

9-1-2000

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## Response of a first-order stream in Maine to short-term *in-stream* acidification

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### Abstract

An experimental short-term acidification with HCl at a first-order stream in central Maine, USA was used to study processes controlling the changes in stream chemistry and to assess the ability of stream substrate to buffer pH. The streambed exerted a strong buffering capacity against pH change by ion exchange during the 6-hour acidification. Streambed substrates had substantial cation and anion exchange capacity in the pH range of 4.1 to 6.5. The ion exchange for cations and  $\text{SO}_4^{2-}$  were rapid and reversible. The speed of release of cations from stream substrates was  $\text{Na}^{1+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{n+} > \text{Be}^{2+}$ , perhaps relating to charge density of these cations.  $\text{Ca}^{2+}$  desorption dominated neutralisation of excess  $\text{H}^+$  for the first 2 hr. As the reservoir of exchangeable Ca diminished, desorption (and possibly dissolution) of  $\text{Al}^{3+}$  became the dominant neutralising mechanism. The exchangeable (and possibly soluble) reservoir of Al was not depleted during the 6-hour acidification. Sulphate adsorption during the acidification reduced the concentration of  $\text{SO}_4^{2-}$  in stream water by as much as  $20 \mu\text{eq L}^{-1}$  (from  $70 \mu\text{eq L}^{-1}$ ). Desorption of  $\text{SO}_4^{2-}$  and adsorption of base cations after the artificial acidification resulted in a prolongation of the pH depression. The streambed had the capacity to buffer stream water chemistry significantly during an acidifying event affecting the entire upstream catchment.

**Keywords:** stream acidification; ion exchange; sediment; sulfate exchange; aluminium; beryllium

### Introduction

Acidification of terrestrial and freshwater systems is a natural process driven by weakly acidic rainfall and the production of carbonic and organic acids in soil. The time scale for this type of acidification is typically in excess of 1000s of years in glaciated terrain. Increased deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^{1-}$  associated with air pollution has accelerated this chronic process of acidification. Short-term episodic acidification processes are superimposed on this longer process. Episodic acidification may be caused by a variety of mechanisms including high discharge (from snow-melt or high rainfall), flushing of partially oxidized organic matter or oxidized S, and pulsed inputs of marine aerosols. Episodic acidification of streams may cause adverse effects to biota, including fish kills. Ecosystems have various buffering processes for changes of pH including: (1) chemical weathering (slow), (2) dissolution of secondary soil “minerals” such as  $\text{Al}(\text{OH})_3$ ,  $\text{FeO}(\text{OH})$ , and  $\text{MnO}(\text{OH})$  (intermediate kinetics), (3) ion exchange (rapid), and (4) changes in speciation of aqueous species (nearly instantaneous) which include the  $\text{H}_2\text{CO}_3 - \text{HCO}_3^{1-} - \text{CO}_3^{2-}$

equilibria, and other weak acid systems (especially organic acids and Al). Better understanding of these buffering mechanisms and their capacity is critical for predicting the severity of and recovery from chronic and episodic acidification. Most buffering mechanisms are attributed to soil-soil water interaction (Cosby *et al.*, 1985; Dahlgren *et al.*, 1990).

The role of stream substrate in neutralising acidity that has survived soil acid neutralising processes has been explored experimentally (Tipping and Hopwood, 1988; Norton *et al.*, 1990, 1992; Watne *et al.*, 1992) although the capacity of the stream bed to neutralise acidity has rarely been quantified. Capacity is clearly related to the relative area of terrestrial drainage, soil volume, and area (or volume) of the interacting stream bed. All other factors being equal, larger catchments should overwhelm any effects of the stream substrate on buffering changes in water quality. A small low alkalinity headwater stream in Maine, USA was acidified to evaluate the release of potentially toxic amounts of Al and Be, as well as to identify and quantify the mechanisms of acid neutralisation and buffering of pH by the stream bed during episodic

acidification. Speciation of metals in acidifying stream water is important because of influence on potential toxicity by the dissolved metals, adsorption-desorption equilibria, and dissolution/precipitation reactions. Therefore, the variations of Al and Be aqueous species during the cycle of acidification were calculated.

## Methods

### SITE DESCRIPTION

We acidified an unnamed first-order stream (henceforth Beryllium Stream) in the Halfmile Stream sub-catchment of the Union River catchment, approximately 20 km west of Lead Mountain and 32 km east of Bangor, Maine, USA. The catchment elevation ranges from 90 m to 180 m, just above the post-glacial marine limit in Maine (Thompson and Borns, 1985). The catchment above the point of the acidification is approximately 2 km<sup>2</sup>. Soil depth ranges from 0 to 1 m. The soils are well-developed spodosols on till. The Wisconsinian till is derived largely from the underlying Lucerne Granite (Wones, 1980). This biotite granite has relatively high F (ca. 0.1%) and Be (ca. 15 mg kg<sup>-1</sup>) (Vesely *et al.* in press). Mixed forests (mainly northern hardwood and spruce/fir/pine) cover the catchment. The canopy was nearly closed along the riparian zone. The streambed consisted of dominantly sand- and silt-sized quartz and feldspar from the till, with minor exposed bedrock, and organic debris and live *Sphagnum* moss. Kaste (1999) determined that the *Sphagnum* at that locality had an ion exchange capacity up to 225 cmol (+) kg<sup>-1</sup>, nearly ten times as high as for the sand/silt-sized material in the streambed. The stream is typically low in alkalinity (Table 1); dissolved organic carbon (DOC) is typically 1 to 2 mg kg<sup>-1</sup>. The stream was studied for the origin and dynamics of aqueous Be by Rissberger (1993) and Kaste (1999).

