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The response of a small stream in the Lesni potok forested catchment, central Czech Republic, to a short-term in-stream acidification

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Abstract

Lesni Potok stream drains a forested headwater catchment in the central Czech Republic. It was artificially acidified with hydrochloric acid (HCl) for four hours to assess the role of stream substrate in acid-neutralisation and recovery. The pH was lowered from 4.7 to 3.2. Desorption of Ca and Mg and desorption or solution of Al dominated acid-neutralisation; Al mobilisation was more important later. The stream substrate released 4,542 meq Ca, 1,184 meq Mg, and 2,329 meq Al over a 45 m long and 1 m wide stream segment; smaller amounts of Be, Cd, Fe, and Mn were released. Adsorption of SO_4^{2-} and desorption of F^- occurred during the acidification phase of the experiment. The exchange reactions were rapidly reversible for Ca, Mg and SO_4^{2-} but not symmetric as the substrate resorbed 1083, 790 and 0 meq Ca, Mg, and Al, respectively, in a 4-hour recovery period. Desorption of SO_4^{2-} occurred during the resorption of Ca and Mg. These exchange and dissolution reactions delay acidification, diminish the pH depression and retard recovery from episodic acidification. The behaviour of the stream substrate-water interaction resembles that for soil–soil water interactions. A mathematical dynamic mass-balance based model, MASS (Modelling Acidification of Stream Sediments), was developed which simulates the adsorption and desorption of base cations during the experiment and was successfully calibrated to the experimental data.

Keywords: Al, Ca, Mg, base cations, acid-neutralisation, stream acidification, recovery, stream sediment, experiment, modelling, adsorption, desorption, adsorption, Czech Republic, Lesni Potok

Introduction

Episodic changes in stream chemistry occur during snowmelt and rainstorm events. In many streams, episodic acidification is caused by a combination of base cation dilution and the release of natural acidity (organic acids, salt effects, and NO_3^-), and anthropogenic acidity (SO_4^{2-} and NO_3^-). Commonly, one or more strong acid anions (Cl^-, NO_3, SO_4^{2-}) increase. The episodic chemical changes include short-term decreases of pH and acid neutralising capacity (ANC) and increases of ionic Al. The importance of the effects of episodic acidification on in-stream processes has been underestimated in modelling and empirical studies.

Several in-stream acidification experiments have clarified some of the important chemical processes, including adsorption, desorption, and dissolution occurring within the stream itself. Hall *et al.* (1980) were the first to study the ecological response of a stream to experimental addition of acidity (H_2SO_4) during six months of low flow. They demonstrated that the fluxes of Ca, Mg, K, Na, and Al are increased as a consequence of depressing the pH to about 4. Other experiments (Norton *et al.*; 1987, 1992, 2000; Tipping and Hopwood, 1988; Hedin *et al.*, 1990; Hruška *et al.,* 1999) used HCl, HNO_3, or H_2SO_4. The latter two studies focused on the effects of in-stream acidification on organic acidity. Three general processes have been documented for interaction between the acidifying stream water and sediment. Firstly and most importantly, H^+ exchanges with other cations adsorbed on the stream substrate, releasing them into solution. Secondly, adsorption of SO_4^{2-} by stream substrate may occur. Thirdly, dissolution of an Al-rich solid phase occurs, along with trace elements associated with that phase. These reactions are generally reversible during recovery (Norton *et al*., 2000).

This paper describes the results of an in-stream acidification of a small first-order stream (Lesni Potok) on granite bedrock, in the central Czech Republic; evaluation of the effects of acidification on the reversible release of base cations (Ca, Mg, K, Na), trace elements, and Al and Be, and the effect of changing pH on SO_4^{2-} sorption is included. The mechanisms of the in-stream acid neutralisation are described and compared with the findings of several other studies (Norton *et al*., 2000; Hruška *et al*., 2002; Navrátil, 2000). A numerical model describing the adsorption and desorption processes controlling the base cation stream chemistry during the acidification experiment has been developed.

Methods

SITE DESCRIPTION

The Central Czech Republic received very acidic deposition in the 1980s but by the late 1990s, the acidity of deposition had decreased substantially (Kopácek *et al*., 2001; Hruška *et al.,* 2002). This history makes Lesni Potok (henceforth LP) an important 'case study' site for detecting changes in chronic and episodic acidification of surface waters. The LP catchment covers 0.765 km^2 and is located some 30 km east-southeast of Prague. Soils, mostly Gleyic or Dystric Cambisols, are derived from the Rícany Granite. The lower part of the catchment is underlain by 4 to 5 m of sediment. The forest vegetation is 46% Norway spruce (*Picea abies*) and 54% European beech (*Fagus sylvatica*). The mean annual bulk precipitation from 1994–2000 was 600 mm and the corresponding runoff was 68 mm. High evapotranspiration is typical of the area and relatively high concentrations of conservative elements such as Cl result. The evapotranspiration rate based on the water budget is 89%, and about 85% based on the Cl budget. The annual average air temperature is 7°C. Stream discharge was determined at a Thomson weir at 400 m a.s.l. The highest point in the catchment is 495 m a.s.l.

The deposition of SO_4^{2-} on this area of the Czech Republic has decreased significantly since 1990 (Kopácek *et al*. 2001; Hruška *et al*. 2002). At LP catchment, the annual bulk deposition of SO_4^{2-} declined from 58 meq m^{-2} in 1994 to 12 meq m^{-2} in year 1999, while the mean concentration of SO_4^{2-} in precipitation decreased from 90 µeq L^{-1} in 1994 to 29 µeq L^{-1} in 1999 (Table 1). Correspondingly, the annual deposition of SO_4^{2-} in beech and spruce throughfall declined from 191 meq m^{-2} in 1994 to 51 meq m^{-2} in 1999, while dry deposition of SO_4^{2-} declined from 2.5 to 1.8 times bulk deposition.

Shallow groundwater was sampled from a 5 m deep well adjacent to the weir. The lower 0.5 m of the plastic casing was perforated and the well sampling water at least 2 m below the groundwater level. The shallow groundwater at LP had high concentrations of Ca^{2+}, Na^+, Cl^-, H_4SiO_4, $Mn^{2+}$and Fe^{2+}; pH was near neutral (6.6) (Table 1). The high concentrations of Ca^{2+}, Na^+ and H_4SiO_4 originated from weathering of plagioclase. High evapotranspiration explains, in part, high concentrations of many solutes in the groundwater and stream water. The concentrations of Al^{n+}, Be^{2+} and Cd^{2+} are low because of the nearly neutral pH value. The relatively high concentrations of Mn^{2+} and Fe^{2+} are a result of partial anoxia in the groundwater more than 2 m below the groundwater table. During periods of low discharge (usually in summer and autumn), the surface water chemistry is very similar to that of shallow groundwater (Table 1).

