22551844

STATUS: PENDING 20060825 OCLC #: 11749004
REQUEST DATE: 20060825 NEED BEFORE: 20061123 SOURCE: ILLiad
BORROWER: NHM RECEIVE DATE: DUE DATE:
RENEWAL REQ: NEW DUE DATE:
LENDERS: *UB3, MBW, MYG, BOS, BMU

CALL NUMBER: Lender's Holdings: v.36-v.66(1997-2003)
TITLE: Biogeochemistry.
ISSN: 0168-2563
ARTICLE: : The biogeochemistry of basic cations in two forest catchments with contrasting...
VOL: 37 NUM: 2 DATE: 1997 PAGES: 173-202
VERIFIED: OCLC
SHIP TO: University of New Hampshire/Dimond Library-ILL/18 Library Way/Durham NH 03824
BILL TO: same
SHIP VIA: UPS, VAN, US Mail
MAXCOST: COPYRIGHT: CCL AFFILIATION: NELINET, DOCLINE, BLC, Academic r...
FAX: 603-862-2637 EMAIL: ARIEL IP # 132.177.228.62 or email i...
BORROW NOTES: FEIN#02-6000937, CISTI Acct. DD668143, NTIS DA# 99925-0, DLC Deposit Acct. ...
PATRON: Kessler, Will
LEND CHARGES: SHIPPED DATE: SHIP INSURANCE:

Biogeochemistry **37:** 173–202, 1997.

The biogeochemistry of basic cations in two forest catchments with contrasting lithology in the Czech Republic

PAVEL KRÁM[1,2], JAKUB HRUŠKA[2], BRIAN S. WENNER[1],
CHARLES T. DRISCOLL[1] & CHRIS E. JOHNSON[1]
[1]*Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244, USA;* [2]*Department of Geochemistry, Czech Geological Survey, 118 21 Prague 1, Czech Republic*

Received 17 June 1996; accepted 22 October 1996

Key words: acidic deposition, magnesium deficiency, Norway spruce, serpentinite, soil chemistry, weathering

Abstract. The biogeochemistry of Ca, Mg, K, and Na were investigated in two forested catchments in the Czech Republic, one underlain by leucogranite, the other by serpentinite. High weathering rates at the serpentinite site at Pluhův Bor resulted in Mg^{2+} as the dominant cation on the soil exchange complex and in drainage water. Other basic cations (Ca^{2+}, K^+, Na^+) showed relatively low concentrations and outflow in streamwater. The catchment exhibited high base saturation in mineral soils (>70%), and near neutral soil and stream pH, despite elevated inputs of acidic deposition. Slow growth of Norway spruce at Pluhův Bor may be caused by K deficiency, Mg oversupply and/or Ni toxicity. In contrast, the granitic site at Lysina showed low concentrations of basic cations on the soil exchange complex and in streamwater. Soil and drainage water at Lysina were highly impacted by acidic deposition. Soil pH was extremely acidic (<4.5) throughout the soil profile, and the base saturation of the mineral soil was very low (<5%). Supplies of basic cations from atmospheric deposition and soil processes were less than inputs of SO_4^{2-} on an equivalence basis, resulting in low pH and high concentrations of total Al in drainage water. Needle yellowing in Norway spruce was possibly the result of Mg deficiency at Lysina. Because of their extremely different lithologies, these catchments serve as valuable end-members of ecosystem sensitivity to elevated levels of acidic deposition.

Introduction

The cycling of the basic cations (Ca, Mg, K, Na) is important to the biogeochemistry of forest ecosystems; Ca, Mg, and K are essential nutrients for plant growth, and low supply rates may affect forest productivity (Federer et al. 1989; Likens & Bormann 1995). Atmospheric deposition and mineral weathering are the principal sources of soluble basic cations in forest ecosystems, and these inputs are critical in regulating the acid-base status of forest soils and soil solutions (van Breemen et al. 1984). Losses of basic cations occur largely by drainage outflow or, in managed ecosystems, by biomass removal. Internal processes such as vegetation uptake and release, mineralization of soil organic matter, secondary mineral formation, and cation exchange, all influence the distribution of basic cations in the ecosystem, as well as biological availability.