### TREATMENT AND SAMPLING

The acidification experiment was conducted on October 9th, 1999. Twenty-eight moles of HCl were added to the stream over a 6-hour period. The delivery mechanism was a 25 litre carboy with an attached burette to regulate the flow. Chloride was assumed to be conservative in Beryllium Stream. Knowing (1) the total moles of HCl added to the stream over 6 hours and (2) the nearly constant Cl concentration achieved in the middle section of the stream, the stream discharge was calculated to be about 300 L min<sup>-1</sup>.

Stream solution samples were taken at 0 (just above the point of acid addition), 20, 50, and 100 m downstream from the acid addition point repeatedly for 8 hours, including 2 hours after the acid addition stopped. One sample at 0 m was filtered through a 0.2 µm polycarbonate membrane to determine the amount of suspended particulate matter.

Samples were brought back to the laboratory on the same day, stored at 5 °C, and analysed within a week.

### ANALYTICAL TECHNIQUES

Al, Be, Ca, K, Mg, and Na were analysed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin-Elmer, model Optima 3300XL). Cl<sup>1-</sup>, F<sup>1-</sup>, NO<sub>3</sub><sup>1-</sup>, and SO<sub>4</sub><sup>2-</sup> were analysed with an ion chromatograph (IC, Dionex, DX 500 chromatographic system, CD20 conductivity detector, GP50 gradient pump, and AS40 automated sampler). pH was measured with a radiometer meter (Copenhagen, SAC 80 sample changer) after equilibration with standard air containing 300 ppm CO<sub>2</sub>. All the analyses were done at the Environmental Chemistry Laboratory of the George J. Mitchell Center, University of Maine. The chemical equilibrium software MINEQL + ver 3.01b (Schecher and McAvoy, 1998) was used to model changes in ionic speciation during the artificial acidification. Input data were measured pH, CO<sub>2</sub> pressure (10<sup>-3.5</sup> atm), and concentrations of Al, Be, Ca, K, Mg, Na, Cl, F, and SO<sub>4</sub>. Nitrate remained between 0 and 1 µeq L<sup>-1</sup> and DOC remained relatively constant and low (Table 1) and thus neither was considered in the calculations.

## Results

Prior to the acidification, the stream had a pH of 6.42 (± 0.06) (Table 1). If the stream water were in equilibrium with atmospheric PCO<sub>2</sub> (= 10<sup>-3.5</sup> atm.) at 10 °C,

$$K_{\text{CO}_2} = [\text{H}_2\text{CO}_3]/\text{PCO}_2[\text{H}_2\text{O}] \quad (1)$$

$$[\text{H}_2\text{CO}_3] = K_{\text{CO}_2}\text{PCO}_2 = (10^{-1.27})(10^{-3.5}) = 10^{-4.77} \quad (2)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^{1-}]/[\text{H}_2\text{CO}_3] \quad (3)$$

$$\begin{aligned} \text{Thus, } [\text{HCO}_3^{1-}] &= 10^{-6.46}[\text{H}_2\text{CO}_3]/[\text{H}^{1+}] \\ &= 10^{-6.46}10^{-4.77}/10^{-6.42} = 10^{-4.81} \text{ (moles L}^{-1}\text{)} \quad (4) \end{aligned}$$

This value is approximately 16 µeq L<sup>-1</sup> a value that is probably low because of general over-saturation of this stream with CO<sub>2</sub>. Calculated alkalinity, based on [(sum of strong base cations) - (sum of strong acid anions)], was +25 µeq L<sup>-1</sup>. Kaste (1999) determined that alkalinity ranged from about +25 to slightly less than 0 µeq L<sup>-1</sup>, depending on discharge. Titration (protonation) of HCO<sub>3</sub><sup>1-</sup> during the artificial acidification to nearly pH = 4 would be nearly complete. The HCO<sub>3</sub><sup>1-</sup> contributes little to the charge balance of the water compared to SO<sub>4</sub><sup>2-</sup> and Cl<sup>1-</sup> (Table 1). Marine aerosols in the stream water contribute approximately 12 µeq Mg L<sup>-1</sup>, 50 µeq Na L<sup>-1</sup>, 61 µeq Cl L<sup>-1</sup>, and 6 µeq SO<sub>4</sub><sup>2-</sup> from atmospheric

Table 1. Chemistry of water samples from the experimental acidification. Delta equals [(concentration at a sampling site and time)-(the concentration from above the point of acid addition)].

