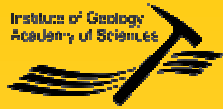


# Chemistry and modeling of the response of a small stream to a short-term in-stream acidification



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## 1. Abstract

Several in-stream acidification experiments have identified three interactions between the acidifying stream water and sediment. First and most important, H<sup>+</sup> exchanges with other cations adsorbed on the stream substrate, releasing them into solution. Second, adsorption of SO<sub>4</sub><sup>2-</sup> by stream substrate may occur. Third, dissolution of an Al-rich solid phase occurs, along with trace elements associated with that phase. The behavior of stream substrate-water interaction may be a good analog for soil – soil water interactions. A mathematical model based on mass balance, MASS Modeling Acidification of Stream Sediments, was developed to simulate the adsorption and desorption of base cations during the experiment.

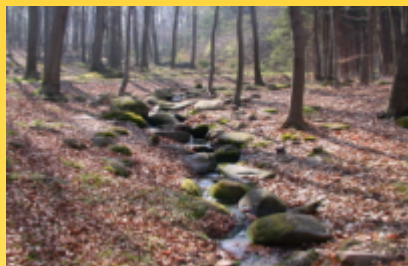


Fig.1 Lesní Potok stream and surrounding European beech forest

## 2. Description of Site and Methods

Recent changes in acidic deposition make Lesní Potok (LP) an important “case study” site for detection of changes in chronic and episodic acidification of surface waters. The LP catchment is located in central Czech Republic approximately 30 km east-southeast of Prague. The catchment covers 0.765 km<sup>2</sup>. Soils at LP, mostly Gleyic or Dystric Cambisols, are derived from the Ricany Granites. The lower part of the catchment is underlain by 4 to 5 m of sediment. The forest vegetation is 46% coniferous (mostly *Picea Abies*) and 54% deciduous (mostly *Fagus Sylvatica*). The average annual bulk precipitation during the period 1994-2000 was 600 mm. The runoff during the same period was 68 mm. The high evapotranspiration is typical for the area and produces relatively high concentrations for conservative elements such as Cl. The evapotranspiration rate based on the water budget is 89%, and about 85% based on the Cl budget. The annual average air temperature at LP 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 acidification experiment was conducted on May 11<sup>th</sup>, 2001. The air temperature was 20°C and the stream water temperature was 11°C. Discharge at the start of acidification was 2.73 L s<sup>-1</sup> (0.128 mm h<sup>-1</sup>, high flow). Twenty-two moles of HCl (4.709 M) were added to the stream during 4 hours at a point just below the stream weir. The discharge of the acid from the Mariotte bottle was approximately 20 ml min<sup>-1</sup>. Point A was 1 m below the acid addition point (weir) - only pH measurements were taken there. Samples of the stream water were taken concurrently at points W (weir, above the acid addition), B, C and D. Points B, C, and D were 20 m, 45 m and 70 m downstream from the weir, respectively.

## 3. pH changes

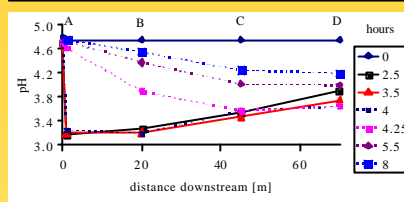


Fig.2 Streamwater pH changes during the experiment

- pH was lowered from 4.7 to 3.2 at point A (1 m downstream)
- pH was lowered from 4.7 to 3.2 at point C (70 m downstream)
- 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.
- the increase of pH was slower during the recovery period than the initial decrease during acidification phase.

## 4. Changes of selected anions and cations concentrations at point C (45 m)

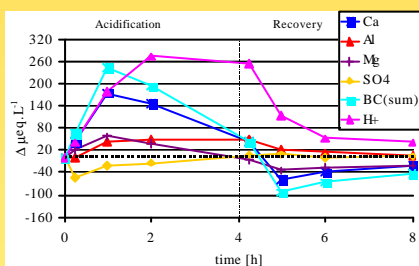


Fig.3 The delta concentrations of dissolved analytes ( $c_i - c_{i0}$ ; in  $\mu\text{eq L}^{-1}$ )

Fig.3

- When the Ca-Mg exchangeable pool became depleted, release of Al gradually replaced release of Ca-Mg as the principal acid-neutralizing mechanism.
- The concentration of SO<sub>4</sub><sup>2-</sup> decreased first during the acidification phase but then increased as the pH increased due to decreasing acidification.

Fig. 4

- The relatively most mobile element was Al, its concentration increased by almost 50%.
- Trace elements associated with amorphous Al solids, such as Be, were mobilized.
- Calcium concentration increased by 25% during the acidification and during the recovery it decreased to 90% of the initial concentration due to its readsorption to stream sediment. Magnesium exhibited similar behavior.