Lithology may have a strong influence on element cycling and the chemistry of drainage waters. A few comparative studies from experimental catchments have demonstrated the critical role of bedrock geology in regulating the biogeochemistry of forested catchments including: Pond Branch, Maryland, USA (schist) vs. Soldiers Delight, Maryland, USA (serpentinite; Cleaves et al. 1974); Hubbard Brook, New Hampshire, USA (glacial till, schist) vs. Sleepers River, Vermont, USA (calcareous glacial till, calcareous schist; Thorne et al. 1988); and Glendye, Scotland, UK (glacial till, granite) vs. Peatfold, Scotland, UK (glacial till, gabbro; Creasey et al. 1986). Generally, these studies have shown soils and streamwaters in areas underlain by igneous and metamorphosed igneous rock types (e.g. granites, granitic gneisses, and schists) exhibit lower concentrations of basic cations and higher acidity than soils and drainage waters in areas underlain by more reactive rock types (e.g. serpentinite, carbonates, and mafic rocks). These patterns are ultimately due to differences in weathering reactions in these areas.

There is considerable interest in the biogeochemistry of areas underlain by granite and granite-derived rocks because their typically low weathering rates result in high vulnerability to acidic atmospheric deposition (Chadwick et al. 1991). Serpentinite is also intriguing because enrichment of Mg, Fe, Ni, Cr, Co and B, and undersupply in Ca, K, P, Mo and Zn, leads to an unusual chemical environment, resulting in dwarf forms of vegetation (Roberts & Proctor 1992). Only a few detailed biogeochemical studies have been conducted in forested ecosystems underlain by serpentinite (Gasser et al. 1994; Gasser & Dahlgren 1994; Kaupenjohann & Wilcke 1995).

Depletion of soil pools of basic cations by elevated inputs of strong acids may result in nutrient deficiency (Zech et al. 1985; Zoettl et al. 1989) or diminish the long-term productivity of forest stands (Federer et al. 1989). Elevated inputs of strong acid anions to sites with low supply rates of basic cations may result in elevated concentrations of Al and H^+ in drainage waters (Johnson et al. 1981), and conditions which may be toxic to forest vegetation (Cronan & Grigal 1995) or downstream aquatic organisms (Baker & Schofield 1982).

Disturbance associated with acidic atmospheric deposition is particularly severe in the region from the North Bohemian Coal Basin in the Czech Republic, to the southeast of former East Germany, to the Silesian Coal Basin in Poland (the "Black Triangle"; Fanta 1994). Atmospheric deposition of H^+ and SO_4^{2-} to the western part of this region are among the highest values reported in the world. Throughfall fluxes as high as 230 mmol m^{-2} yr^{-1} of H^+, and 470 mmol m^{-2} yr^{-1} of SO_4^{2-} have been reported (Černý 1993), resulting in extreme acidification of drainage waters and forest dieback (Pačes 1986; Moldan & Schnoor 1992).

Managed stands of Norway spruce (*Picea abies*) cover 55% of the forested areas in the Czech Republic. From 1958 to 1992 at least 473 km^2 of dead or dying Norway spruce stands were cut in the Czech Republic. An additional 59 km^2 or more of Czech conifer forests have experienced very heavy damage with more than 50% of the foliage loss, as measured in June 1992 (Anonymous 1993). Large plantations of Norway spruce died in the Ore Mountains (Krušné hory, Erzgebirge) and Jizera Mountains (Jizerské hory, Góry Izerskie) (Moravčík & Černý 1995). It is generally assumed that air pollution from industrial activities in the North Bohemian Coal Basin and Zittau Coal Basin contributed to forest decline in these mountains. The mortality of Norway spruce appears to be due to a combination of high SO_2 concentrations, acidic deposition, poor nutritional status in highly acidic soil (especially low Mg), and climatic stress (wind, cold, rime), followed by irruptions of insect pests (Innes 1993).

Despite generally high inputs, there is considerable site-to-site variability in the response of forest catchments to acidic deposition in the Black Triangle region. It appears that this variability is largely due to differences in lithology. The objective of this study was to compare biogeochemical patterns of basic cations in two forested catchments in the Czech Republic exhibiting extremely different lithologies which serve as end-members of ecosystem sensitivity to acidic deposition.