hrs	dist. m	Be ueq/L	Al ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	Cl ueq/L	SO4 ueq/L	H ueq/L	F ueq/L		
0*	0	0.2	16.9	49.2	22.5	104.0	4.8	61.6	72.9	0.4	6.4	9.9	
0	0	0.2	16.2	49.1	23.4	99.2	5.0	62.0	72.9	0.3	6.5	9.8	
4	0	0.2	16.2	48.4	23.2	102.7	4.7	60.3	72.5	0.4	6.4		
6.5	0	0.2	15.5	47.6	23.5	103.1	4.3	60.0	72.1	0.3	6.5		
avg.		0.2	16.2	48.6	23.1	102.2	4.7	61.0	72.6	0.4	6.4		
hrs	dist.	Be ueq/L	Al ueq/L	Ca ueq/L	Mg ueq/L	Na ueq/L	K ueq/L	Cl ueq/L	SO4 ueq/L	H ueq/L	EqpH	EqpH	
		delta	delta	delta	delta	delta	delta	delta	delta	delta	delta	delta	
0.5	20	0.4	27.9	70.4	21.8	6.4	2.6	0.5	72.0	-5.3	1.6	1.2	5.8
1	20	0.5	33.0	76.4	27.8	7.7	10.9	0.0	86.0	-5.4	2.3	2.0	5.6
2	20	1.5	106.3	116.8	68.2	17.4	7.4	0.5	265.0	-16.8	45.7	45.3	4.3
4	20	2.0	154.6	138.3	68.7	15.6	8.3	0.1	404.0	-20.1	87.1	86.7	4.1
6	20	1.3	94.6	87.8	39.3	8.5	1.3	0.0	280.0	-5.7	56.2	55.9	4.3
6.5	20	1.4	108.1	91.9	34.8	7.4	2.2	0.1	258.0	2.3	45.7	45.3	4.3
7	20	0.7	43.4	27.2	7.8	1.0	-9.6	0.0	128.0	14.7	14.1	13.7	4.9
7.5	20	0.5	32.2	16.0	1.0	0.2	3.0	-0.3	97.9	15.4	5.1	4.7	5.3
8	20	0.4	27.0	10.8	-4.9	-0.9	0.0	-0.4	81.5	14.1	3.5	3.1	5.5
0.5	50	0.2	16.1	-0.1	-0.4	-0.7	-6.5	0.1	64.4	-0.3	0.3	0.0	6.5
1	50	0.3	20.1	3.9	6.8	3.4	7.8	0.2	81.6	-1.7	0.6	0.2	6.2
2	50	0.5	33.4	17.2	31.8	8.6	1.3	0.4	150.0	-8.0	1.6	1.2	5.8
4	50	1.1	75.2	59.0	58.7	14.7	0.4	0.3	253.0	-12.4	10.5	10.1	5.0
6	50	1.8	120.1	103.9	74.2	17.1	3.9	0.0	333.0	-15.9	30.9	30.5	4.5
7	50	1.8	130.1	113.9	65.7	16.5	5.7	-0.2	333.0	-13.5	37.2	36.8	4.4
8	50	0.8	51.7	35.5	22.8	4.9	-2.6	-0.3	154.0	9.6	8.7	8.3	5.1
2	100	0.3	18.9	2.7	7.3	2.4	-2.2	0.5	78.5	-2.1	0.4	0.0	6.4
4	100	0.8	48.3	32.0	66.2	18.6	7.4	0.5	220.0	-15.6	2.8	2.4	5.6
6	100	1.5	99.4	83.2	98.2	23.7	6.5	0.6	324.0	-22.2	7.4	7.0	5.1

\* = filtered.

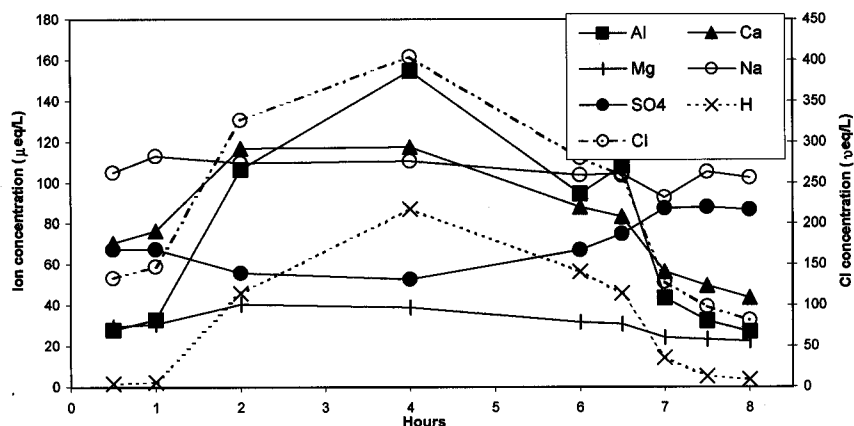


Fig. 1. Chemical changes through time (h) in Beryllium Stream during the artificial acidification, at 20 m downstream from the point of acid addition.

pollution is about  $67 \mu\text{eq L}^{-1}$ . Background concentrations did not vary significantly over the course of the experiment.

Prior to the acidification, the patterns of the aqueous concentrations (in  $\mu\text{eq L}^{-1}$ ) were  $\text{Na} > \text{Ca} > \text{Al}$  (Fig. 1). The concentration of all analytes in Table 1 were virtually identical in the filtered and unfiltered samples taken at 0 m at the start of the experiment, so suspended material was nearly zero. Concentrations of all the base cations and Al increased quickly as a consequence of the HCl addition. The  $\text{Na}^{1+}$  response peaked in the first hour of the 6-hour HCl addition. By 2 hr at the 20 m site, however, the concentration pattern shifted to (in  $\mu\text{eq L}^{-1}$ )  $\text{Al} > \text{Ca} > \text{Na}$ . The shape of response curves shows that the release of  $\text{Na}^{1+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  was faster and more short-lived in response to the acidification than  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$ . The peak of  $\text{Ca}^{2+}$  was less sharp than that of  $\text{Na}^{1+}$  and occurred about 2 hr after the acidification started. The concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  declined after 2 hr even as  $\text{Cl}^{1-}$  concentration continued to increase up to 4 hr, indicating a decline in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  released from stream substrates. The release of  $\text{Al}^{3+}$  from stream substrates contributed the most neutralisation followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . At 8 hr after the start of acidification, 2 hr after cessation of acid addition, the concentrations of both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the 20 m site were lower than the background concentrations. Essentially the same temporal response in cation concentrations at 20 m occurred later further downstream. At 50 m and 100 m downstream, the  $\text{Cl}^{1-}$  concentration was nearly equal at 6 hr. The faster response of Ca than Al during the first hour at 20 m also occurred during 4 to 6 hr at 100 m downstream.

