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Hydrochemical fluxes and bedrock chemistry in three contrasting catchments underlain by felsic, mafic and ultramafic rocks

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Abstract

Bedrock chemistry from three drill cores and fluxes of precipitation, throughfall and runoff from the 2015 water year were examined in three forested catchments in the western Czech Republic. The coefficient of alkalinity of rocks at the granitic (felsic) LYS catchment fall in the low chemical reactivity category. Rocks from the amphibolitic (mafic) NAZ catchment have high reactivity and rocks from the serpentinitic (mostly ultramafic) PLB catchment have high or even very high reactivity. Streamwater fluxes reflected the composition of the underlying bedrock lithologies, especially for magnesium, nickel and chromium at PLB, and for calcium, arsenic and sulfur at NAZ. Streamwater at LYS reflected incomplete neutralization of acidic deposition in the catchment and had mostly negative alkalinity and correspondingly very high fluxes of potentially toxic inorganic monomeric aluminum. Internal cycling of magnesium and calcium in spruce canopy throughfall was influenced by substrate chemistry at PLB and NAZ. About half of streamwater nitrogen left the catchments in the organic form.

Peer-review under responsibility of the organizing committee of WRI-15
Keywords: granite; amphibolite; serpentinite; Norway spruce; magnesium; coefficient of alkalinity of rocks

1. Introduction

Chemical weathering of rocks and soils buffers terrestrial and freshwater ecosystems from anthropogenic adification. The focus of this contribution is to compare bedrock chemistry and hydrochemical fluxes in three

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different Czech catchments with substrates that can serve as examples of differing catchment vulnerability to anthropogenic acidification.

2. Study area and methods

The study catchments are situated 5–7 km apart in the Slavkov Forest, western Bohemia, Czech Republic and are forested mainly by even-aged stands of Norway spruce (*Picea abies*). They have similar areas, altitude, annual mean air temperature (5–6 °C), and atmospheric deposition but geochemically differing bedrocks and soils (Tab. 1). Lysina (LYS) and Pluhův Bor (PLB) are in the Czech GEOMON network of catchments and in the international ecological network (ILTER). Moreover, LYS is part of two International Cooperative Programs (ICP) – Integrated Monitoring and Waters. All three catchments formed the Slavkov Forest CZO[1] in 2010, one of the main Critical Zone Observatories of the former European SoilTrEC project.

Table 1. Characteristics of the three study catchments in the Slavkov Forest. Most of the data are from[2], except for the forested area for 2015 from[3] and the biomass growth based on data from[4,5] and recalculated for 2015.

Catchment	Area (km^2)	Altitude (masl)	Prevailing rock	Prevailing soil	Closed-canopy forest[3] (%)	Spruce (%)	Age (yrs)	Above-ground biomass (t/ha)	Above-ground biom. growth[4,5] (t/ha/yr)
Lysina	0.273	829-949	Granite	Podzol	98	100	42	101	4.9
Na Zeleném	0.55	736-802	Amphibolite	Cambisol	89	97	97	277	6.4
Pluhův Bor	0.216	690-804	Serpentinite	Stagnosol	81	88	114	169	0.84

Stream water discharge has been monitored using V-notch weirs and mechanical water level recorders since the 1990 water year (November–October) at LYS, since the 1992 water year at PLB and by a pressure recorder since 2015 at Na Zeleném (NAZ). Stream water was collected at regular intervals (weekly at LYS and PLB and monthly at NAZ) for chemical analysis at these three sites over the last 6 years. Weekly samples or older data were not evaluated for this contribution. Bulk precipitation and canopy throughfall were collected monthly (in total) by 6 and 25 collectors, respectively. Water analyses performed in the Czech Geological Survey (CGS) using standard laboratory methods, which were described previously in detail[2]. Aluminum fractions were measured using colorimetry and cation exchange resin[6]. Calculations of element fluxes in precipitation and throughfall in the 2015 water year were based on 12 samples of each, and runoff calculations were based on 13 samples from each catchment. Rock samples from boreholes drilled to 26-30 m depth in September 2012 were processed and their elemental content was analyzed mostly by FAAS or RFA, also in the accredited CGS laboratories. Sulfur was analyzed by combustion on an elemental analyzer (ELTRA). The coefficient of alkalinity for the rocks was calculated (Eq. 1)[7,8] using individual concentrations (mol kg^{-1}).

$$CAlk = \frac{\mathbf{Na+K+Li+Ca+Mg+Ba+Sr}}{\mathbf{Si+Ti+Al+Fe+Mn+Na+K+Li+Ca+Mg+Ba+Sr}} \quad (1)$$

