organic and mineral horizons from May to August of 2003.

Concentrations ( $\mu\text{mol/L}$ )		Precipitation	Storm water			Stream water			Soil water					
									Organic horizon		Mineral horizon			
			W1	W6		W1	W6		W1	W6	W1	W6		W1
pH	x	4.39	5.23	>	5.12	5.33	≈	5.25	4.49	>	4.11	4.58	≈	4.57
	SD	0.30	0.15	III	0.27	0.11	IV	0.21	0.45	III	0.23	0.31	IV	0.56
ANC ( $\mu\text{eq/L}$ )	x	−49.00	1.23	>	−0.20	1.91	≈	1.37	−33.8	>	−84.1	−18.3	≈	−18.4
	SD	28.80	4.25	I	9.11	3.33	IV	4.69	72.30	II	49.10	28.19	IV	43.67
$\text{Ca}^{2+}$	x	3.18	31.72	>	18.95	33.80	>	17.23	54.97	>	18.30	27.62	>	12.23
	SD	1.89	2.06	III	1.21	2.70	III	1.54	30.25	III	14.18	15.51	III	16.36
$\text{Mg}^{2+}$	x	0.61	8.28	<	9.92	7.53	<	9.61	7.45	≈	7.41	5.31	≈	5.05
	SD	0.48	0.70	III	1.16	0.47	III	0.58	3.81	IV	3.07	2.22	IV	5.15
$\text{Na}^+$	x	1.99	36.17	<	38.42	37.16	<	55.79	26.37	>	15.94	30.39	≈	30.00
	SD	1.41	3.60	III	4.97	9.01	I	25.00	21.32	II	8.43	17.33	IV	10.44
$\text{K}^+$	x	1.16	2.56	<	3.70	1.81	≈	2.54	22.02	≈	23.85	6.71	≈	5.50
	SD	0.88	0.99	III	2.17	1.26	IV	1.21	21.44	IV	25.88	10.23	IV	5.10
$\text{Al}_i$	x	0.15	2.15	<	2.62	2.15	>	1.68	4.63	≈	5.74	9.42	≈	9.94
	SD	NA	0.39	III	0.43	0.44	I	0.48	5.05	IV	4.46	5.74	IV	5.06
$\text{NH}_4^+$	x	6.87	1.25	≈	0.76	3.18	≈	2.98	11.75	>	6.46	4.68	≈	3.19
	SD	5.26	3.25	IV	0.64	8.34	IV	4.85	9.92	I	12.36	6.42	IV	6.77
$\text{SO}_4^{2-}$	x	24.43	45.54	>	40.49	48.49	>	44.58	32.93	≈	29.52	42.10	>	33.82
	SD	14.18	2.32	III	4.11	2.78	II	3.14	9.49	IV	7.37	10.48	III	6.86
$\text{NO}_3^-$	x	20.89	6.71	>	4.89	5.32	≈	4.47	34.63	≈	40.19	17.84	≈	16.02
	SD	9.34	3.64	III	1.01	0.44	IV	2.22	55.99	IV	41.60	19.98	IV	35.31
$\text{Cl}^-$	x	8.34	14.26	>	13.16	13.31	<	15.08	12.32	≈	10.30	13.16	≈	12.80
	SD	3.49	1.77	III	1.54	1.91	I	1.97	6.12	IV	5.94	5.49	IV	5.51
$\text{F}^-$	x	NA	1.26	≈	1.24	1.48	≈	1.33	1.19	>	0.67	1.19	≈	0.99
	SD	NA	0.19	IV	0.18	0.30	IV	0.24	0.79	II	0.45	0.57	IV	0.66
$\text{H}_4\text{SiO}_4$	x	4.90	126.7	>	77.94	136.59	>	89.15	160.0	>	75.50	163.51	>	78.15
	SD	2.54	7.73	III	9.46	5.97	III	12.81	50.90	III	48.10	58.02	III	28.95
DOC	x	173	183.4	>	154.2	182.7	>	153.36	2418	≈	2077	875	≈	866.6
	SD	47.40	23.03	III	26.65	35.2	I	22.93	2189	IV	1325	1285	IV	603.2
DIC	x	81.76	47.41	>	44.82	36.59	≈	46.70	249.0	>	157.6	237.6	≈	186.8
	SD	16.55	10.12	I	8.86	17.09	IV	25.60	200.4	I	141.6	222.8	IV	188.2

NA = not available; x = arithmetic mean; SD = standard deviation.

Both alternative hypotheses ( $\text{W1} > \text{W6}$  or  $\text{W1} < \text{W6}$ ) and null hypotheses ( $\text{W1} \approx \text{W6}$ ) are tested by two sample *t*-test based on *p*-value, using the significance level of 0.05 and 95% confidence intervals for all tests. The strength of these results indicate I( $p < 0.05$ ), II( $p < 0.01$ ), III( $p < 0.001$ ), and IV( $p > 0.05$ ).