Combining all samples from all locations across time, correlations between  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$ , and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are extremely high ( $r^2 = 0.99$  and  $0.98$ , respectively). This tight linkage suggests that these ion pairs were being desorbed, and later adsorbed, in the same proportion, regardless of pH.

Sulphate concentration at 20 m declined below the background value during acidification and then increased above

the background after 7 hr. The concentration of  $\text{SO}_4^{2-}$  was negatively correlated with  $\text{H}^{1+}$  ( $r^2 = 0.74$ ) across all the samples. Nitrate remained at  $1 \mu\text{eq L}^{-1}$ . Fluoride and DOC were low and measured only for background samples.

## Discussion

### CATION RESPONSES TO pH CHANGES

Several lines of evidence support the conclusion that ion exchange occurred between the stream substrates and the stream water as a consequence of the addition of  $\text{H}^{1+}$ . Concentrations of all the base cations, Al, and Be increased concurrently with the increase in  $\text{Cl}^{1-}$  and  $\text{H}^{1+}$ . Two types of equilibria probably occur. Exchange with  $\text{H}^{1+}$  is clearly occurring. Using Ca as an example:



for which an equilibrium constant can be defined:

$$K_{\text{exch.}} = (\text{Ca}^{2+})[\text{H}_2\text{-Substrate}]/(\text{H}^{1+})^2[\text{Ca-Substrate}] \quad (6)$$

where brackets denote the mole fraction on the exchange site (analogous to base saturation) and parentheses indicate activity of the cation in solution. Rearranging the terms and making the assumption that the exchange site occupancy for  $\text{Ca}^{2+}$  and  $\text{H}^{1+}$  remains proportionally the same,

$$K_{\text{exch.}} = \{(\text{Ca}^{2+})/(\text{H}^{1+})^2\} * \{[\text{H}_2\text{-Substrate}]/[\text{Ca-Substrate}]\} \quad (7a)$$

$$K'_{\text{exch.}} = \{(\text{Ca}^{2+})/(\text{H}^{1+})^2\} \quad (7b)$$

As long as the occupancy of exchange sites by the two competing species remains proportionately constant, the ratio  $(\text{Ca}^{2+})/(\text{H}^{1+})^2$  in solution should remain constant. If two base cations (e.g. Ca and Mg) compete for the same site

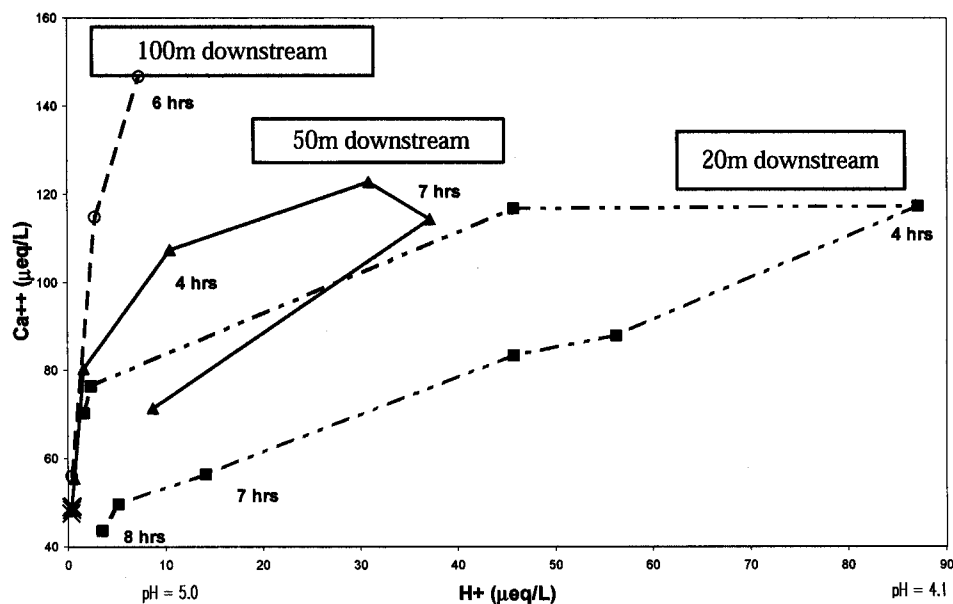
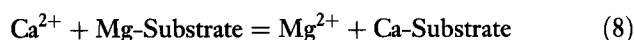


Fig. 2. Concentration of  $\text{Ca}^{2+}$  versus  $\text{H}^{1+}$  through time (h) in Beryllium Stream at different locations.