3. Results and discussion

All eight analyzed rock core samples from LYS are felsic (with SiO_2> 65%), with individual contents from 65.4 to 74.7% of SiO_2. Of nine NAZ rock samples analysed, seven are mafic (SiO_2 45–55%), and two are ultramafic (43–44%). Drill core samples from PLB are the most diverse: of fourteen samples analysed, six are ultramafic (SiO_2 < 45%), with SiO_2 contents from 37.7 to 43.7%, five samples are mafic, and three samples contain 55-58% SiO_2 which correspond to the intermediate category[9,10]. The largest content of MgO (38.7%) and Ni (0.1%) was detected in the uppermost serpentinite (Fig. 1a) and, naturally, this sample also contains the lowest contents of K_2O and CaO (just 0.01% and 0.04%), as a typical feature of the ultramafic rock. Relatively large concentrations of sulfur (Fig. 1b) were detected at NAZ (up to 0.63%), perhaps partially in the form of arsenopyrite related to elevated concentrations of total arsenic in bedrock (up to 77 ppm). Coefficient of alkalinity values at LYS fall in the low reactivity category (0.1–0.2), whereas almost all values from NAZ and two thirds of values from PLB fall in the high reactivity category (0.25–0.4). Five rock core samples from PLB fall in the very high reactivity category (>0.4), with the highest recorded value (0.56) in the uppermost serpentinite.

Streamwater chemistry at LYS, NAZ and PLB reflected composition of the underlying substrates[2]. Strikingly different concentrations of Mg are shown in Fig. 2a, the high concentrations were recorded only during baseflow, lower values during high flow.

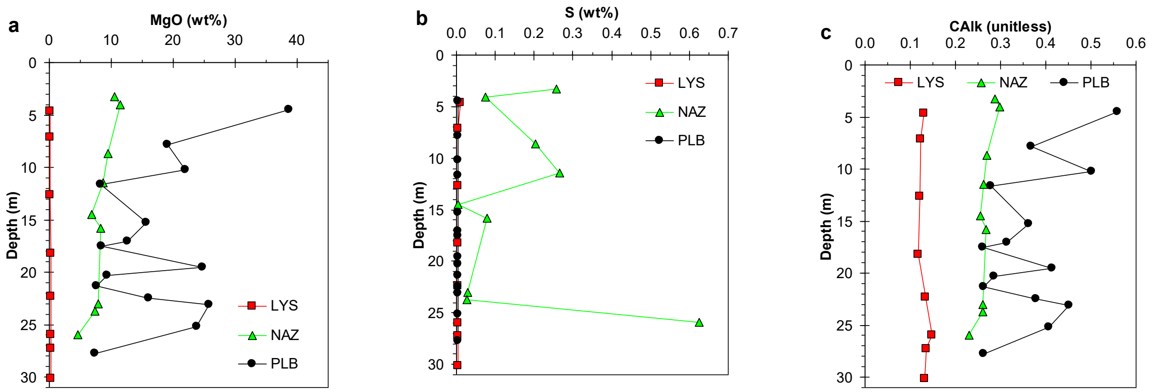

Fig. 1. Chemical composition of rock samples (weight percents) from the drill cores at Lysina (LYS), Na Zeleném (NAZ) and Pluhův Bor (PLB) for (a) magnesium; (b) sulfur; (c) coefficient of alkanitity according to Equation 1.

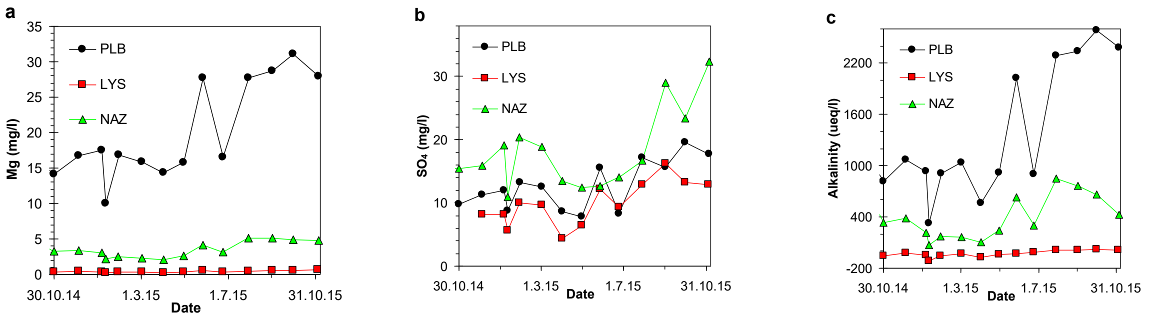

Fig. 2. Streamwater concentrations at Lysina (LYS), Na Zeleném (NAZ) and Pluhův Bor (PLB) in the water year 2015 for (a) magnesium; (b) sulfate; (c) Gran titration alkalinity.