relative to values observed in stream water. Due to acidic conditions and contact of water with soil, concentrations of inorganic monomeric Al ( $Al_i$ ) were elevated in soil water compared to stream water (Palmer et al., 2004). The O-horizon soil water in the treated watershed had a higher ANC than values in the reference catchment largely due to the supply of  $Ca^{2+}$  associated with wollastonite dissolution. In contrast, the ANC of W6 in mineral horizon solutions was similar to that of W1 due to the increase in  $SO_4^{2-}$  concentration that occurred coincident with the increase in  $Ca^{2+}$  concentration (Table 3). W1 also exhibited higher concentrations of  $H_4SiO_4$  in all soil, stream, and storm waters due to the wollastonite application. Sulfate concentrations were relatively uniform in soil water, stream, and storm waters within a relatively narrow range of 33–48  $\mu\text{mol/L}$  in the treated watershed which were generally higher than the reference watershed (30–40  $\mu\text{mol/L}$ ). This characteristic can be explained by  $SO_4^{2-}$  deposition and the buffering of  $SO_4^{2-}$  by sorption reactions with reactive mineral surfaces in the soil (discussed below). As expected,  $Ca^{2+}$  and  $H_4SiO_4$  were the most strongly regulated by the

addition of wollastonite (Table 3). Mean concentrations of  $Mg^{2+}$  ( $p>0.05$  in both the organic and the mineral soil solutions),  $Na^+$  ( $p>0.05$  in the mineral soil solution),  $K^+$  ( $p>0.05$  in both the organic and the mineral soil solutions),  $Al_i$  ( $p>0.05$  in both the organic and the mineral soil solutions),  $NH_4^+$  ( $p>0.05$  in the mineral soil solution),  $NO_3^-$  ( $p>0.05$  in both the organic and the mineral soil solutions),  $Cl^-$  ( $p>0.05$  in both the organic and the mineral soil solutions),  $F^-$  ( $p>0.05$  in the mineral soil solution), DOC ( $p>0.05$  in both the organic and the mineral soil solutions), and DIC ( $p>0.05$  in the mineral soil solution) showed similar values between W1 and W6 soil solutions through the two sample  $t$ -test. Concentrations of  $Na^+$  ( $p<0.01$ ),  $NH_4^+$  ( $p<0.05$ ),  $F^-$  ( $p<0.01$ ), and DIC ( $p<0.05$ ) in organic soil water of W1 were greater than those of W6 (two sample  $t$ -test).

There was a general consistency in concentrations of the chemical constituents (pH, ANC,  $Ca^{2+}$ ,  $Al_i$ ,  $SO_4^{2-}$ , and  $H_4SiO_4$ ) of organic soil water and storm flow between W1 and W6. Concentrations in pH, ANC,  $Ca^{2+}$ ,  $SO_4^{2-}$ , and  $H_4SiO_4$  of stream water during the storm events in the

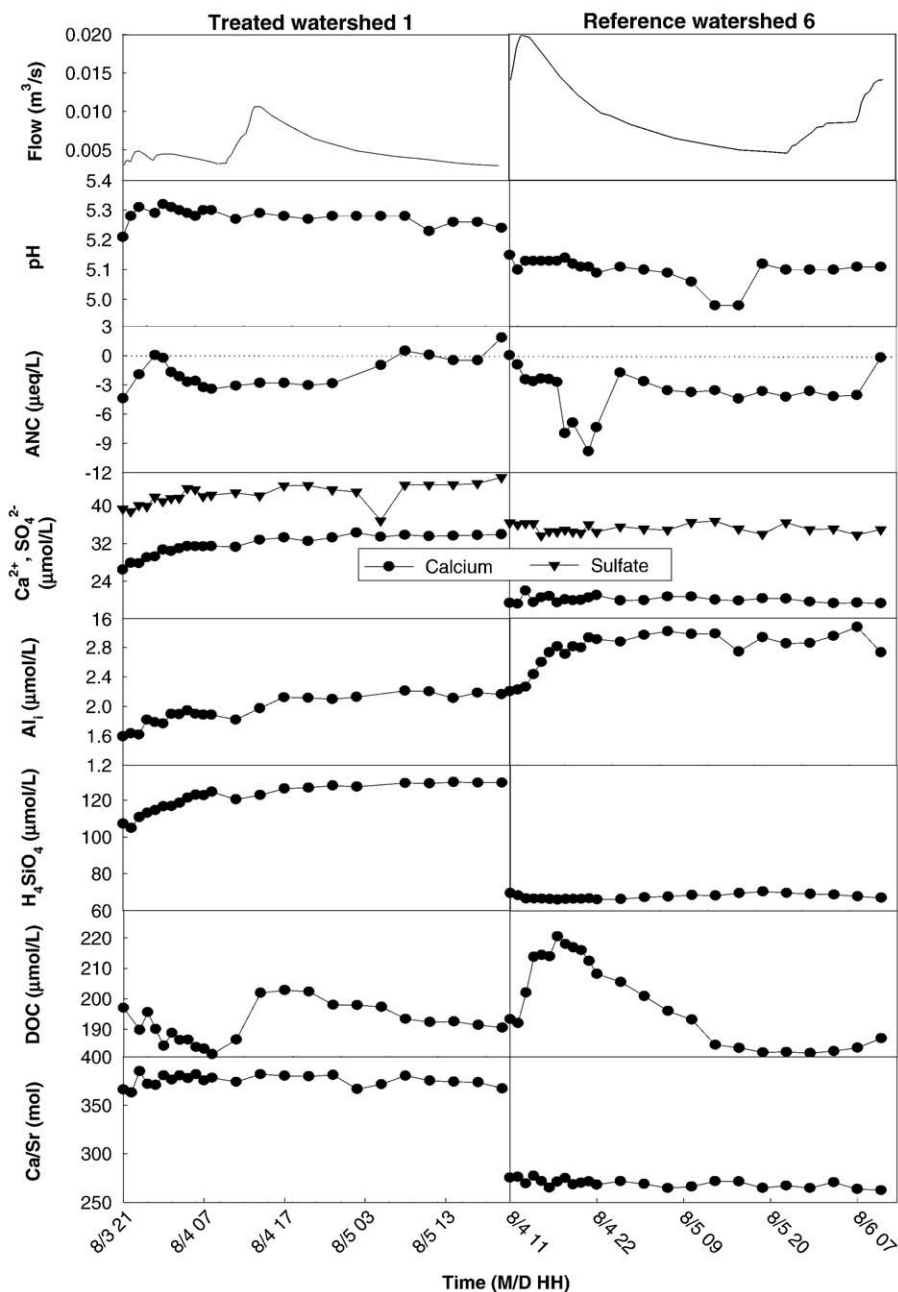


Fig. 2. Hydrochemical response (discharge, pH, ANC,  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $Al_i$ ,  $H_4SiO_4$ , DOC, and Ca/Sr) of W1 and W6 at the HBEF during a 3–6 August 2003 storm event.