Methods

Site descriptions

Two experimental catchments in western Bohemia were chosen to explore the role of lithology in regulating the chemistry of soil and drainage waters and forest nutrition status under high loadings of acidic deposition. The site selection criteria for the catchments included proximity, similar atmospheric deposition and differing lithology (Figure 1, Table 1). The two catchments are located 7 km apart in the Slavkov Forest (Slavkovský les), south of the heavily damaged Ore Mountains. The region is forested with planted Norway spruce (*Picea abies*) monocultures and some European beech (*Fagus sylvatica*) at lower elevations. The original forests were composed of silver fir (*Abies alba*), European beech, and Norway spruce until the beginning of 19th Century. Approximately 10 km north of the catchments is a highly

Table 1. Characteristics of the study catchments.

Catchment	Lysina	Pluhův Bor
Location	50°03′ N, 12°40′ E	50°04′ N, 12°46′ E
Drainage area (km^2)	0.273	0.220
Altitude (m)	829–949	690–804
Mean slope (%)	11.5	13.0
Aspect	North-East	South-East
Avg. precipitation (mm) (1931–1980)	950	850
Avg. runoff (mm) (1992–1993)	419	226
Avg. air temperature (°C) (1931–1980)	5.0	6.0
Vegetation	Forest >20 years (70%), Young forest and grass (30%)	Forest >20 years (94%) Young forest and grass (6%)
Major tree species	Norway spruce (*Picea abies*) (100%)	Norway spruce (*Picea abies*) (92%), Scots pine (*Pinus sylvestris*) (8%)
Avg. spruce tree:		
Age (yr)	45	115
Height (m)	16	21
Diameter at breast height 1.3 m (cm)	18	24
Prevailing soils	Podzolic brown earth	Eutrophic brown earth
Glacial deposits	None	None
Bedrock	Leucogranite	Serpentinite

industrialized region, including large power production facilities (Tisová and Vřesová; near the town of Sokolov), supplied by high sulfur coal (2–12% S by weight) from several open-pit coal mines in the Sokolov basin.

The Lysina catchment is underlain by leucogranite composed mainly of quartz and feldspars. The oxides SiO_2 and Al_2O_3 comprise 87% of the rock by weight (Table 2). The CaO content of the leucogranite is 0.52%, one-fourth of the world average for granites, while the MgO content, 0.11%, is one-sixth of the world average (Pačes 1983). Soils in the catchment are largely podzolic brown earths and peaty gleys. The catchment is forested with second generation Norway spruce, with an average stand age of approximately 45 years, but with individual stands ranging from a few years to more than 120 years. Semi-mature plantations (>20 years) cover 70% of the catchment.

The Pluhův Bor catchment is underlain by serpentinite consisting primarily of antigorite ($Mg_3Si_2O_5(OH)_4$). The concentrations of the major oxides (SiO_2, MgO and Fe_2O_3) at Pluhův Bor (Table 2) are similar to calculated average values for serpentinite (Roberts & Proctor 1992). However, the