Higher concentrations of sulfate at NAZ (Fig. 2b) probably reflected significant content of S in bedrock at NAZ (Fig. 1b). The strongly anthropogenically acidified streamwater at LYS reflected incomplete neutralization of acidic atmospheric deposition and had chronically low streamwater alkalinity (Fig. 2c) and pH[11] (not shown), especially during high flow periods. Precipitation and throughfall fluxes in the 2015 water year reflect the recent reduction in atmospheric deposition of pollutants in Central Europe[12]. Total deposition of S calculated from the precipitation and throughfall fluxes (Tab. 2) and the forest cover of catchments (Tab. 1) was 3.7, 5.1 and 4.8 kg ha^{-1} yr^{-1} at LYS, NAZ and PLB, respectively. Corresponding net loss of S was 0.7 kg ha^{-1} yr^{-1} at LYS and PLB and 1.3 kg ha^{-1} yr^{-1} at NAZ which could reflect that approximately half of the S output at NAZ was from internal sources (Fig. 1b). Dry deposition and internal cycling of nutrient base cations were estimated proportionally to Na flux, assuming negligible internal vegetation flux of Na[13]. Throughfall fluxes reflected substrate chemistry, e.g., the largest internal cycling of Mg (84% of the throughfall flux) was calculated at PLB and the largest internal cycling of Ca (74%) was calculated for NAZ and correspondingly the lowest (22%) for LYS. Runoff fluxes (Tab. 2) of elements like Mg, Ni and Cr strongly reflected the composition of the underlying substrates[2,9,10] (Fig. 1). Comparable output of phosphorus at LYS and PLB (Tab. 2) is surprising because mean P concentrations in granite at LYS[9] are 5.7 times larger than mean P content in bedrock at PLB[10], where spruce trees suffer P deficiency[14]. Perhaps extremely slow above-ground biomass growth of trees at PLB (Tab. 1) and corresponding limited net tree uptake of P are partially responsible for that situation. About half of runoff N left all three catchments in the form of DON. Incomplete neutralization of incoming acidity at LYS, acidity generation from previously stored S and production of organic acids, caused higher H^+ output flux than input flux (Tab. 2). This acidic environment caused a large runoff output of potentially toxic inorganic monomeric Al (Ali)[6] at LYS.

Table 2. Open area bulk precipitation fluxes, canopy throughfall fluxes and streamwater fluxes of selected elements and compounds at the three study catchments for the 2015 water year (Nov. 2014 – Oct. 2015). Ali = inorganic monomeric Al (potentially toxic species[6]), Alo = organic monomeric Al, Alp = particulate Al, DIN = dissolved inorganic N (sum of NO_3-N and NH_4-N), DON = dissolv. organic N, nd = not determined.

Elem.	Unit	LYSINA			NA ZELENÉM			PLUHŮV BOR		
		Precip.	Through.	**Runoff**	Precip.	Through.	**Runoff**	Precip.	Through.	**Runoff**
Mg	kg ha^{-1} yr^{-1}	0.31	1.0	**0.53**	0.30	1.9	**3.42**	0.33	4.2	**21.71**
Ca	kg ha^{-1} yr^{-1}	2.0	3.0	**2.1**	1.3	5.4	**6.74**	1.3	6.4	**2.14**
K	kg ha^{-1} yr^{-1}	1.7	12.2	**0.60**	2.2	14.6	**1.06**	1.7	9.1	**0.46**
Na	kg ha^{-1} yr^{-1}	1.6	1.9	**3.45**	1.2	2.9	**4.58**	1.2	2.3	**1.54**
Si	kg ha^{-1} yr^{-1}	nd	nd	**12.4**	nd	nd	**10.2**	nd	nd	**20.9**
P	g ha^{-1} yr^{-1}	298	406	**160**	308	206	**71**	373	216	**151**
Ali	g ha^{-1} yr^{-1}	nd	nd	**462**	nd	nd	**8.5**	nd	nd	**12.3**
Alo	g ha^{-1} yr^{-1}	nd	nd	**935**	nd	nd	**219**	nd	nd	**322**
Alp	g ha^{-1} yr^{-1}	nd	nd	**1376**	nd	nd	**581**	nd	nd	**1954**
Ni	g ha^{-1} yr^{-1}	27.1	4.8	**2.3**	5.0	3.3	**3.2**	5.2	13.9	**265.2**
Cr	g ha^{-1} yr^{-1}	2.4	1.10	**1.9**	1.1	0.76	**1.8**	1.3	0.99	**60.7**
F	g ha^{-1} yr^{-1}	110	89	**310**	71	71	**110**	77	79	**150**
S	kg ha^{-1} yr^{-1}	1.8	3.7	**4.4**	1.3	5.6	**6.4**	1.5	5.6	**5.5**
DIN	kg ha^{-1} yr^{-1}	5.30	3.7	**0.56**	3.82	10.5	**0.73**	4.46	9.5	**1.63**
DON	kg ha^{-1} yr^{-1}	0.0	1.6	**0.55**	0.2	3.2	**0.68**	0.1	3.4	**1.67**
DOC	kg ha^{-1} yr^{-1}	12.6	50.0	**58.4**	11.3	65.9	**20.3**	11.0	64.6	**72.1**
H^+	g ha^{-1} yr^{-1}	77.3	66.0	**222.4**	69.7	65.2	**1.0**	69.9	63.0	**0.3**

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