treated watershed were greater than those in the reference watershed, and an  $Al_i$  concentration in W1 was lower than in W6. These patterns were similar to patterns of concentrations of the organic soil solution between W1 and W6. Those solute concentrations of storm water were influenced by concentrations of soil water in organic horizon within the experimental watersheds. In particular, the dissolution products of wollastonite increased pH ( $p < 0.001$ , two sample  $t$ -test), ANC ( $p < 0.05$ , two sample  $t$ -test),  $Ca^{2+}$  ( $p < 0.001$ , two sample  $t$ -test),  $SO_4^{2-}$  ( $p < 0.001$ , two sample  $t$ -test), and  $H_4SiO_4$  ( $p < 0.001$ , two sample  $t$ -test) and decreased  $Al_i$  ( $p < 0.001$ , two sample  $t$ -test) in storm waters of W1 in comparison to W6.

### 3.3. Hydrochemical responses to storm events

The precipitation amounts for each storm event of the 2003 summer season are shown in Table 2. The 3–6 August storm event was characterized by a relatively high amount of precipitation (36.8 mm).

In contrast, the 9–11 June event had relatively low precipitation (6.4 mm). To illustrate the range of hydrochemical response for the treated and the reference watersheds (Table 2), we focus our analyses on the high discharge storm occurring 3–6 August and the low discharge storm occurring 9–11 June (Figs. 2 and 3). W6 (area of 13.2 ha) exhibited higher discharge than W1 (area of 11.8 ha) during the high (W6:  $0.3996 \text{ m}^3/\text{s}$ , W1:  $0.2075 \text{ m}^3/\text{s}$ ) and the low flow (W6:  $0.0691 \text{ m}^3/\text{s}$ , W1:  $0.0209 \text{ m}^3/\text{s}$ ) storm periods due to its larger area (Table 2, Figs. 2 and 3).

During the first 2 h of the 3–6 August event, W1 experienced a slight increase in flow. A large increase in stream discharge occurred 16 h (1:42 p.m. 4 August) after the start of the event when additional precipitation increased the flow to  $0.011 \text{ m}^3/\text{s}$ . The discharge gradually decreased to  $0.003 \text{ m}^3/\text{s}$  at the end of the sampling period (approximately 47 h (8:00 p.m. 5 August); Fig. 2). In W6 during the large storm event, peak discharge occurred 2 h (12:54 p.m. 4 August) after the event began with a maximum