The major cations in the LP surface water during 1999 were Ca^{2+} (45%), Mg^{2+} (31%), Na^+ (22%) and K^+ (2%) (Table 1). Eighty-eight percent of the strong acid anion (SAA) concentration is SO_4^{2-}, the remainder is Cl^-, F^- and NO_3^-. The dissolved organic carbon (DOC) concentrations in the surface water are typically ~ 8 mg L^{-1}.

Higher discharge events during snowmelt in spring or during summer or autumn rainstorms involve shallower flow paths for much of the runoff. Stream chemistry varies substantially between high flow ($Q > 2.5$ L s^{-1}), intermediate flow ($0.5 \leq Q \leq 2.5$ L s^{-1}), and low flow periods ($Q < 0.5$ L s^{-1}) (Table 1). As flow increases, pH decreases and concentrations of Ca^{2+}, Mg^{2+}, Al^{n+}, K^+, Be^{2+}, Cd^{2+}, SO_4^{2-}, F^-, and NO_3^- increase. This unusual behaviour of base cations is related to the high evapotranspiration, biomass mineralisation, and chemical weathering. Concentrations of Na^+, Cl^-, H_4SiO_4, Fe^{2+} and Mn^{2+} decreased at higher discharges.

From 1996 to 2000, the throughfall flux of SO_4^{2-} decreased by nearly 75%, while the average SO_4^{2-} concentration in LP surface water decreased by only 20%. The stream output of SO_4^{2-} in 1999 was twice the throughfall flux. Apparently, some of the SO_4^{2-} deposited in the past and adsorbed on the soils was desorbed and exported from the catchment. The reduction in mean SO_4^{2-} concentration ($\Delta = -298$ µeq L^{-1}) in the surface water between the years 1994 and 1999 was

Table 1. Numerical average values of selected parameters for the stream water of Lesni Potok catchment.

		Wet deposition		Shallow groundwater	Stream water		Data for 1994 - 2000		
		1994	1999	1999	1994	1999	high flow	intermediate	low flow
Q	L s^{-1}				2.53	2.2	>2.5	0.5–2.5	<0.5
pH		4.17	4.48	6.64	5.04	5.25	4.84	4.99	5.65
Na^+	µeq L^{-1}	10	14	670	381	395	346	370	410
K^+	µeq L^{-1}	5	5	26	54	29	34	30	28
Mg^{2+}	µeq L^{-1}	6	6	416	646	566	623	613	563
Ca^{2+}	µeq L^{-1}	28	19	1262	1060	826	949	919	836
Fe^{2+}	µeq L^{-1}	3	2	246	39	17	3	6	18
Mn^{2+}	µeq L^{-1}	0.2	0.2	31	15	10	7	7	15
Al^{3+}	µeq L^{-1}	6	5	1	92	83	84	79	55
Be^{2+}	µeq L^{-1}	0.0111	0.0024	0.03	1.63	0.82	1.44	1.22	0.78
Cd^{2+}	µeq L^{-1}	0.0025	0.0013	0.0004	0.0067	0.0033	0.0064	0.0059	0.0020
Cl^-	µeq L^{-1}	11	30	127	132	121	115	125	130
F^-	µeq L^{-1}	3	1	16	39	38	43	40	37
SO_4^{2-}	µeq L^{-1}	90	29	931	1758	1460	1700	1636	1493
NO_3^-	µeq L^{-1}	39	44	5	60	48	64	42	15

less that the reduction in Ca^{2+}, Mg^{2+} and Al^{3+} ($\Delta = -234$ µeq L^{-1}, -80 µeq L^{-1} and -9 µeq L^{-1}, respectively) resulting in a slight increase in the alkalinity and mean annual pH. Fluoride and chloride remained low and relatively constant from 1994 to 1999.

TREATMENT AND SAMPLING

The acidification experiment was applied on 11th May 2001. The air and stream temperatures were 20°C and 11°C respectively. The catchment had received no precipitation for five days before the experimental treatment but 33 mm of rain had fallen seven days before the experiment. Discharge at the start of acidification was 2.73 L s^{-1} (0.013 mm h^{-1}, high flow) and decreased to 2.43 L s^{-1} (0.011 mm h^{-1}) by the end of sampling, eight hours later. Over four hours, 22 moles of HCl (4.709 M) were added to the stream, by Mariotte bottle at approximately 20 ml min^{-1} at a point just below the weir. At point A, 1 m beyond where the acid was added, only pH was measured. Samples of stream water were taken concurrently at points W (weir, above where the acid was added) and at points B, C and D, respectively 20 m, 45 m and 70 m downstream from the weir. Each sampling event included three samples per site. The first was unfiltered and was used to determine total metal concentration (tot); the second was filtered through a 0.45 µm cellulose membrane filter and was analysed to determine dissolved metals (dis). Both were stabilised with ultra-pure HNO_3. The third sample was unfiltered and was analysed for anions.

ANALYTICAL METHODS

The pH was measured *in situ* with a calibrated portable pH meter (WTW 330). Concentrations of Na, K, Mg, Ca, Al and Fe were determined by flame atomic absorption spectrometry (FAAS; Perkin Elmer 3100), of F^-, Cl^-, SO_4^{2-} and NO_3^- by ion chromatography (HPLC, columns Tessek HEMA-S1000 Q-L 10 mm) and of Be and Cd by Graphite Furnace AAS (GFAAS, VARIAN SpectrAA 300). The speciation calculations used the chemical equilibrium modelling software MINEQL+ (Schecher and McAvoy, 1993).

CALCULATION OF CHANGES IN NET MASSES OF ELEMENTS IN STREAM SEDIMENTS AND STREAM WATER (MASS)

The areas above and below the time versus delta values (c_o–c_i) at point C (45 m beyond where the acid was added) during the eight hours were integrated numerically. This calculation determined the mass balance changes during the interaction of acidified water with the first 45 m of streambed.