(both of which compete with  $\text{H}^+$ ) we may write:



$$K_{\text{exch.}} = \left\{ \frac{(\text{Mg}^{2+})}{(\text{Ca}^{2+})} \right\} / \left\{ \frac{[\text{Ca-Substrate}]}{[\text{Mg-Substrate}]} \right\} \quad (9)$$

As for the  $\text{H}^{1+}$ -base cation exchange equilibria, the ratio of Ca/Mg in the solution should remain constant as long as the proportions of Ca and Mg on exchange sites remain constant. The correlation between Ca and Mg for all samples across all sites was  $r^2 = 0.99$ , indicating that the relative proportions of these two elements on the exchange sites did not change substantially during the acidification.

The relationships between Ca and Mg for all samples and  $\text{H}^{1+}$  or  $(\text{H}^{1+})^2$  are less strong. Concentrations of  $\text{Ca}^{2+}$  (Fig. 2) and  $\text{Mg}^{2+}$  plotted against  $\text{H}^{1+}$  have a clear evolution if sequential water samples are plotted for each stream location. For example, the first two samples at 20 m (0.5 and 1 hr), three samples (0.5, 1, and 2 hr) at 50 m, and three samples (2, 4, and 6 hr) at 100 m have steep positive slopes, indicating rapid desorption of  $\text{Ca}^{2+}$  (and  $\text{Mg}^{2+}$ , not shown). This desorption persisted longer farther downstream probably because  $\text{H}^{1+}$  was lower and water in transit had already acquired additional  $\text{Ca}^{2+}$  from upstream desorption. Sequential sample values moved clock-wise at both 20 m and 50 m. As the  $\text{H}^{1+}$  concentration increased above  $30 \mu\text{eq L}^{-1}$  ( $\text{pH} = 4.5$ ), desorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  decreased significantly. At 20 m and 50 m, for any specific  $\text{H}^{1+}$  concentration, earlier samples always had higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  than later samples. This implies that the exchangeable Ca and Mg pools were depleted during the 6 hr acidification, violating the assumption of (Eqn. 7b). Apparently, exchange site occupancy by Ca and Mg was

decreasing substantially, i.e. occupancy by  $\text{H}^{1+}$  was increasing significantly. A similar behaviour was documented by Wright *et al.*, (1988) where Na replaced Ca and Mg in a simulated marine salt-driven episode of acidification. Other experimental stream acidification studies reported that the early neutralisation of stream acidity was dominated by  $\text{Ca}^{2+}$  desorption followed by  $\text{Al}^{3+}$  desorption, and both were effective for a few hours to a few days (Norton *et al.*, 1990). Dynamics like this are not decipherable in natural individual episodes because of the magnitude of the total exchange capacity of the soils in the catchment. However, during prolonged artificial acidification of a whole catchment at Bear Brook Watershed in Maine, the relationship between Ca and Mg in stream water did change, because of preferential elution of Mg from the soils (Norton *et al.*, 1999).

The last stream sample (8 hr) at 20 m had lower  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations than prior to the acidification (Fig. 3). These depressed concentrations are likely caused by re-sorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and desorption of excess  $\text{H}^{1+}$  from exchange sites, due to the lowered  $\text{H}^{1+}$  in the stream. The streambed should continue to adsorb  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  until the exchanger  $[\text{H}_x\text{-substrate}]/[\text{cation-substrate}]$  recovers to the pre-acidification condition. Because of the  $\text{H}^{1+}$  desorption during this later phase, stream recovery from pH depression is slower than the stream with non-reactive substrate (Norton *et al.*, 1990).

The concentrations of  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$  plotted against  $\text{H}^{1+}$  have very consistent relationships across the entire pH range and through the experiment, supporting the ion exchange model (Eqns. 7a and 7b). The  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$  had a significant exponential relationship against  $\text{H}^{1+}$  ( $\text{Al} = m[\text{H}^{1+}]^{0.4} + c$ ;  $r^2 = 0.91$  for both). The exchangeable Be and Al pools on the stream substrate were sufficiently

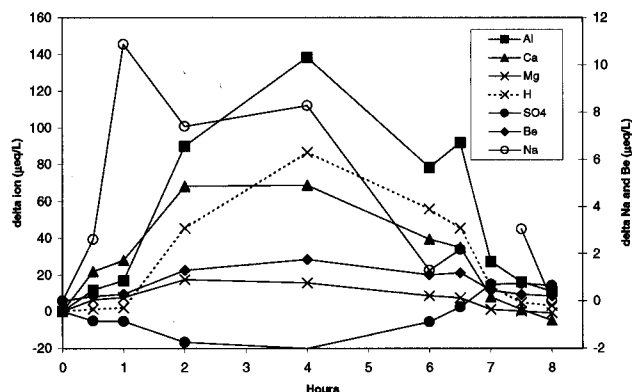


Fig. 3. Changes in ion concentrations through time (h), at 20 m downstream from the point of acid addition, relative to background conditions (delta concentration).

large for the experimental acidification not to deplete these pools significantly, either proportionately (Al versus Be) or absolutely. This is clear from inspection of the temporal changes in Al and Be against  $H^{1+}$  at each sampling location. As a consequence, Al and Be for all samples are strongly correlated ( $r^2 = 0.99$ ).

The nature of the streambed source of elevated Al in the stream water is not clear. It may be  $Al(OH)_3$  precipitated during mixing of emerging acidic soil solutions with higher pH stream water or from increasing pH caused by degassing of excess  $CO_2$  (Norton and Henriksen, 1983). The acidified samples were under-saturated with respect to amorphous  $Al(OH)_3$  but approach saturation with respect to the crystalline form, gibbsite ( $Al(OH)_3$ ). Alternatively, the Al could be truly exchangeable. The Be concentrations in solution are well below saturation. However, Kaste (1999) found that, at low flow, up to 50% of the total Be in the stream samples was particulate. The Be may occur as exchangeable Be, or it may be occluded in, or co-precipitated with  $Al(OH)_3$ . However, the constancy of the Al/Be ratio during the experiment and the lack of particulate matter in the water argue that the elevated Al and Be was from exchangeable pools.