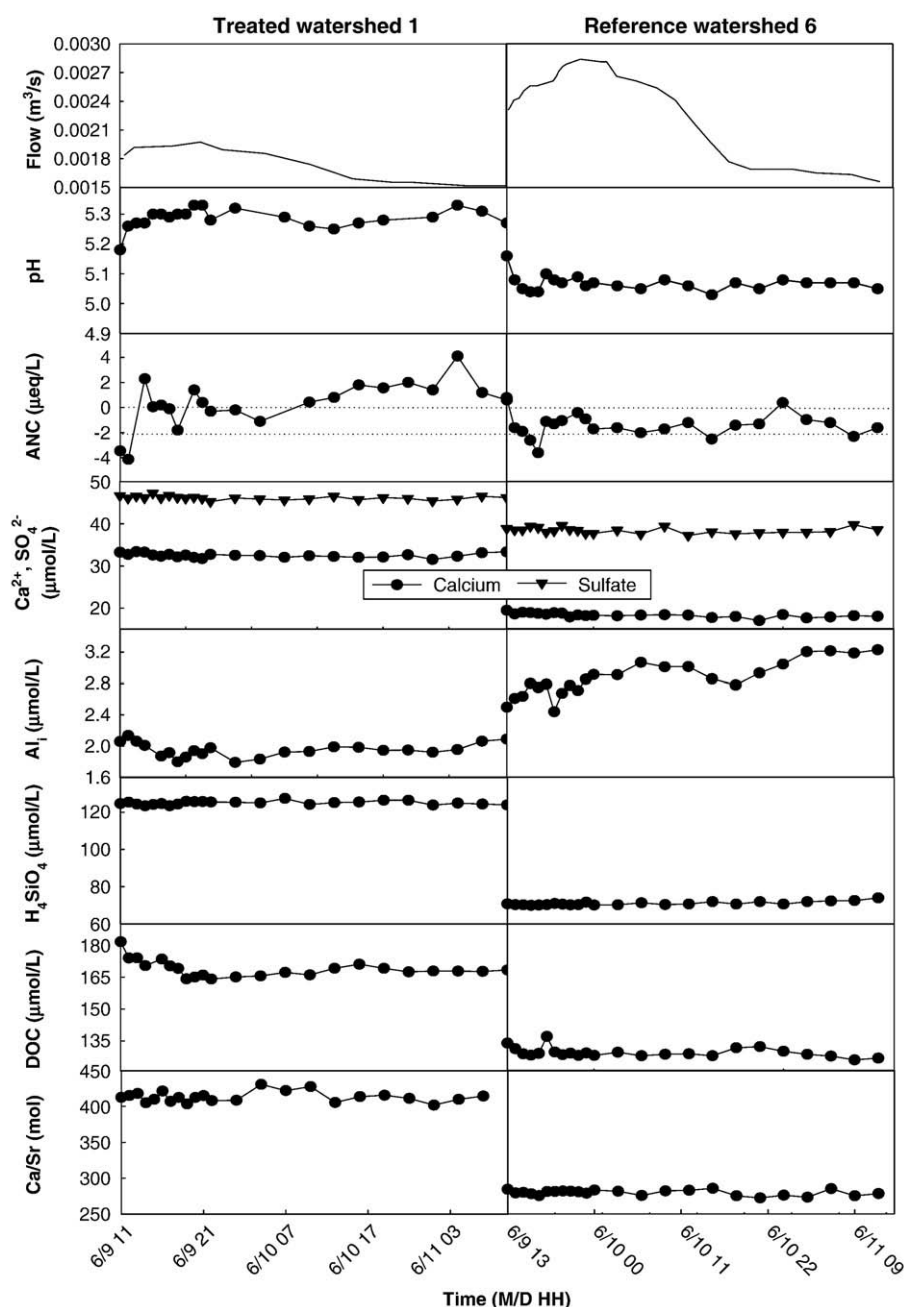


Fig. 3. Hydrochemical response (discharge, pH, ANC,  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $Al_i$ ,  $H_4SiO_4$ , DOC, and Ca/Sr) of W1 and W6 at the HBEF during a 9–11 June 2003 storm event.

discharge of  $0.020 \text{ m}^3/\text{s}$ , and decreased steadily until 36 h (10:54 p.m. 5 August) later when discharge reached a minimum of  $0.005 \text{ m}^3/\text{s}$ . At 36 h additional precipitation increased the discharge for the remainder of the event (Fig. 2). During the low flow event (9–11 June, 2003) the rising limb of the hydrograph in W1 increased to  $0.002 \text{ m}^3/\text{s}$  within 10 h (9:12 p.m. 9th of June) followed by a steady decrease. W6 experienced a peak storm discharge at 10 h (10:36 p.m. 9th of June) of  $0.003 \text{ m}^3/\text{s}$  and the discharge decreased during the remainder of the event (Fig. 3).

Interactions between  $\text{Ca}^{2+}$  availability and the acid–base status of storm waters suggest that soil  $\text{Ca}^{2+}$  depletion is a key factor which leads to acidic episodes in streams (Lawrence, 2002). The stream draining the treated watershed exhibited pH values ranging from 5.21 to 5.31 and ANC values from  $-4.4$  to  $1.9 \mu\text{eq/L}$  during the high flow storm (3–6 August), and pH from 5.18 to 5.33 and ANC from  $-4.1$  to  $4.1 \mu\text{eq/L}$  during the small storm (9–11 June). Concentrations of  $\text{Al}_i$  ranged from  $1.6$  to  $2.2 \mu\text{mol/L}$  during the large storm event and from  $1.8$  to  $2.1 \mu\text{mol/L}$  during the small storm event. In contrast, the reference watershed exhibited pH ranging from 4.98 to 5.15 during the large flow event and from 5.03 to 5.16 during the small event, and ANC ranging from  $-9.8$  to  $0.04 \mu\text{eq/L}$  and from  $-3.6$  to  $0.8 \mu\text{eq/L}$  during the large and the small events, respectively. The relatively small difference in acidity responses (i.e. pH, ANC) in W1 and W6 streams during storm events suggests that the  $\text{Ca}^{2+}$  treatment has had modest impacts on the acid–base chemistry of summer storm water. This limited response may have been due to the 4 year lag between the wollastonite treatment and the study period and because of limited supply of water along shallow flowpaths during summer low flow conditions. We expect that there might be a comparatively larger difference in pH and ANC responses between the two streams during the storm periods immediately after the application, since mean pH (5.58; unpublished data) and ANC ( $18.3 \mu\text{eq/L}$ ; unpublished data) values in stream water of W1 from May to August in 2000 were greater than those (pH: 5.07, ANC:  $4.3$ , unpublished data) of W6.

Concentrations of  $\text{Al}_i$  increased from  $2.2$  to  $3.1 \mu\text{mol/L}$  during the large event and from  $2.4$  to  $3.2 \mu\text{mol/L}$  during the small event. The addition of  $\text{Ca}^{2+}$  in the treated watershed decreased the mobilization of  $\text{Al}_i$  in the forest floor (Table 3) and subsequent transport to the stream water (Figs. 2 and 3). The solubility of Al is pH dependent with decreases in solubility associated with increases in pH from acidic values. Greater increases in  $\text{Al}_i$  concentrations were observed in W6 stream waters which had a greater pH decline during events. In contrast, increases in  $\text{Al}_i$  during storm events were more modest in the wollastonite treated watershed. Stream water draining W1, with an enhanced supply of  $\text{Ca}^{2+}$  within the soil, was less acidic. In contrast, W6 experienced acidic episodes under the range of storm flow conditions observed in this study (Figs. 2 and 3). W1 had higher storm flow  $\text{Ca}^{2+}$  (from  $26.5$  to  $34.3 \mu\text{mol/L}$  during the large event; from  $31.6$  to  $33.4 \mu\text{mol/L}$  during the small event) and  $\text{H}_4\text{SiO}_4$  (from  $105$  to  $130 \mu\text{mol/L}$  during the large event; from  $123$  to  $127 \mu\text{mol/L}$  during the small event) than W6 ( $\text{Ca}^{2+}$  and  $\text{H}_4\text{SiO}_4$  ranged from  $19$  to  $22 \mu\text{mol/L}$  and from  $66$  to  $70 \mu\text{mol/L}$  during the large event;  $\text{Ca}^{2+}$  and  $\text{H}_4\text{SiO}_4$  from  $17$  to  $20 \mu\text{mol/L}$  and from  $70$  to  $74 \mu\text{mol/L}$  during the small event, respectively). The corresponding increase in  $\text{H}_4\text{SiO}_4$  at W1 is likely due to the dissolution of added wollastonite.