MODELLING THE ACIDIFICATION OF STREAM SEDIMENTS (MASS)

Modelled interactions of cation adsorption and desorption from the stream sediment and subsequent resorption, or adsorption were based on the common reaction:

$$Me^{S} + H^{+} \longleftrightarrow Me^{+} + H^{S} \tag{1}$$

The model assumes steady state equilibrium between metals in the stream solution (Me^{+}) and homogenous stream sediment (Me^{S}) throughout the stream before the episodic experimental acidification. The cation desorption from the stream sediment and its subsequent resorption are described as:

$$(c_{Me^{+}})_{l} = k_{1}c_{H^{+}}c_{Me^{S}} - k_{2}c_{Me^{+}}c_{H^{S}} \tag{2}$$

$$c_{H^{+}} = c^{0}_{H^{+}} + \alpha\left(c^{0}_{Me^{+}} - c_{Me^{+}}\right) \tag{3}$$

where, c_{H+} is the concentration of hydrogen ions in the stream water, c_{Me+} is the concentration of the modelled cation in the streamwater, and $c_{Me}{}^{S}$ and $c_{H}{}^{S}$ are the leachable concentrations of the modelled cation Me^{+} and H^{+} sorbed to the solid phase (sediment), respectively. The k_{i} values are rate constants. The parameter α reflects the proportional charge of the modelled ion and the relative loss of H^{+} in the solution corresponding to all other solutes that are being desorbed at the same time as the modelled Me^{+}. The concurrent desorption of other cations follows from Eqn. (3) and is consistent with the behaviour of modelled Me^{+}. This formulation assumes a stream velocity that permits solution-sediment equilibration. The changes of Me^{+} and H^{+} concentrations are given by the derivative with respect to distance downstream, *l*. The time to any state is determined by the amount of exchangeable *Me* on the sediment, $c_{Me}{}^{s}$. For the whole stream length, conservation of mass yields

$$(c_{Me^{S}})_{t} = -(c_{Me^{+}})_{l} \qquad dt = \frac{dl}{v} \tag{4}$$

where *v* is the stream velocity (m s^{-1}). The temporal change of the cation concentration in sediment at any distance (*l*) from the point of the acid addition corresponds to enrichment or depletion of c_{Me+}, the element of interest.

$$\left(\int_{0}^{L} c_{Me^{S}}\,dl\right)_{t} = c^{0}_{Me^{+}} - c_{Me^{+}}(L,t) \tag{5}$$

This means that:

$$c_{Me^{S}}(l,\tau) = c^{0}_{Me^{S}} - \int_{0}^{\tau} (c_{Me^{+}}(l,t))_{l}\,dt \tag{6}$$

The concentration of the H^{+} sorbed on the solid phase at any time is:

$$c_{H^{S}} = c^{0}_{H^{S}} + \alpha\int_{0}^{\tau} (c_{Me^{+}})_{l}\,dt \tag{7}$$

Using Eqns, (5), (6) and (7), the solution of Eqn. (2) is:

$$c_{Me^{+}}(L,\tau) = e^{-z}\left[c^{0}_{Me^{+}} + k_{1}\left(c^{0}_{H^{+}} + \alpha c^{0}_{Me^{+}}\right)\right.$$
$$\left.\int_{0}^{L}\left(c^{0}_{Me^{S}} - \int_{0}^{\tau}(c_{Me^{+}}(l,t))_{l}\,dt\right)e^{z}\,dl\right] \tag{8}$$
$$z = \alpha\left(k_{2} - k_{1}\right)\int_{0}^{\tau}\left(c_{Me^{+}}(l,t) - c^{0}_{Me^{+}}\right)dt + \alpha k_{1}c^{0}_{Me^{S}}\,l + k_{2}c^{0}_{H^{S}}\,l$$

Equation (8) was solved iteratively with respect to *t*. The derivative of c_{Me+} with respect to *l* was obtained from Eqn. (2) in the previous time step. This approach was consistent with the physical aspects of the experiment. The flowing water interacts with a static solid phase that may be represented with respect to time in small time steps as:

$$(c_{Me^{S}}(l,t+1))_{t} = -(c_{Me^{+}}(l,t))_{l} \tag{9}$$

This approach to modelling desorption and adsorption in a small stream enabled more accurate results than by using purely numerical methods. This dynamic model was based on mass-balance. The input parameters (rate constants) must be calibrated empirically against data from a specific stream (in this case, Lesni Potok). It is, however, a general model, containing processes that can be parameterised. The various k_{i}s correspond to the adsorption and desorption processes and would have different values in other systems. Metabolic processes of living organisms on the solid and in the liquid phases were assumed to have a negligible impact on the metals being considered.

Results

pH

The pH of the stream water above the acid addition was 4.8. After 3.5 hours of acid addition, pH was nearly 3.2 at points A and B, 3.5 at point C, and 3.7 at point D (Fig. 1). The pH value ~3.2 occurred at point A 20 minutes after the start of the experiment and remained constant until the acid addition was stopped at t = 4 hours. At point B, the pH value reached ~3.2 after three hours of acidification and remained at 3.2 until the end of the addition. It required nearly three hours to acidify the first 20 m of the stream to pH value ~ 3.2. At 4.25 hours (15 minutes after the end of the addition), the pH at point A recovered to 4.62, and after an additional 30 minutes, pH was almost back to its initial value. At point B the pH increased during the first 15 minutes of the recovery to 3.9. After four hours of recovery, pH increased only to 4.55. The increase in pH was slower during the recovery period than the reduction during the acidification phase (Fig. 1).

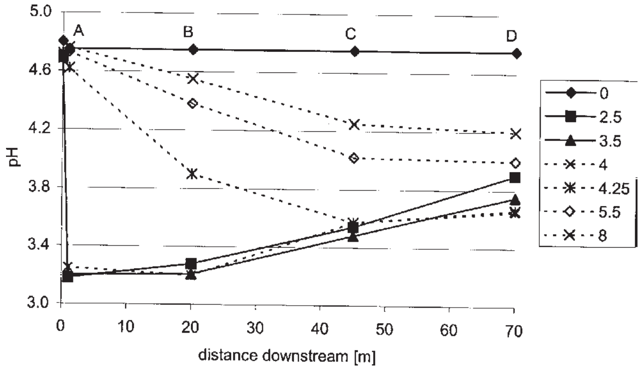


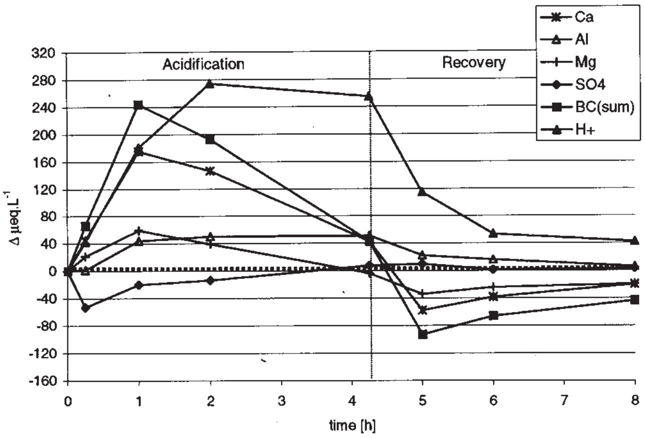
Fig. 1. *Streamwater pH at sites in the experimental stream reach. Solid lines represent changes during the acidification phase; dashed lines represent changes during the recovery. The number in the explanation is time (hours) from the beginning of experiment.*