#### DIFFERENCES IN BEHAVIOR OF CATIONS

Despite the high correlation between  $Ca^{2+}$  and  $Mg^{2+}$ , and between  $Al^{3+}$  and  $Be^{2+}$ , their response to the acid addition was slightly different, reflecting the differences in charge density and perhaps the substrate selectivity. The  $Ca^{2+}/Mg^{2+}$  ratio reveals that  $Ca^{2+}$  was desorbed preferentially when pH of the solution was decreasing and re-adsorbed preferentially compared to  $Mg^{2+}$  when pH started decreasing. This may be explained by the lower charge density of  $Ca^{2+}$  than  $Mg^{2+}$ . Essentially no trend was present between  $Al^{3+}$  and  $Be^{2+}$ , perhaps because of the smaller difference in charge density between  $Al^{3+}$  and  $Be^{2+}$

and also because of a larger pool of exchangeable Al and Be, relative to that for Ca and Mg. This is consistent with the finding that  $Al^{3+}$  versus  $Be^{2+}$  had a slightly stronger correlation than  $Ca^{2+}$  versus  $Mg^{2+}$ . Cation selectivity of streambed substrates is likely to affect  $Ca^{2+}$  and  $Mg^{2+}$  more significantly than  $Al^{3+}$  and  $Be^{2+}$  because the reservoir size of exchangeable Ca and Mg is small relative to desorption rate. Significant desorption of  $Ca^{2+}$  and  $Al^{3+}$  from mosses occurred at two streams experimentally acidified in southern Norway (Henriksen *et al.*, 1988). The selectivity of that moss to different cation is unknown.

In soil from the Bear Brook Watershed, approximately 30 km to the east, there has been a similar cation response to catchment-scale artificial acidification (Norton *et al.*, 1999). For those spodosol Bs soils, Dahlgren *et al.* (1990) demonstrated that the exchangeable reservoir size was  $Al \gg K = Ca > Na$ .

#### ANION RESPONSE TO pH CHANGES

Sulphate concentration changed dramatically and rapidly during the experimental acidification. Sulphate adsorption occurred during the acidification, presumably as a response to lower pH producing protonation of  $Al(OH)_3$ , thereby increasing the anion adsorption capacity (Fig. 4). During the acid addition, total equivalents of  $SO_4^{2-}$  adsorbed were less than the equivalents of  $Ca^{2+}$  desorbed. The rapid shift by  $SO_4^{2-}$  from sorption to desorption happened before  $Ca^{2+}$  switched from desorption to adsorption, suggesting that the anion exchange capacity for  $SO_4^{2-}$  is smaller than for  $Ca^{2+}$ ; i.e. the water had nearly equilibrated with the sediment with respect to  $SO_4^{2-}$  before the acidification stress ceased. The desorption and adsorption trajectories as a function of pH were not equivalent, as they were for Ca and Mg (contrast Figs. 2 and 4).

#### THE IMPACT OF ION EXCHANGE BY STREAM SUBSTRATE ON EPISODIC ACIDIFICATION

Anion adsorption and cation desorption occurred during acidification of the stream water. This process (Eqn. 5) was reversed during decreasing acid stress. Consequently, the depth of pH depression during episodic acidification was reduced and the time necessary for recovery was increased. Norton *et al.* (1990) suggested the role of exchangeable cations in moderating episodic acidification and recovery. However, the effect of  $SO_4^{2-}$  dynamics has not been observed in streams during experiments because most of the experiments used  $H_2SO_4$  as the acid, due to its well-established role in anthropogenic acidification. The majority of recovery of pH and concentrations of other cations and  $SO_4^{2-}$  should take only hours because of the reversibility and speed of the reactions, and the rate of supply by stream water.

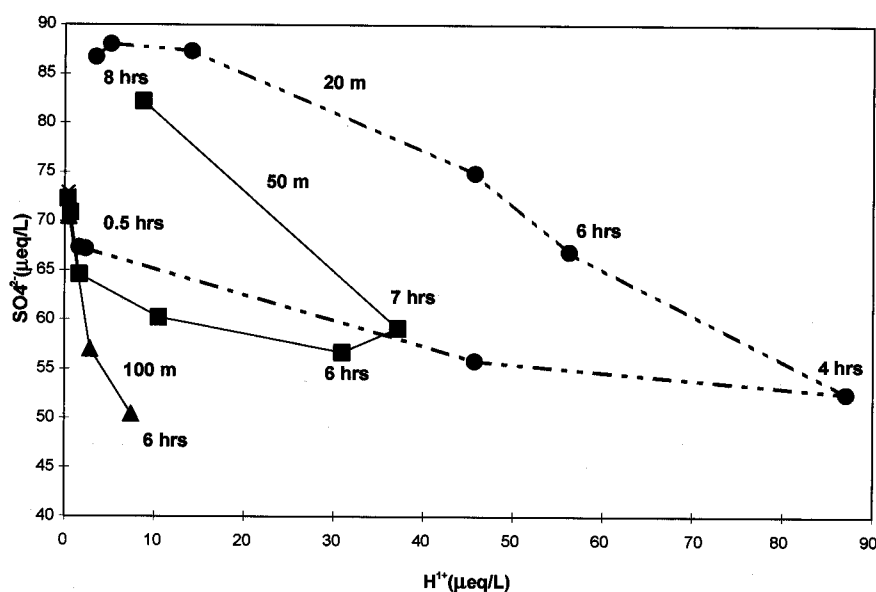


Fig. 4. Changes in  $\text{SO}_4^{2-}$  concentration versus  $\text{H}^{1+}$  through time (h) in Beryllium Stream at different locations.