Concentrations of DOC increased with flow in W1 and W6 during the large event, with the maximum DOC concentrations corresponding with the time of peak stream discharge (Fig. 2). This observation supports the importance of flow through the upper organic horizon and is consistent with numerous studies using DOC as a tracer of flowpaths (Hornberger et al., 1994). DOC concentrations showed no clear relationship with discharge during the small event (Fig. 3) probably due to precipitation onto an already wet soil. DOC is released through the breakdown of organic matter in organic horizons, leading to an increase in DOC to soil water and flushing of soil water during summer storm events and spring snowmelt (Brown et al., 1999; Hornberger et al., 1994).

Concentrations of  $\text{SO}_4^{2-}$  in the treated watershed were higher than those in the reference watershed across the range of flow condition (Table 3, Figs. 2 and 3). The higher  $\text{SO}_4^{2-}$  concentrations in W1 suggest that the increase in pH associated with the wollastonite treatment may have facilitated the desorption of  $\text{SO}_4^{2-}$  from soil adsorption sites. It is also possible that sulfate may have been released from sulfide minerals through enhanced mineral weathering or enhanced mineralization of organic S in soil (Holloway and Dahlgren, 2001; Novak et al., 1996). Previous investigators at the HBEF have shown that stream  $\text{SO}_4^{2-}$  concentrations are strongly influenced by pH-dependent soil adsorption (Fuller et al., 1985; Mitchell et al., 1989; Nodvin et al., 1988). Increases in  $\text{Ca}^{2+}$  concentrations and concomitant decreases in  $\text{H}^+$  concentration at W1 likely facilitated the desorption of  $\text{SO}_4^{2-}$  from soil resulting in higher  $\text{SO}_4^{2-}$  concentrations in soil and stream water. This pattern was evident under base flow conditions, and storm events did not result in significant changes in stream  $\text{SO}_4^{2-}$  concentrations.

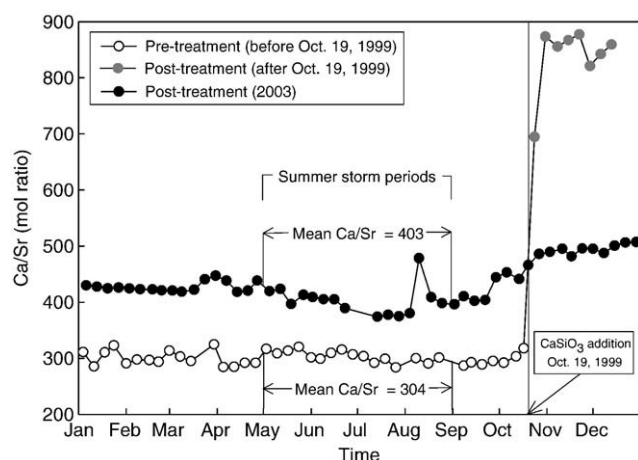
The relatively higher concentrations of  $\text{Ca}^{2+}$  during storm events in W1 diminished episodic acidification compared with W6. The higher  $\text{SO}_4^{2-}$  concentrations in W1 off-set somewhat the increase in  $\text{Ca}^{2+}$  concentrations derived from the added wollastonite, therefore limiting the ANC increase in W1 compared to W6. Nevertheless, the wollastonite addition helped attenuate the magnitude of episodic acidification in W1 in comparison with W6.

One mitigation strategy for acidic deposition is liming (i.e., base treatment) to help restore depleted soil pools of exchangeable  $\text{Ca}^{2+}$  and enhance the supply of  $\text{Ca}^{2+}$  to surface waters, which decreases acidity associated with elevated concentrations of hydrogen ion and strong acid anions (i.e.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), and limits the mobility of  $\text{Al}_i$  to stream water. Watershed liming has been used to treat acidic surface waters. In Woods Lake watershed in the Adirondack region of New York addition of calcium carbonate limited episodic acidification (Newton et al., 1996). As observed at Woods Lake, W1 experienced higher concentrations of  $\text{Ca}^{2+}$  than W6 during storm events, as well as increased pH and ANC, and decreased  $\text{Al}_i$  due to the wollastonite dissolution, despite increased concentrations of  $\text{SO}_4^{2-}$  (Table 3; Figs. 2 and 3). The mitigation of acidic deposition and the modest improvement in associated episodic acidification of stream water likely starts before precipitation infiltrates the soils. The enhanced supply of  $\text{Ca}^{2+}$  is likely initiated with the leaching of exchangeable  $\text{Ca}^{2+}$  from foliage. Minocha et al. (2005) showed foliar exchangeable (soluble or biologically available)  $\text{Ca}^{2+}$  increased in five species (American beech, red spruce, sugar maple, paper birch, and yellow birch) after the application in W1.

#### 3.4. Relationship between Ca/Sr ratio and Ca from wollastonite

In both the large flow and small flow events of W1 and W6 Ca/Sr (mol) ratios were found to be nearly independent of discharge, exhibiting a slight decrease during the large flow event (mean values of  $\text{Ca/Sr (mol)} = 376$  for W1 and  $270$  for W6) compared with the small flow event (mean values of  $\text{Ca/Sr (mol)} = 413$  for W1 and  $279$  for W6). An increase in Ca/Sr ratio in the treated watershed was due to an increase in Ca availability derived from wollastonite (Figs. 2 and 3).