ANIONS

A pH of 3.2 caused by the addition of the HCl to water with an original pH of about 4.8 should add about 610 µeq Cl L^{-1} to the water. The Cl^- concentration initially was 107 µeq L^{-1} should have increased to about 720 µeq L^{-1} if Cl^- were conservative in the stream. The maximum Cl^- measured was 540 µeq L^{-1}, so either the minimum pH was slightly higher than measured (pH should be 3.35 for the maximum measured Cl^-) or Cl^- was underestimated. There are no data for Cl at point A but at point C (45 m) Cl^- reached 258 µeq L^{-1} after 15 minutes, 536 µeq L^{-1} after 1 hour and remained at ~540 µeq L^{-1} until the end of the acidification. Ten minutes after the acid addition ended (4.25 hours from the start), Cl^- concentration at point C decreased to 403 µeq L^{-1}. Three hours later, the concentration of Cl^- had decreased to its initial value, ~110 µeq L^{-1} at point C (Table 2). The water's residence time in the experimental reach was approximately 15 minutes.

Sulphate, the most abundant anion (1450 µeq L^{-1}), decreased by 4% (51 µeq L^{-1}) at point C during the first 15 minutes of the experiment. After reaching its minimum value (1400 µeq L^{-1}), SO_4^{2-} started to increase gradually. During the recovery stage, the SO_4^{2-} reached its maximum concentration (1,463 µeq L^{-1}) six hours after the start of the acid treatment. Thereafter, it remained virtually constant (~1455 µeq L^{-1}) to the end of experiment (Fig. 2).

Nitrate increased slightly above background levels during the acidification experiment and decreased slightly during the recovery but the total variation was only 25 µeq L^{-1}. This variation is less than the increase in NO_3^- during high discharge events. At point C, F^- concentration increased from 35 to 44 meq L^{-1}, one hour after the acidification started and than decreased to slightly above background values even as the pH continued to decline (Table 2).



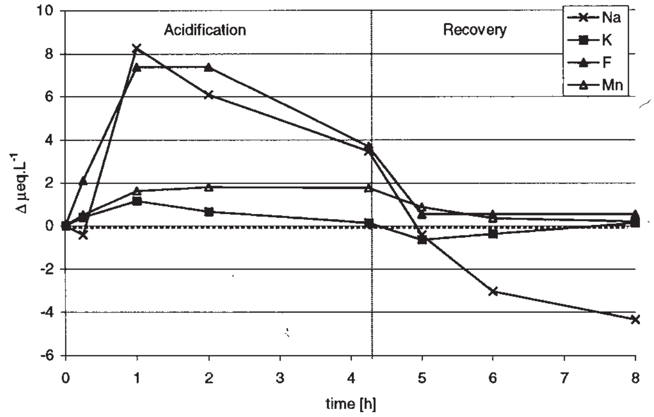


Fig. 2. *The delta concentrations of dissolved analytes ($c_i - c_0$; in µeq L^{-1}) at point C, 45 m below the point of acid addition. The dashed line represents no change. BC = the sum of base cations (Ca, Mg, Na, and K).*

BASE CATIONS

Concentrations of Ca and Mg increased significantly and rapidly. Calcium release neutralised the most acid; its concentration increased by 25% (175 µeq L^{-1}) at maximum concentration. Magnesium concentration increased rapidly but only to a maximum of 11% (58 µeq L^{-1}). In the first 20 m of the stream, sources of Ca and Mg were depleted after the first hour of the acidification and their concentrations in the solution gradually decreased (Fig. 2). Shortly after the acidification ceased (t = 4.25 hrs), Ca and Mg concentrations decreased below their background values (at t = 0) and then started to increase slowly toward but not to the background concentration. The correlation between Ca and Mg for all samples was R = 0.97. However, at t = 4 hours at point B, the concentration of Mg reached background concentration, indicating steady state equilibrium between the stream and sediment, but with the exchange complex depleted of Mg and no desorption (Fig. 2). Desorption of Ca was very low by this time (e.g. four

Table 2. Stream chemistry at various points on the experimental reach W (weir), B (20 m below W), C (45 m), and D (70 m).

site	time	pH	H	Ca(tot)	Mg(tot)	Na(tot)	K(tot)	Al(tot)	Al(dis)	Mn(tot)	Mn(dis)	Fe(tot)	Fe(dis)	Cd(dis)	Be(dis)	Cl	NO_3	SO
W	0	4.80	11	706	510	364	23	108	88	5.0	4.1	5.7	3.8	0.004	1.3	109	23	1,4
	360	4.76	17	712	514	359	23	108	NA	4.3	NA	5.0	NA	NA	NA	105	21	1,4
	Avg.		**14**	**709**	**512**	**361**	**23**	**108**	**88**	**4.7**	**4.1**	**5.4**	**3.8**	**0.004**	**1.3**	**107**	**22**	**1,4**
B	15	3.60	251	797	542	372	24	123	112	5.5	4.6	6.4	4.9	0.006	1.5	NA	NA	N
	60	3.38	417	760	527	372	23	128	93	5.5	4.6	7.2	5.1	0.006	1.6	556	36	1,4
	240	3.20	631	727	508	361	23	125	88	5.3	4.6	7.2	5.2	0.005	1.5	578	23	1,4
	360	4.55	28	709	503	355	23	107	55	4.4	4.0	5.4	4.6	0.003	1.2	107	21	1,4
C	15	4.25	56	753	533	361	23	109	NA	5.2	NA	6.1	NA	NA	NA	258	27	1,4
	60	3.71	195	884	571	370	24	152	93	6.3	5.4	7.9	5.5	0.009	1.7	536	32	1,4
	120	3.54	288	856	551	368	24	158	104	6.5	5.6	7.5	5.5	0.009	1.8	547	24	1,4
	255	3.57	269	751	508	365	23	159	112	6.4	5.5	8.6	5.8	0.008	1.8	403	22	1,4
	300	3.89	129	651	478	361	22	130	83	5.5	4.7	6.7	4.9	0.005	1.4	134	16	1,4
	360	4.17	68	670	488	358	23	124	86	5.0	4.6	7.2	4.8	0.004	1.3	123	22	1,4
	480	4.25	56	689	493	357	23	114	76	4.9	4.4	6.8	4.8	0.004	1.2	111	10	1,4
D	270	3.73	186	803	532	365	23	173	83	7.6	6.7	7.2	5.8	0.010	1.9	426	20	1,4
	360	4.08	83	660	482	369	22	129	86	6.3	5.2	6.4	5.1	0.006	1.5	125	18	1,4

* all values in µeq.L^{-1}, time in minutes, and pH in units

hours at Point B). The concentrations of Ca and Mg for the entire sample group were insignificantly related to H^+.