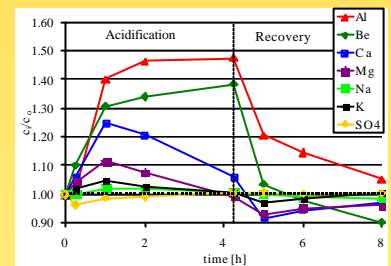


Fig.4 The relative change ( $c/c_0$  equivalents/equivalents) of concentrations of dissolved analytes versus time at point C

## 5. Acid neutralization mechanisms at point C (45 m)

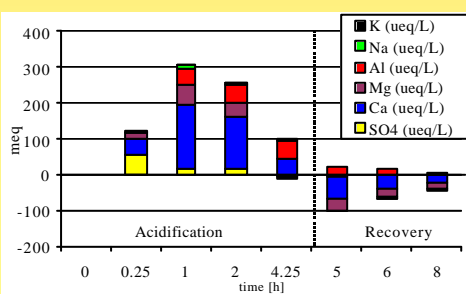
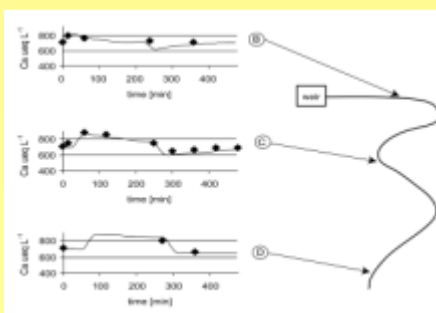


Fig.5 Acid neutralization through time at point C, the x-axis is not proportional.

The stream substrate at LP has three important mechanisms of acid neutralization.

1. adsorption of SO<sub>4</sub><sup>2-</sup>
  2. ion exchange of H<sup>+</sup> for the divalent base cations Ca<sup>2+</sup> and Mg<sup>2+</sup> on the cation exchange sites of the stream substrate, and
  3. ion exchange of H<sup>+</sup> for Al<sup>3+</sup> on the cation exchange sites of the stream substrate or dissolution of a solid phase Al(OH)<sub>3</sub> of the stream substrate.
- The contribution of the individual elements to acid-neutralization (Fig. 5) early in the experiment was SO<sub>4</sub>>Ca>Mg>Al (t = 0.25 h), then Ca>Mg>Al>SO<sub>4</sub> (t = 1 h), and finally Al>Ca>Mg>SO<sub>4</sub> (t = 4 h).
  - The maximum acid neutralization by release of base cations (BC = Ca+Mg+K+Na) and SO<sub>4</sub><sup>2-</sup> adsorption was about 170  $\mu\text{eq L}^{-1}$ .
  - The total contribution of adsorption of SO<sub>4</sub><sup>2-</sup> (59 meq) to neutralization of the acid over the 70 m stretch of stream was small compared to that of Ca (4,542 meq), Al (2,329 meq), and Mg (1,184 meq).
  - If acid neutralization had not occurred, the pH at point C would have decrease to 3.75, 3.31, 3.27 and 3.45 at time 0.25, 1, 2 and 4.25 h, respectively.
  - During recovery, the pH would have increased faster if the resorption of base cations and desorption of SO<sub>4</sub><sup>2-</sup> had not occurred.

## 6. Modeling



### Modeling

A dynamic model (MASS – Modeling the Acidification of Stream Sediment) was developed. It reproduces the behavior of the base cations that are involved in ion exchange equilibria. The master variables include pH, which is controlled partly by cation and anion exchange (primarily SO<sub>4</sub><sup>2-</sup>) and partly by dissolution or precipitation of Al(OH)<sub>3</sub>. MASS does not model the anion exchange nor solid phase equilibria with Al(OH)<sub>3</sub>. The significant consistency between modeled and measured base cation concentrations suggests that the assumptions of the modeling approach may be realistic. Clearly, stream sediment minimizes the magnitude of episodic acidification and delays recovery.

$$c_{Me^+}(L, t) = e^{-z} \left[ c_{Me^+}^0 + k_1 (c_{H^+}^0 + \alpha c_{Me^+}^0) \int_0^L (c_{Me^+}^0 - \int_0^t (c_{Me^+}(l, t))_l dt) e^{-l} dl \right]$$

$$z = \alpha (k_2 - k_1) \int_0^L (c_{Me^+}(l, t) - c_{Me^+}^0) dt + \alpha k_1 c_{Me^+}^0 L + k_2 c_{H^+}^0 L$$

$Me^+$  metals in the stream solution,  $Me^+$  metals in homogenous stream sediment  
 $c_{H^+}$  activity of hydrogen ions in the stream water  
 $c_{Me^+}$  concentration of the modeled cation in the stream water  
 $c_{Me^+}^0$  exchangeable concentrations of the modeled cation  $Me^+$   
 $c_{Me^+}^s$  concentration of H<sup>+</sup> sorbed to the solid phase (sediment)  
 $\alpha$  proportional charge of the modeled ion and the relative loss of H<sup>+</sup> in the solution corresponding to all other solutes that are being desorbed at the same time as the modeled  $Me^+$   
 $l$  distance downstream,  $t$  = time,  $k_i$  = rate constants

### Acknowledgments

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For more information about the Lesní potok catchment, visit <http://www.gli.cas.cz/lesnipotok/>