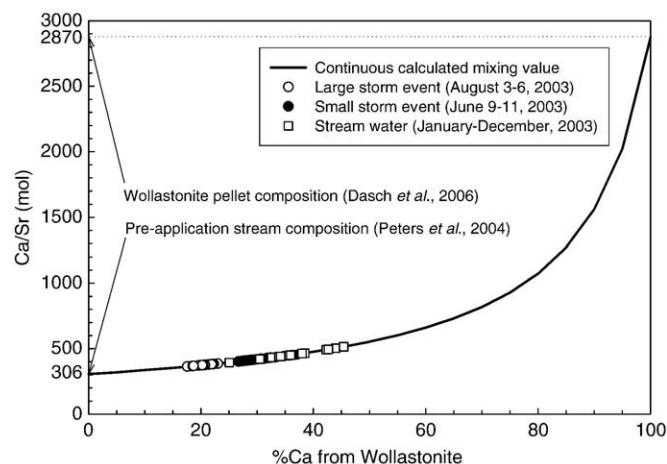
Weekly stream water samples have been collected at the weir of W1 to evaluate the watershed response to the wollastonite treatment (Peters et al., 2004). Ca/Sr ratios indicated that wollastonite contributions in W1 increased Ca/Sr up to  $877$  (mol ratio) immediately after the application (October 19, 1999) and the ratio remained higher during the summer storm period in 2003 (average  $\text{Ca/Sr} = 403$ ) than during the same periods in 1999 (average  $\text{Ca/Sr} = 304$ , Fig. 4). Although Ca/Sr ratios in 2003 were smaller than those in fall 1999 following the treatment, ratios during snowmelt (mean  $\text{Ca/Sr} = 429$  from March to April), summer storm events (mean  $\text{Ca/Sr} = 403$  from May to August), and late fall periods (mean  $\text{Ca/Sr} = 476$  from October to November) were higher than those ratios



**Fig. 4.** Ca/Sr (mol) ratio in weekly stream water between the pre-treatment period (prior to October 19, 1999) and the post-treatment period (2003) at watershed 1.

prior to the treatment (mean Ca/Sr = 299, 304, and 304, respectively). Initial high values (from 694 to 877) of Ca/Sr in 1999 were attributed by direct input of wollastonite into the stream channel (Peters et al., 2004). Subsequently,  $\text{Ca}^{2+}$  derived from the wollastonite dissolution was transported to the stream channel of W1 via supply from shallow flowpaths (Table 3).

The increase in  $\text{Ca}^{2+}$  concentration in the treated watershed was expected as the result of the  $\text{CaSiO}_3$  addition. A distinct Ca/Sr ratio compared to other sources at Hubbard Brook (e.g. precipitation, weatherable minerals) enables us to trace the fate of the added  $\text{Ca}^{2+}$  in the ecosystem, assuming a constant Sr content and constant Sr isotopic composition (Blum et al., 2000; Peters et al., 2004; Dasch et al., 2006). Dasch et al. (2006) showed that  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  derived from wollastonite and incorporated into hardwood foliage, generally retains its characteristic Ca/Sr ratio (~10-fold higher than background values), with only a small (<16%) discrimination upon foliar uptake. Therefore, the Ca/Sr ratio can be used to quantify the amount of wollastonite-derived  $\text{Ca}^{2+}$  in stream water, even if some is derived from foliar leaching. The percent of  $\text{Ca}^{2+}$  derived from wollastonite added to W1 as a function of the ratio of  $\text{Ca}^{2+}$  to  $\text{Sr}^{2+}$  during the large and small storm events, as well as monthly stream water samples are shown in Fig. 5. During the large event the amount of  $\text{Ca}^{2+}$  derived from wollastonite ranged from 17.6 to 22.9% (mean value: 20.7%), while during the small event values were approximately 26.7 to 32.4% (mean value: 29.0%). The percent of  $\text{Ca}^{2+}$  derived from the



**Fig. 5.** Relationship between Ca/Sr (mol) ratio and %  $\text{Ca}^{2+}$  from wollastonite during the large event (○), the small event (▲), and monthly stream water (□) at the treated watershed. Solid line (calculated mixing values; Peters et al., 2004) describes continuous computed mixing relationships between the pre-application stream water (Ca/Sr (mol) = 306) and wollastonite pellet composition (Ca/Sr (mol) = 2870).

wollastonite during the monthly stream water samples from May to August, 2003 was 31.4% (Table 4).

Calcium concentrations, Ca/Sr (mol) ratios, and %  $\text{Ca}^{2+}$  from wollastonite during the large storm event were smaller than values during the small storm event and monthly samples of stream water. The small storm event also showed statistically smaller values of Ca/Sr ( $p < 0.05$ , two sample  $t$ -test) and %  $\text{Ca}^{2+}$  ( $p < 0.05$ , two sample  $t$ -test) derived from wollastonite than monthly samples of stream water (Table 4). During the large storm event, elevated discharge related to precipitation amounts decreased the  $\text{Ca}^{2+}$  derived from wollastonite, while the small storm event with lower discharge had either no effect, or slightly decreased the  $\text{Ca}^{2+}$  derived from the wollastonite. This pattern was probably impacted by groundwater and pre-event water concentrations. To explain the possible role of groundwater and subsurface flow on the  $\text{Ca}^{2+}$  derived from added wollastonite, we hypothesize that by 2003  $\text{Ca}^{2+}$  from the dissolution of  $\text{CaSiO}_3$  was not transported to groundwater and was retained in subsurface horizons. High water table is expected during the large storm and this high water table may encourage groundwater to dilute the  $\text{Ca}^{2+}$  concentration derived from wollastonite in subsurface flow which drains into stream channel. On the other hand, low water table during the small storm period may either limit dilution of  $\text{Ca}^{2+}$  derived from the added wollastonite or not, and the old subsurface water concentration is likely to control stream concentrations. Changes of solute

**Table 4**  
Relationships between Ca/Sr ratio and % Ca derived from wollastonite dissolution in storm water and stream water of W1.

