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Bedrock weathering and stream water chemistry in felsic and ultramafic forest catchments

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Abstract

Two small forested catchments, each underlain by geochemically contrasting silicate rock types, were studied in the western Czech Republic. The felsic (granitic) Lysina catchment exhibited low resilience to anthropogenic acidic deposition and therefore low pH, Mg and high concentration of toxic species of Al in drainage water. Pluhův Bor, underlain by ultramafic rocks (especially serpentinite), exhibited very high resilience to acidic deposition and also peculiar drainage water chemistry due to the lithology (high pH, Mg, Ni and Cr). A significant depletion trend in Mg was observed from the unweathered to weathered rocks and to the topsoils at both sites. Enrichment profiles of K and Ca within the topsoil at Pluhův Bor indicated biocycling of these limiting nutrients.

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Keywords: granite; serpentinite; Norway spruce; stream water; borehole core; chemical weathering; element mobility; base cations; acidification

1. Introduction

Chemical weathering of rocks and soils buffers forest ecosystems from anthropogenic acidification. Several comparative papers about small forested catchments on contrasting rock types demonstrated their role in regulating drainage water chemistry[1,2]. The focus of this contribution was to compare and contrast hydrochemical and geochemical patterns in two Czech catchments with geochemistry that can serve as examples of differing catchment resilience to anthropogenic acidification. There is substantial evidence that acidic atmospheric deposition depleted exchangeable pools of base cations in Central European forest soils during the past decades[3]. This has had the detrimental effect of decreasing the capacity of forest soils to neutralize incoming acidity. Chemical weathering of

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rocks and soils has been of great succour through its significant and positive contribution in supplying nutrient base cations (Ca, Mg, K) for plants and for neutralization of soil acidity. In this study the effect of weathering processes on selected base cations and their cycling and mobility is investigated at the base-poor granitic catchment Lysina and at the magnesium-rich Pluhův Bor catchment.

2. Study area and methods

The study catchments are situated 7 km apart in the Slavkov Forest (Slavkovský les), western Bohemia, Czech Republic and are forested by Norway spruce (*Picea abies*) plantations[2,3,4]. They have a similar area, altitude, air temperature, and atmospheric deposition but geochemically differing bedrocks and soils (Tab. 1). They are in the Czech GEOMON network of catchments and in the International Long-Term Ecological Research network. Moreover, Lysina is in the International Cooperative Programme – Integrated Monitoring ICP IM and the ICP Waters. Lysina became one of the four main Critical Zone Observatories of the SoilTrEC project[5] and the Pluhův Bor was included in the project as a paired site. Stream water discharge has been monitored using V-notch weirs and mechanical water level recorders since 1989 at Lysina and since 1991 at Pluhův Bor. Stream water was collected weekly for chemical analysis at both sites. Laboratory methods of water analyses performed in the Czech Geological Survey were described previously in detail[2]. Rock and soil samples were collected from boreholes with depths reaching up to 30 m at Lysina and 28 m at Pluhův Bor and also from an additional soil pit at Lysina. These samples were dried down, homogenized, weighed, dissolved via acid digestion and analysed for their elemental concentrations by ICP-OES[6,7]. Normalized concentration profiles (i.e. tau values) of alkaline earth metals were generated as a function of depth through the regolith profile, using an immobile element (Ti, titanium) as a reference for the normalization[8,9]. This approach allowed us to quantify the degree of depletion and/or enrichment of selected alkaline earth metal through the weathering profile[6,7].

Table 1. Characteristics of the three study catchments in the Slavkov Forest.

Catchment	Area km^2	Altitude m a.s.l.	Prevailing rock	Prevailing soil	Temperat °C	Spruce %
Lysina	0.273	829-949	Granite	Podzol	5	100
Pluhův Bor	0.216	690-804	Serpentinite	Stagnosol	6	88

3. Results and discussion

Aquatic chemistry reflected the geochemical composition of the underlying substrates within the studied catchments[2] and exhibited diverse pH values (Fig. 1). The strongly anthropogenically acidified soil waters at Lysina exhibited incomplete neutralization of acidic atmospheric deposition and had chronically low streamwater pH, especially during high flow periods (Fig. 1). Pluhův Bor exhibited the most efficient neutralization of mineral acids by the weathering of magnesium-rich silicates and high pH stream water, especially during baseflow conditions. Lysina exhibited very low Mg concentrations (around 0.4 mg l^{-1}) in stream water; Pluhův Bor contained extremely high concentrations (around 18 mg l^{-1}) of Mg, both negatively related to stream water discharge. Very low pH values (Fig. 1) and high inorganic monomeric aluminum (Ali) concentrations were found in the surface water draining granite[2]. Concentrations of Ali were usually above the toxic level for fish (0.05 mg l^{-1}) and toxic levels for different species of benthic macroinvertebrates (0.14 - 0.3 mg l^{-1})[10]. Extremely high mean Ali concentrations (0.7 mg l^{-1}) were observed in stream water at Lysina in the first half of the 1990s. These Ali concentrations were among the highest values reported in literature[11]. Serpentinite stream water exhibited high pH (Fig. 1). Trace metals of geogenic origin (Ni and Cr) were very high in stream water at Pluhův Bor[2].

Contrasting stream water compositions of the studied catchments were generated according to MAGIC modeling simulations mainly by differences in chemical weathering rates of base cations[3]. Chemical weathering reactions buffer terrestrial and aquatic ecosystems from acidification[2]. Despite very different drainage water acidity, dissolved organic carbon (DOC) concentrations were similar at Lysina and Pluhův Bor. The DOC concentrations in drainage waters at Lysina and Pluhův Bor increased[12] during the measured period 1993-2014. In contrast, in response to

decreased atmospheric deposition of anthropogenic sulfur mainly in the 1990s, streamwater sulfate declined in the study catchments. Moreover, the sulfate decline at Pluhův Bor was one of the most pronounced worldwide[13].