The concentration of Na did not vary significantly during the experiment. The maximum increase of Na concentration at point C was 2% (8 µeq L^{-1}). The maximum increase for K concentration was only 1 µeq L^{-1} and its contribution (ca. 20 µeq L^{-1}) to the sum of cations is negligible.

ALUMINUM

The Al(tot) concentration did not change significantly during the first 15 minutes of the acidification but then increased about 50% (Fig. 3) and stabilised for three hours. The Al concentration in filtered samples Al(dis) was still increasing at four hours at point C. The Al(dis) increased a maximum of 35% (23 µeq L^{-1}). After the acid addition, the concentration of both Al(tot) and Al(dis) decreased, but Al(tot) did not reach the initial concentration. Al(dis) decreased below background during the recovery. Although lower pH produced higher Al(dis), the statistical relationship was poor. The dominant species of Al before the experiment were AlF^{2+} and AlF_2^+. Over 70% of the Al(dis) concentration was AlF^{2+} during the experiment. AlF_2^+ accounted for ~18% before the treatment but decreased to 10% as Al reached its highest concentration (t = 4.25 hrs). Other species of Al were Al^{3+}, AlF_{3aq} and $AlSO_4^+$. Al^{3+} became more important at the highest Al(dis) concentration.

TRACE METALS

Concentrations of dissolved and particulate manganese were low (*c.* 4 µeq L^{-1}) and increased only by 1 to 2 µeq L^{-1} at the lowest pH. Total and filtered Mn concentrations (tot) and (dis) were highly correlated during the acidification (R = 0.95) and both correlated strongly with Fe and Al. Concentrations of (tot) and (dis) Fe were low and increased only by ~2 µeq L^{-1} during the acidification. During the recovery stage Fe (tot) and Fe(dis) concentrations remained higher than initial concentrations. The Be concentration increased by up to 0.5 µeq L^{-1} (Fig. 3) at the peak of acidity and then decreased to background during recovery. The correlation of Be with Al was significant (R = 0.88), as it was with Mn(tot), Mn(dis), Fe(tot) and Fe(dis). Cadmium concentration doubled at point C but its contribution to acid neutralisation was trivial.

MODELLING THE ACIDIFICATION OF STREAM SEDIMENT (MASS) - STREAM WATER-SUBSTRATE INTERACTION

The distribution of cations (including H^+) and anions between the liquid and solid phases is a result of ion

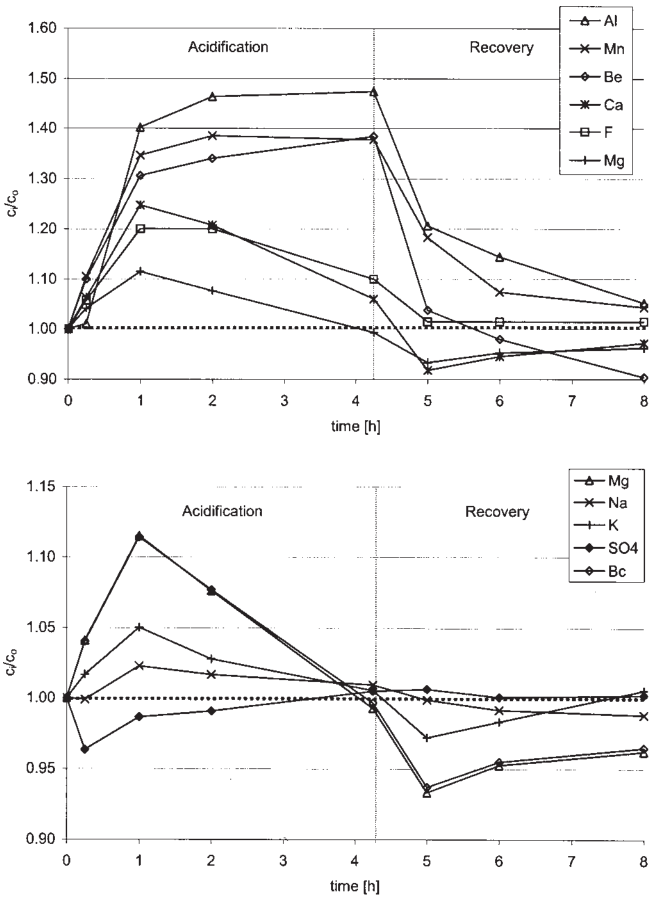


Fig. 3. *The relative change (c_i/c_0; equivalents/equivalents) of concentrations of dissolved analytes versus time at point C, 45 m below the acid addition point, (Bc = Ca + Mg + K).*

exchange (adsorption or desorption) and dissolution or precipitation. The concentrations and proportions of ions in solution affect these interactions. The concentrations of base cation metals in bulk sediment are generally much higher than in solution. However, not all of the metals are exchangeable. The limited sorption sites on the solid surfaces have different binding energies and affinities for different ions. The MASS model must be parameterised for each element using appropriate values of rate constants (k_is).

The dynamic model describes only adsorption and desorption of cations. No dissolution (e.g. of Al) is included. The fit between experimental observations of Ca and the modelled value is shown at Fig. 7. A good match of the modelled dependencies for c_{Me+} with the experimental data was obtained with $k_1/k_2 = 1.25$ and $\alpha = 2.4$. The modelled decrease of c_{H+} and increase of c_H^S is not in good agreement with the measurements without taking into account the depletion of H^+ by other desorbed cations and dissolved Al. This additional interaction of H^+ with other cations through ion exchange, Al, Fe, Mn dissolution and sulphate adsorption is calibrated through the α parameter.

Discussion

ANIONS

The SO_4^{2-} concentration declined rapidly suggesting adsorption of the SO_4^{2-} during the acidification phase (Fig. 3). As the surfaces of the in-stream solid phases gain positive charge by adsorption of H^+, the SO_4^{2-} becomes bound to the solid phase because of the increasingly positive surface charge (Nodvin *et al.*, 1986). As the concentration of the H^+ ions in the stream and on the substrate decreases, SO_4^{2-} is desorbed to the solution. The SO_4^{2-} concentration normally increases during high discharge events (Table 1). The total variation of SO_4^{2-} during the experiment was about 50 μeq L^{-1}, substantially less than the variation seen during low and high flow, 206 μeq L^{-1}, the highest of all measured parameters. Consequently it is concluded that a stream water – sediment interaction plays only a small role in buffering SO_4^{2-} concentration. The mean free F^- concentration decreased by 1 μeq L^{-1} from 1994 to 1999 but, during variable discharge, it ranged from 37 (low discharge) to 43 μeq L^{-1}. During the artificial acidification, F^- increased comparably. Fluoride may be released from exchange sites as H^+ displaces OH^-. An additional explanation for the increase in F at lower pH is that as Al is liberated from the stream substrate during acidification, F complexed to the solid is released to the solution. Further, at lower pH, F complexed with Al should become liberated as Al speciation shifts toward Al^{3+}.