		Storm water		Stream water	
		Large event (August 3–6, 2003)		Monthly intervals (May–August, 2003)	
$\text{Ca}^{2+}$ ( $\mu\text{mol/L}$ )	$\bar{x}$	31.6	32.5	33.8	
	SD	2.2	0.5	2.7	
	$n$	24	24	7	
	$p$		0.034	0.268	
Ca/Sr (mol)	$\bar{x}$	375.7	413.1	426.0	
	SD	5.84	7.26	16.0	
	$n$	24	23	7	
	$p$		0.000	0.042	
% Ca from wollastonite	$\bar{x}$	20.7	29.0	31.4	
	SD	1.43	1.44	3.16	
	$n$	24	23	7	
	$p$		0.000	0.048	

$\bar{x}$  = arithmetic mean; SD = standard deviation;  $n$  = numbers;  $p$  =  $p$ -value (< sign of inequality) is test result between large and small events, or between small event and stream water by two sample  $t$ -test or paired  $t$ -test based on  $p$ -value, using the significance level of 0.05 and 95% confidence intervals for all tests.

<sup>a</sup> Paired  $t$ -test.

<sup>b</sup> Two sample  $t$ -test.

<sup>c</sup> The  $\text{Ca}^{2+}$  concentration in the small event is not statistically different from the monthly stream water values.



**Table 5**

Statistical analysis for improving precision of the comparison of mean values in acid neutralizing capacity and evaluating  $\text{Ca}^{2+}$  as a factor increasing ANC values in W1 of the HBEF during the storm events.

Category	Storm water ( $\mu\text{mol/L}$ ) <sup>a</sup>		Hypothesis <sup>b</sup>	Test	<i>p</i> -Value	95% confidence interval	Test result <sup>c</sup>	Conclusion <sup>d</sup>
	W1	W6						
Ca <sup>2+</sup>	32	19	H <sub>a</sub> : $\mu_{W1-\text{Ca}} > \mu_{W6-\text{Ca}}$ H <sub>o</sub> : $\mu_{W1-\text{Ca}} \leq \mu_{W6-\text{Ca}}$	Two sample <i>t</i> -test	0.00	12.4–13.2	Reject H <sub>o</sub>	$\mu_{W1-\text{Ca}} > \mu_{W6-\text{Ca}}$
Mg <sup>2+</sup>	8.3	9.9	H <sub>a</sub> : $\mu_{W1-\text{cations}} < \mu_{W6-\text{cations}}$	Paired <i>t</i> -test	0.07	–3.0–0.7	Fail to reject H <sub>o</sub>	$\mu_{W1-\text{cations}} \approx \mu_{W6-\text{cations}}$
Na <sup>+</sup>	36	38	H <sub>o</sub> : $\mu_{W1-\text{cations}} \geq \mu_{W6-\text{cations}}$ OR		0.15	–1.4–5.4	Fail to reject H <sub>o</sub>	$\mu_{W1-\text{anions}} \approx \mu_{W6-\text{anions}}$
K <sup>+</sup>	2.6	3.7	H <sub>a</sub> : $\mu_{W1-\text{cations}} \neq \mu_{W6-\text{cations}}$					
NH <sub>4</sub> <sup>+</sup>	1.3	0.8	H <sub>o</sub> : $\mu_{W1-\text{cations}} = \mu_{W6-\text{cations}}$					
SO <sub>4</sub> <sup>2–</sup>	46	40	H <sub>a</sub> : $\mu_{W1-\text{anions}} > \mu_{W6-\text{anions}}$	Paired <i>t</i> -test	0.08	–1.4–5.4	Fail to reject H <sub>o</sub>	$\mu_{W1-\text{anions}} \approx \mu_{W6-\text{anions}}$
NO <sub>3</sub> <sup>–</sup>	6.7	4.9	H <sub>o</sub> : $\mu_{W1-\text{anions}} \leq \mu_{W6-\text{anions}}$ OR		0.16			
Cl <sup>–</sup>	14	13	H <sub>a</sub> : $\mu_{W1-\text{anions}} \neq \mu_{W6-\text{anions}}$					
F <sup>–</sup>	1.26	1.24	H <sub>o</sub> : $\mu_{W1-\text{anions}} = \mu_{W6-\text{anions}}$					

<sup>a</sup> Data for all solute concentrations are taken from the analysis of stream samples of W1 ( $n = 133$ ) and W6 ( $n = 144$ ) during storm events.

<sup>b</sup>  $H_a$  is an alternative hypothesis thought to be true and  $H_o$  is a null hypothesis that is the logical opposite of the  $H_a$ .

<sup>c</sup> Test result by rejection region: reject  $H_o$  if  $p\text{-value} < \alpha = 0.05$  and fail to reject  $H_o$  if  $p\text{-value} > \alpha = 0.05$ .