#### SINKS FOR ADDED $\text{H}^{1+}$

$\text{H}^{1+}$  may interact with organic matter in the stream (particulate or dissolved), reducing variations of pH through either ion exchange or protonation. Norton *et al.* (1987) found a 25% increase (but a small absolute amount) in total organic carbon in a stream during a similar acidification experiment. In Beryllium Stream, dissolved organic C concentration is typically less than  $2 \text{ mg L}^{-1}$ . The experiment was conducted in autumn and hardwood deciduous leaves were abundant in the stream. Their contribution to pH neutralisation could not be isolated from the more stable organic and inorganic streambed substrate. However, the concentration of K, an abundant leachate from fresh litter, varied little during the experiment. During the maximum pH depression, ion balance ( $\mu\text{eq L}^{-1}$ ) is maintained as follows ( $\text{K}^{1+}$  is trivial,  $\text{F}^{1-}$  remains constant):

$$\Delta \text{ Ion balance} = (\Delta \text{ anions}) - (\Delta \text{ cations}) \quad (10a)$$

$$\Delta \text{ Ion balance} = (\Delta \text{Cl} + \Delta \text{SO}_4 + \Delta \text{HCO}_3 + \Delta \text{Org}^-) - (\Delta \text{H} + \Delta \text{Al} + \Delta \text{Be} + \Delta \text{Ca} + \Delta \text{Mg} + \Delta \text{Na}) \quad (10b)$$

$$\Delta \text{ Ion balance} = (+342 - 20 - 25 - 5) - (90 + 154 + 3 + 68 + 17 + 6) \quad (10c)$$

$$\Delta \text{ Ion balance} = (292) - (338) = -46 \text{ ueq L}^{-1}, \text{ unaccounted for} \quad (10c)$$

This deficit is partly attributable to increases in the effective charge of Al as a result of changes in speciation from hydroxyfluoride complexes to dominantly free Al and the formation of free F. Additional uncalculated changes

include the decrease of the  $\text{CaHCO}_3^{1+}$  and  $\text{MgHCO}_3^{1+}$  complexes during acidification.

#### CHANGES IN SPECIATION DURING THE EXPERIMENTAL ACIDIFICATION

Before the acidification, approximately 20% of Ca and Mg occurred as  $\text{CaHCO}_3^{1+}$  and  $\text{MgHCO}_3^{1+}$ . At the peak of acidification, as Ca and Mg increased dramatically and with pH lowered below 5, the  $\text{HCO}_3$  complexes decreased nearly to zero (as does  $\text{HCO}_3^{1-}$ ) and Ca and Mg were present dominantly as  $2+$  ions. The principal species of Al and Be (potentially toxic to biota) that occurred during the acidification experiment are listed in Table 2.

Hydroxycomplexes  $(\text{Al}(\text{OH})_x)^{(3+)-x}$  of Al were  $> 80\%$  of the total Al before the start of acidification, at  $\text{pH} = 6.36$  (Fig. 5a).  $(\text{Al}(\text{OH})_x)^{(3+)-x}$  decreased to 50% after 1 hour ( $\text{pH} = 5.63$ ) and to  $< 10\%$  after 2 hours ( $\text{pH} = 4.34$ ).  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_2^{1+}$  decreased to  $< 1\%$ ;  $\text{Al}(\text{OH})^{2+}$  at the lowest pH (4.06) was  $< 10\%$ . Two hours after the acid addition ceased,  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_2^{1+}$  recovered to  $\sim 40\%$  and  $\text{Al}(\text{OH})^{2+}$  virtually disappeared. For pH below 4.5, the most abundant form of Al was  $\text{Al}^{3+}$ . The  $\text{Al}^{3+}$  dominates when most  $\text{F}^{1-}$  is bound as  $\text{AlF}^{2+}$  and pH is too low for appreciable  $(\text{Al}(\text{OH})_x)^{(3+)-x}$ . When pH was higher than 4.5, total Al was lower and a larger percentage was complexed by  $\text{F}^{1-}$  or  $(\text{OH})^{1-}$ .  $\text{AlF}^{2+}$  was important in the transition from high to low pH comprising as much as 30% of total Al. Similarly, the  $\text{AlF}_2^{1+}$  was important only in the transition between high and low pH.

Before the acidification, Be species were dominated by  $\text{Be}^{2+}$ ,  $\text{BeF}^{1+}$ , and  $\text{Be}(\text{OH})^{1+}$  (Fig. 5b).  $\text{BeF}_2^0$  and  $\text{BeF}^{1+}$  became minor because of strong dependence on pH and



Table 2. Principal Al and Be species in Beryllium Stream during the acidification.