CATIONS

The LP surface water has high ionic strength due to a combination of chemical weathering and high evapotranspiration in the catchment. The mean annual concentrations of Ca and Mg in the surface water have decreased from 1994 to 1999 and they increase during high discharge events (Table 1). The Ca and Mg concentrations in the experiment did not exceed the range in the long-term monitoring data (Table 1). The range of the Ca/Mg ratio (1.36–1.55) during the experiment is within the range of the Ca/Mg ratio (1.2–2.22) determined during the seven years of monitoring the LP catchment. The increased SO_4^{2-} and H^+ concentrations induced the desorption of Ca and Mg. Initially, release of the divalent base cations Ca and Mg was the most important component of the acid neutralisation. As this reservoir became depleted, release of more Al contributed to the neutralisation of the acid input. The Ca/Mg ratio was highest at one to two hours, indicating desorption of Ca in greater proportion to Mg from the stream substrate (Fig. 4). The lowest ratio occurred at five hours, representing the start of the Ca and Mg resorption during the recovery stage. At 5 hours (Fig. 4), Mg was resorbed in greater proportion to its stream concentration than was Ca. Two hours after the acid addition stopped, Ca and Mg concentrations started slowly to increase (Fig. 2). Although the Ca/Mg ratio recovered to its original value by the end of the experiment, the concentrations had not. The rate of recovery was slower than the mobilisation of base cations during the acidification phase. The shape of the curve for "sum of base cations (BC)" through time (acidification and recovery) is consistent with the conceptual model of Norton *et al*. (1999).

Sodium behaved contrary to Ca, Mg, and K. The long-term concentration of Na correlates negatively with discharge (Table 1) but was unaffected in the experiment. High discharge events normally slightly enhance the export of K from the catchment but the difference between the mean concentrations for low and high discharges is small (Table 1). The concentration of K changed less than 1 μeq L^{-1} from the background value. Sodium and K are relatively unaffected by in-stream processes.

The mean Al(tot) concentration in the LP surface water has decreased from 92 μeq L^{-1} in 1994 to 83 μeq L^{-1} in 1999 as SO_4^{2-} and H^+ have declined. The concentration of Al(tot) in the surface water increased as pH decreased (Table 1). The mean values of Al(tot) for low and high flow discharges differ by 29 μeq L^{-1}. During the first 15 minutes of the experimental acidification, little Al(tot) was mobilised from the substrate, compared to Ca or Mg. The concentration of Al(tot) started to increase in the first hour of the acidification and reached its maximum after four hours of acidification. The increase in Al(tot) during the experiment was approximately twice the natural range (Tables 1 and 2). The concentrations of F^- in the surface water increased at higher flows, likely enhancing Al mobility by formation of Al–F complexes. The Al(tot) was higher than mean values for any flow in the 1994–2000 period. It is concluded that Al stream chemistry is affected by water-sediment interaction, principally decreasing the rate and magnitude of episodic acidification and recovery.

TRACE METALS

The export of Mn from the catchment has decreased by 5 μeq L^{-1} from 1994 to 1999. The highest mean concentrations were at low discharge (Table 1). Iron in surface water normally decreases with increasing discharge and decreasing pH. Thus, the small increase of Fe in the experiment suggests some in-stream release of Fe. Beryllium and Cd were normally mobilised during high discharge events (Table 1). Their concentrations during the experiment rose to relatively high values, suggesting that the stream sediments may contribute much of the Be and Cd at high flow. On a percentage basis, Cd was the most mobilised metal. Its concentration increased rapidly due to the elevated H^+ and decreased immediately as pH rose at the end of experiment, falling below the initial concentration. The average concentrations of Cd and Be have decreased in the surface waters of LP between 1994–1999 (Table 1) (Navrátil *et al*., 2002). Possible causes are decreased deposition of Be and Cd to the catchment (Skrivan *et al*., 2000) and the streamwater pH increase.

The Be geochemistry at LP has been reported in detail by Skrivan *et al*. (1993, 1994 and 2000) and Navrátil (2000, 2002). The most important species of Be in the LP surface water were Be^{2+} and BeF^+ (Navrátil, 2000). Before the acidification experiment, Be^{2+} was ~10% higher than BeF^+, BeF_2, $BeSO_4$ and $BeOH^+$ accounted for < 3% during the experiment. During the acidification phase, Be^{2+} became more dominant as the F became preferentially bound to Al, particularly at the end of the acidification. As the Al concentration decreased during the recovery stage, the relationship between the Be^{2+} and BeF^+ reversed. Similar behaviour of Be species was observed during episodic events at the LP catchment in 1999 (Navrátil, 2000).

ACID NEUTRALISATION MECHANISMS THROUGH TIME

The stream substrate at LP is involved in three important mechanisms of acid neutralisation:

(1) adsorption of SO_4^{2-}
(2) ion exchange of H^+ for the divalent base cations Ca^{2+} and Mg^{2+} on the cation exchange sites of the stream substrate, and
(3) ion exchange of H^+ for Al^{3+} on the cation exchange sites of the stream substrate or dissolution of a solid phase $Al(OH)_3$ of the stream substrate.

The contribution of the individual elements to acid-neutralisation (Fig. 6) early in the experiment was SO_4^{2-} > Ca > Mg > Al (t = 0.25 h), then Ca > Mg > Al > SO_4^{2-} (t = 1 h), and finally Al > Ca > Mg > SO_4^{2-} (t = 4 h). The maximum acid neutralisation by base cation release and SO_4^{2-} adsorption was about 170 μeq L^{-1}. The adsorption of SO_4^{2-} was the fastest process. However, the total contribution of this process (59 μeq) to neutralisation of the acid over the 70 m stretch of stream was small compared to that of Ca (4542 μeq), Al (2329 μeq), and Mg (1184 μeq). The mass