<sup>d</sup>  $\mu_{W1-i}$  is population mean of  $i$  (i.e.,  $\text{Ca}^{2+}$ , cations ( $\text{Mg}^{2+}$ – $\text{Na}^+$ – $\text{K}^+$ – $\text{NH}_4^+$ ), or anions ( $\text{SO}_4^{2-}$ – $\text{NO}_3^-$ – $\text{Cl}^-$ – $\text{F}^-$ )) concentration at W1 and  $\mu_{W6-i}$  is population mean of  $i$  (i.e.,  $\text{Ca}^{2+}$ , cations ( $\text{Mg}^{2+}$ – $\text{Na}^+$ – $\text{K}^+$ – $\text{NH}_4^+$ ), or anions ( $\text{SO}_4^{2-}$ – $\text{NO}_3^-$ – $\text{Cl}^-$ – $\text{F}^-$ )) concentration at W6 during storm events.

concentrations in stream chemistry are often linked to changes in the hydrologic flowpaths of water (Robson et al., 1995). Genereux and Hopper (1998) found that through the application of oxygen isotopes to storm event studies, the majority of storm flow (more than 80%) was derived from old water in a small watershed before the start of the event. Storm waters derived from different hydrologic flowpaths are characterized by distinct solute chemistries related to the biological and geological processes occurring along these flowpaths (Hogan and Blum, 2003). The changes in stream  $\text{Ca}^{2+}$  concentrations during storm events in W1 were more associated with  $\text{Ca}^{2+}$  concentrations released from the wollastonite application in the organic soil water along shallow subsurface flowpaths than in the mineral soil water in comparison with W6 during the study period (Table 3).

### 3.5. Controls on change in stream ANC during storm events

By analyzing ionic solutes that contribute to stream water ANC (as indicated in Eq. (2)) the mechanisms driving changes in ANC can be determined and the causes of episodic acidification quantified. This approach allowed for examination of contributing ionic solute concentrations and their changes associated with ANC values.

W6 experienced significantly greater flow for each event than W1. However, event size did not have an impact on the mechanisms driving the changes in ANC for the storms investigated. Comparisons in calculated mean ANC values ( $\text{ANC}_c$  using the Eq. (2) and the mean values in Table 3) of the six storm waters were 6.7 and 0.35  $\mu\text{eq/L}$  for the treated watershed and the reference watershed during storm events, respectively. These values were slightly higher, but correspond with the mean measured ANC values (ANC) of 1.2 and  $-0.2 \mu\text{eq/L}$  at W1 and W6 (Table 3) during the storm periods. This difference between measured and calculated ANC values is likely due to the presence of unmeasured organic acids, which depress ANC values (Driscoll et al., 1995).

The data in Table 5 represent the concentrations of cations and anions found in W1 and W6 streams at the HBEF. The watershed with lower concentrations of strong acid anions will have higher ANC (Eq. (2)), and the watershed with higher  $\text{Ca}^{2+}$  concentrations and similar strong acid anion concentrations will also have higher ANC. To test this hypothesis, the null and the alternative hypotheses were established. The test results are shown in Table 5, including hypothesis, confidence interval, *p*-value, and a brief summary of each test. We conclude that the  $\text{Ca}^{2+}$  concentration in W1 is greater than that in W6 and there is insufficient evidence to claim that concentrations of ions except  $\text{Ca}^{2+}$  between two watersheds are different during storm events.

The major factor responsible for the difference in ANC between two watersheds is the difference in  $\text{Ca}^{2+}$  ( $p < 0.001$ , two sample *t*-test; Table 5) in spite of slightly higher concentrations of strong acid anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ;  $p > 0.05$ , two sample *t*-test) in the treated watershed compared to the reference watershed. Calcium concentrations were higher under all flow conditions of W1 than those of W6. In fact, the  $\text{Ca}^{2+}$  added due to the wollastonite addition, facilitated increases in pH and ANC and alleviated episodic acidification in W1 in comparison with W6.

## 4. Conclusions

The variability in the hydro-biogeochemical interactions between a Ca-treated watershed (W1) and a reference watershed (W6) at the HBEF were examined during six storm events. Detailed analyses of the response of individual chemical species during storm episodes helped elucidate factors that control storm event chemistry.

The  $\text{Ca}^{2+}$  concentrations were higher in stream water of W1, which was treated by wollastonite in 1999, resulting in higher pH and ANC and lower  $\text{Al}_i$  concentrations compared to the reference watershed (W6). Historical acidic deposition has depleted pools of exchangeable  $\text{Ca}^{2+}$  in the forest floor, making acidification of surface waters more severe during episodes. However, stream water draining W1 had either no decrease or only slight dilution in  $\text{Ca}^{2+}$  concentrations compared to pre-event water and still exhibited a positive mean ANC value (1.2  $\mu\text{eq/L}$ ) even during storm events, in comparison with stream water draining W6. This phenomenon probably resulted from the transmission of water through organic horizon with elevated  $\text{Ca}^{2+}$  in soil water. This shift in hydrologic flowpath supplied available  $\text{Ca}^{2+}$  derived from wollastonite dissolution in this horizon into the stream channel. The enhanced supply of  $\text{Ca}^{2+}$  was a major factor increasing ANC during storm events compared to other cations and anions. The difference between pre-event ANC and the minimum ANC was also calculated for each storm event. The changes of ANC were 0.0 and  $-9.9 \mu\text{eq/L}$  during the large event, and  $-0.7$  and  $-4.4 \mu\text{eq/L}$  during the small event at W1 and W6, respectively. Although the differences in pH, ANC, and  $\text{Al}_i$  between W1 and W6 were relatively small following the wollastonite treatment, Ca and  $\text{H}_4\text{SiO}_4$  concentrations were significantly greater in the treated watershed. This treatment bolstered stream  $\text{Ca}^{2+}$  concentrations and therefore limited the intensity of episodic acidification in summer storms in comparison with the reference watershed. We anticipate changes in biological structure and function associated with the watershed treatment which might include increases in stream microbial activity and

macroinvertebrate diversity and production in the stream ecosystem due to the increase in pH and the decrease in Al.

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