Al			Be		
Ion	Hydroxycomplexes	Fluorocomplexes	Ion	Hydroxycomplexes	Fluorocomplexes
Al <sup>3+</sup>	Al(OH) <sup>2+</sup> Al(OH) <sub>2</sub> <sup>1+</sup> Al(OH) <sub>3</sub> <sup>0</sup>	AlF <sup>2+</sup> AlF <sub>2</sub> <sup>1+</sup>	Be <sup>2+</sup>	Be(OH) <sup>1+</sup>	BeF <sup>1+</sup> BeF <sub>2</sub> <sup>0</sup>

lowered concentration of F<sup>1-</sup> due to competition with increasing Al as acidification developed. Fluoride is preferably bound in Al complexes. Be<sup>2+</sup> increased from 25% of total Be initially to > 90% at the lowest pH. The relative % of Be(OH)<sup>1+</sup> depends largely on the activity of (OH)<sup>1-</sup>. During low pH values Be(OH)<sup>1+</sup> became negligible, but initially was about 20%.

Changes in speciation occur downstream as a consequence of variations of pH, total concentration of metals that compete for the same ligands, and the concentration of the ligands (Fig. 5a, 5b). For Beryllium Stream, maximum

toxicity may vary for different biota, depending on whether they are sensitive to the fluoride complexes, the hydroxy complexes, or the uncomplexed ion.

### Conclusions

The streambed of Beryllium Stream exerted a strong buffering capacity against pH change by ion exchange during the experimental short-term acidification with HCl. Streambed substrates demonstrated both CEC and AEC in

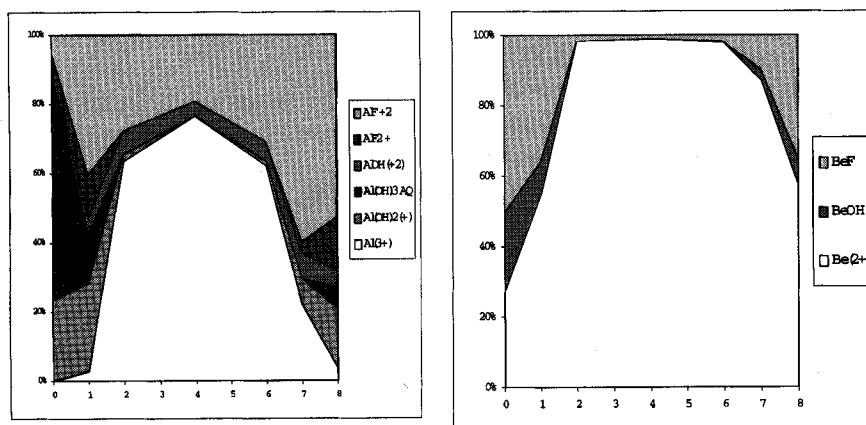


Fig. 5a and 5b. Changes (%) of Al and Be species through time (h), 20 m downstream from the point of acid addition.

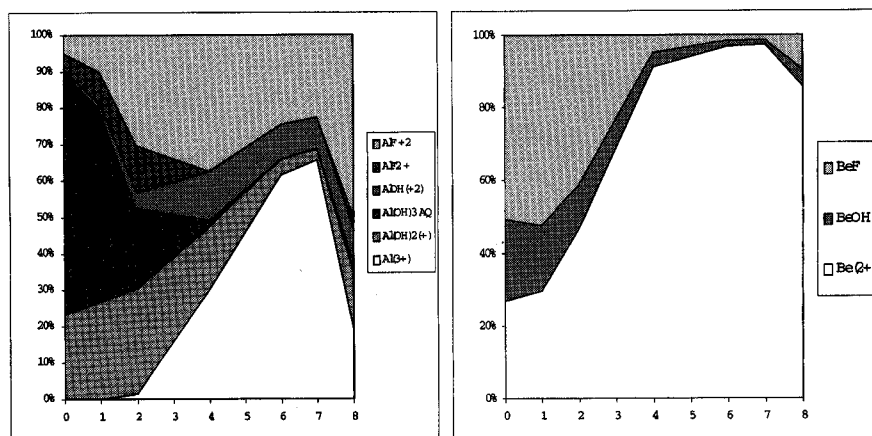


Fig. 6a and 6b. Changes (%) of Al and Be species through time (h), 50 m downstream from the acid addition.

the pH range of 4.1 to 6.5. The response of cations on streambeds was fastest for  $\text{Na}^{1+}$ , then  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , followed by  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$ , corresponding in part to the difference in charge density of these cations. During the experimental acidification,  $\text{Ca}^{2+}$  desorption dominated neutralisation of excess  $\text{H}^{+}$  for the first 2 hr, followed by  $\text{Al}^{3+}$ . Later, release of  $\text{Al}^{3+}$  dominated. Relationships between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  did not vary through the acidification as the base saturation of the stream substrate decreased. However, the release of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  relative to  $\text{H}^{+}$  declined through time, suggesting depletion of these two cations from the substrate. The relationship between  $\text{Al}^{3+}$  and  $\text{Be}^{2+}$  also remained constant, indicating there was no observed depletion of either reservoir. Strong  $\text{SO}_4^{2-}$  adsorption occurred during the acidification. All the exchange reactions were reversible. The total stream ion exchange capacity, scaled up to the catchment, indicates that this headwater streambed can measurably impact stream chemistry during episodic acidification. The depression of the pH is damped and the recovery to pre-acidification conditions is delayed.

## Acknowledgements

This research was supported by the U. S. National Science Foundation (Grant EAR-9725705 to Norton), the Czech Republic Ministry of Education (Grant ME147, 1998 to J. Vesely), the Czech Geological Survey, and Charles University, Czech Republic (Navratil).

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