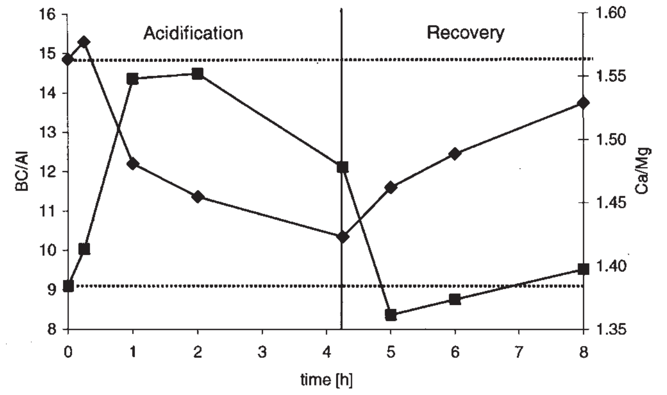


Fig. 4. *The Ca/Mg ratio (equivalents/equivalents) (squares, right Y axis) and BC/Al (dis) ratio (equivalents/equivalents) (diamonds, left Y axis) versus time at point C, 45 m below the acid addition point.*

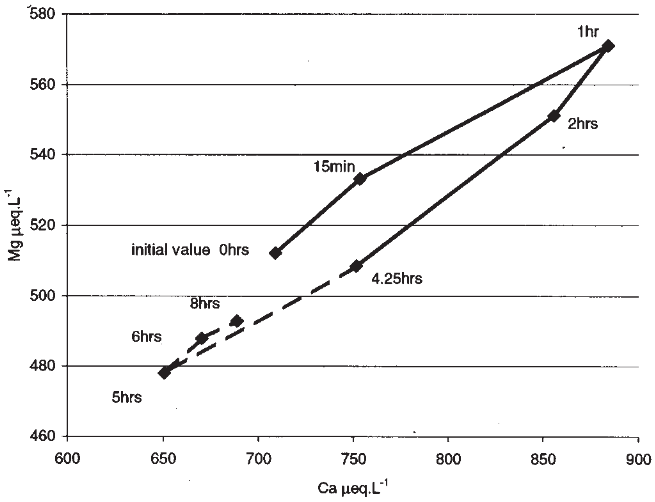


Fig. 5. *The concentration of Ca versus Mg at point C, 45 m below the acid addition point. The solid line represents acidification; the dashed line represents the recovery; numbers represent time in hours.*

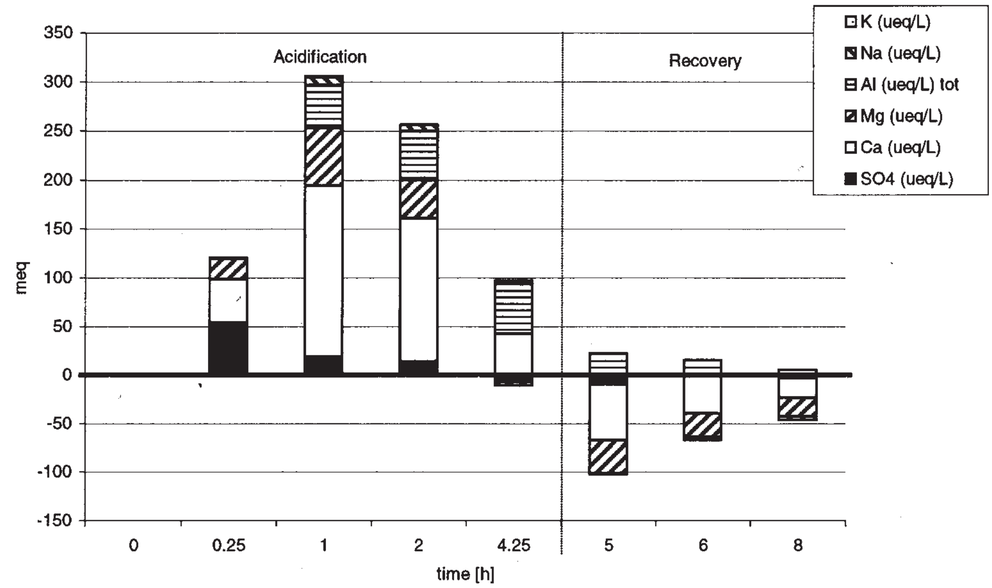


Fig. 6. *Acid neutralisation through time at point C, 45 m below the acid addition point. The x-axis is not proportional.*

of BCs (5961 µeq) desorbed from the stream sediment exceeded the integrated mass of BCs resorbed back to the substrate over a similar time; recovery was slower than acidification. Even after Cl and SO_4^{2-} concentrations had returned to background values, Ca, Mg, and Al had not recovered. Mg had the highest resorption to substrate (approximately 790 µeq or 67% of the desorbed amount) during the 4-hour recovery. Of the desorbed Ca, Na, and K, 24%, 39% and 39%, respectively, were resorbed. But the contribution of Na and K to the total acid neutralisation was minor. Sodium and K are 4% and 10%, respectively, of the total base cations extracted from soil but only 1% and 2%, respectively, from stream sediment with 0.1M HNO_3 (Navrátil, unpublished). Consequently, little Na and K are available for ion exchange in the stream.

The Fe and Mn were exported in lower amounts (195 µeq and 83 µeq, respectively). If acid neutralisation had not occurred, the pH at point C would have decreased to 3.75, 3.31, 3.27 and 3.45 at times 0.25, 1, 2 and 4.25 hours, respectively. During recovery, the pH would increase faster

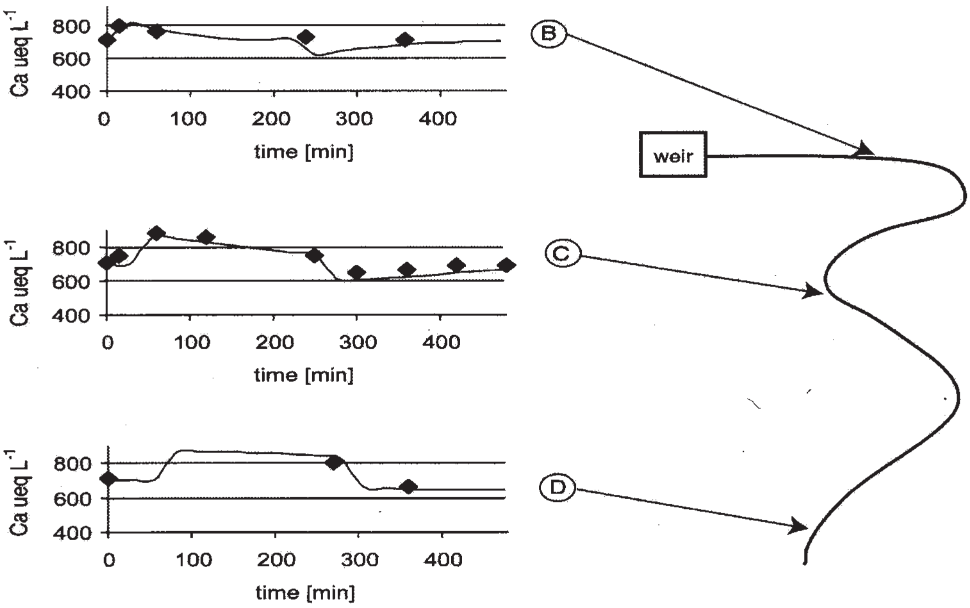


Fig. 7. *Measured Ca concentration (diamonds) and modelled response for Ca concentration (solid line) at points B, C, and D versus time.*

if the resorption of base cations and desorption of SO_4^{2-} had not occurred. The pH should have returned to its initial value (4.71) after 2 hours of recovery, based on Cl^- concentration, and assuming no sediment-water interaction.