Sampled rocks and soils from Lysina showed that Ca, Mg and K experienced significant depletion in the topsoil, whereas Ba revealed an enrichment profile at the shallower depths[6]. Specifically, Ca was highly depleted closer to the organic-rich topsoils (tau values up to -0.97), and Mg also showed a depletion trend but with lower magnitudes (tau values about -0.8). This observation supports the fact that Ca often out-competes Mg with respect to the intensity of element leaching from the soils and rocks due to weathering and biological processes. Similarly, the normalized weathering profile of Sr showed a depletion trend (tau values about -0.7) that, however, is less pronounced compared to Ca or Mg. Conclusively, results from the acidified base-poor forest ecosystem at Lysina show that the behaviour of base cations during weathering and soil formation follows a trend where Ca is leached most readily from the system, followed by Mg and Sr. The extremely negative tau values of Ca, Mg and Sr trends in the upper part of the weathering profile (from -0.7 up to -0.97) are likely a consequence of the long-term and severe acid deposition history at Lysina[6]. Interestingly, results from Lysina also confirmed a strong and systematic enrichment trend for Cr closer to the organic-rich topsoils (tau values reaching up to +8), suggesting deposition and accumulation of Cr at this site from external sources[6]. Elemental analysis of rocks and soils from Pluhův Bor confirmed, in agreement with the prevous visual examination of the borehole core, that there are major lithological changes with the depth: ranging from ultramafic rocks (serpentinite, tremolitic schist and actinolitic schists) to the mafic amphibolite[7]. The serpentinitic part of the core showed a surprisingly significant depletion in the topsoil for Mg, and enrichment profiles toward the topsoil for Ca and especially for K, the major deficient nutrient base cation at Pluhův Bor, indicating the influence of biocycling. A similar enrichment profile to Ca was observed for Sr. Both Ni and Cr profiles indicated enrichment trends in the deeper parts, but closer to the surface, both potentially toxic metals show strong depletion trends, indicating their high mobility at Pluhův Bor. Strong coupling of Ni and Cr was observed ($R^2 = 0.88$, $p < 0.05$) along the entire weathering profile at Pluhův Bor[7].

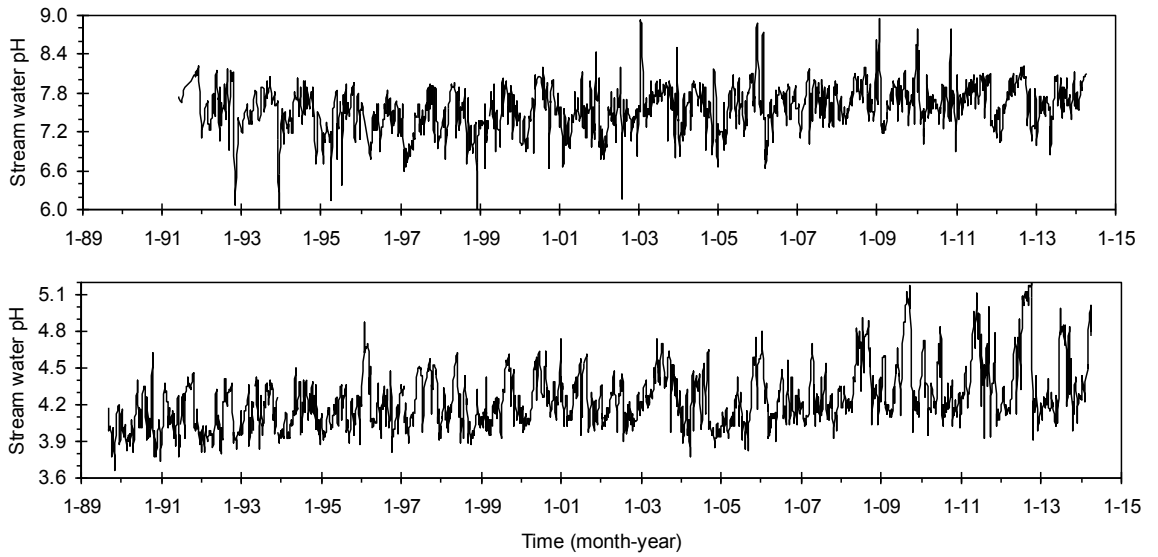

Fig. 1. Temporal patterns of streamwater pH values at Pluhův Bor (top) and Lysina (bottom) between September 1989 (Lysina), June 1991 (Pluhův Bor) and April 2014. High pH values generally represent baseflow conditions and low pH values represent floods.

4. Conclusions

Monolithologic Czech catchments served as valuable representatives of spruce ecosystem resilience to anthropogenic acidification. The granitic Lysina catchment exhibited low resilience and therefore low stream water pH, Mg and high concentration of toxic inorganic monomeric Al. The ultramafic Pluhův Bor represented sites with

very high resilience and also peculiar stream water chemistry due to geogenic reasons (high pH, Mg, Ni and Cr, low K). Rock and soil samples showed depletion patterns in the topsoil for Ca, Mg and K at Lysina and for Mg at Pluhův Bor. Enrichment profiles of K and Ca in the topsoil at Pluhův Bor indicated biocycling of these essential, but deficient nutrients. Both Ni and Cr showed depletion trends closer to the surface, indicating their high mobility in these more oxic and alkaline conditions, and these elements also showed a strong coupling at Pluhův Bor. This is in contrast with the behavior of Cr at the granitic Lysina where it showed a strong enrichment trend, which points to a lack of Cr mobility, likely related to highly acidic conditions there.

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