THE MASS MODELLED RESPONSE

During the experimental acidification phase, the pH increased downstream toward the value prior to the acidification because of the interactions between the acidified water and the stream substrates. The acidic water caused desorption of exchangeable base cations and Al from the substrate and, therefore, H^+ was lost from solution. Increased concentrations of the BCs in water may then shift the equilibrium downstream between sediment and water if pH does not override the increased concentrations of cations. Some adsorption of excess cations may occur downstream. The dominant factor controlling the chemical changes in stream water is the concentration of H^+. As the pH decreased to 3.5, the concentrations of the divalent cations in the solution increased significantly. The H^+ ions were very competitive during ion exchange at the interface of hydrophilic oxide (silicate and alumosilicate) and organic matter surfaces and the aqueous solution. Sorption sites of the solid surfaces were unsaturated with bases during the experiment. If this were not true, there would have been no initial equilibrium (Eqn. 1). Concurrent with the cation desorption, polyvalent anions (mostly SO_4^{2-}) are sorbed (their concentration in solution decreases) as a result of increasing positive charge of the solid surfaces, caused by the increased concentration of H^+ in solution and on the exchange surface. A lag of the c_{Me+} maxima (peak concentrations) at each sampling site is caused by lower mean effective stream flow velocity than was calculated from the measured discharge. This lower stream velocity corresponding to the modelled calculation can be attributed to water turbulence, non-homogeneous velocity within the stream and solute-substrate penetration (hyporheic infiltration).

COMPARISON WITH OTHER EXPERIMENTS

In all artificial stream acidification experiments where appropriate data have been collected, base cations are released by desorption, Al is dissolved from an Al-rich phase or desorbed, and SO_4^{2-} is adsorbed during the acidification trajectory. The amounts and proportions of base cations released differ among experiments, probably depending on the acidification status of the catchment soils prior to the experiment (and, thus, of the stream sediment properties) as well as the exchange properties (e.g. selectivity for a specific cation) of the stream substrate. During recovery, these reactions are reversible but have unequal rates so that the chemical recovery does not retrace the acidification trajectory. The rate of establishment of a new equilibrium during acidification is $SO_4^{2-} >$ base cations > Al. The recovery process rates are more complex and less uniform from study to study. None of the studies has data taken over a sufficiently long period to determine when stream chemistry returns to normal at some specified distance downstream from the acid addition. For the LP study, the concentration of Cl returned to normal within two and eight hours at 20 and 50 m downstream, respectively. Yet the base cations had still not completely recovered. Al dynamics are even more complex, involving the probable precipitation of $Al(OH)_3$ on the stream substrate, as well as recharging Al sites as part of the exchange acidity of the sediment. Water chemistry probably returns asymptotically to normal within several days. During the experiment, the stream was at the lower threshold for high discharge (Table 1) and acidic. The artificial depression of pH was dramatically below normal variations. Acid neutralisation under more normal episodic acidification would be somewhat less effective, but more prolonged. It is concluded that stream sediment has the ability to reduce the pH depression during acidification and prolong recovery through cation and anion exchange, and Al exchange, dissolution and precipitation.

Conclusions

In response to the addition of HCl directly to the stream at Lesni Potok, F^- increased and SO_4^{2-} decreased. This difference in behaviour must be caused by site-specific exchange mechanisms. The variation in free F^- is likely to be caused by dissolution of particulate $Al(OH)_3$ and release of exchangeable F at the lower pH, rather than by changes in Al speciation. The SO_4^{2-} behaviour is dominated by pH-related changes in anion exchange capacity, with adsorption increasing at lower pH. During the recovery stage, the stream substrate desorbed SO_4^{2-}. This experiment supports the conclusions from Hruška *et al*. (2002) who examined the release of SO_4^{2-} from other catchments in Europe. In general, atmospheric deposition rates of SO_4^{2-} have decreased in Europe and North America. Excess SO_4^{2-} in soils and stream sediment is being desorbed and exported from many catchments.

The experiment demonstrated the reversible exchange processes between H^+ and base cations, particularly Ca^{2+} and Mg^{2+}. As the Ca-Mg exchangeable pool became depleted, Al release gradually replaced Ca-Mg release as the principal acid-neutralising mechanism. The Ca/Mg ratio in the stream was highest during the acidification and lowest at the start of the recovery. During recovery, Mg resorbed faster than Ca. The BC/Al ratio increased at first but decreased sharply as BCs became depleted and Al mobilisation increased. The BC/Al ratio did not return to its initial value during the recovery period. The reversible desorption of BC, dissolution of Al and adsorption of SO_4^{2-} delayed acidification, diminished the pH depression and prolonged the recovery. Recovery is slower than acidification, there is hysteresis in the pattern of recovery and the recovery lags behind the flushing of the added Cl (as HCl).

During the acidification, Al^{3+} and AlF^{2+} become more important species of dissolved Al. Calculated Be speciation was controlled by abundance of the Al species, pH, and the availability of free F^-. Iron and Mn were both mobilised during the artificial acidification phase but their concentration normally decreases during natural episodic acidification events, likely because of dilution and oxidation of the Fe- and Mn-rich shallow groundwater. The mobilised Mn and Fe, although increasing over 40% above their initial concentration, were unimportant as an acid-neutralising mechanism because of their low concentrations. Although clear evidence of resorption of Al, Fe, and Mn is lacking (no values below background), the recovery of these three elements to background values could be delayed by resorption.

A dynamic model (MASS — Modelling the Acidification of Stream Sediment) was developed. It reproduces the behaviour of the base cations that are involved in ion exchange equilibria. The master variables include pH, which is controlled partly by anion exchange (primarily SO_4^{2-}) and partly by dissolution or precipitation of $Al(OH)_3$. MASS does not model the anion exchange or solid phase equilibria with $Al(OH)_3$. The significant consistency between modelled and measured base cation concentrations suggests that the assumptions of the modelling approach may be realistic. Clearly, stream sediment (somewhat analogous to catchment soils) minimises the magnitude of episodic acidification and delays recovery.

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