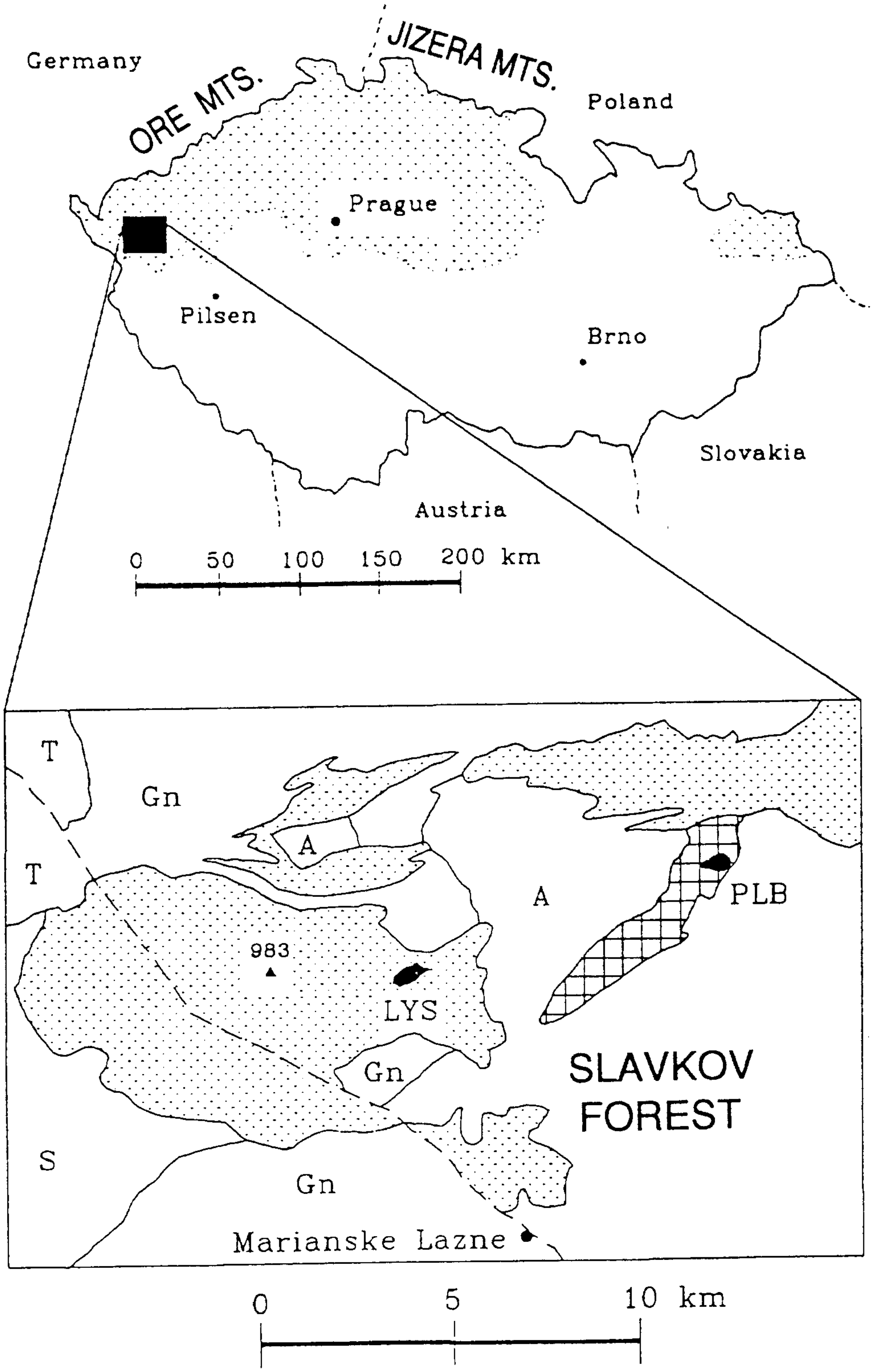

Figure 1. Upper panel: map of the Czech Republic, showing areas with annual average SO_2 concentrations above 30 $\mu g\ m^{-3}$ in ambient air (dotted) (modified after Moldan & Schnoor 1992). Lower panel: map of the Slavkov Forest with the locations of the experimental catchments Lysina (LYS) and Pluhův Bor (PLB), and major geologic formations (dotted – granite, cross-hatched – serpentinite, A – amphibolite, Gn – gneiss, S – mica shist, T – tertiary sediments, dashed line – fault).

Table 2. Average elemental composition of bedrock at the study areas (calculated using data of Fiala 1961).

	Leucogranite (Lysina)	Serpentinite (Pluhův Bor)
	mass%	
SiO_2	72.9	38.4
Al_2O_3	14.0	0.61
CrO_2	0.001	0.41
Fe_2O_3	0.73	6.6
FeO	1.4	1.7
MnO	0.07	0.13
MgO	0.11	36.8
CaO	0.52	Trace
Li_2O	0.12	Trace
Na_2O	2.9	1.3
K_2O	4.4	0.29
P_2O_5	0.30	0.01
CO_2	BD	0.15
F	0.84	BD
S	Trace	0.04
H_2O^+	1.2	12.7
H_2O^-	0.3	0.65
NiO	BD	0.24

BD – below detection limit

serpentinite at Pluhův Bor contains greater amounts of K_2O (ten times) and Na_2O (six times) than "average" serpentinite, and a lower amount of Al_2O_3, one-fourth the "average" value. Only trace quantities of CaO are present, which is atypical for serpentinite (the average value from the literature is 1.5%, range: 0.04–8.9%). The dominant soils are eutrophic brown soils and peaty gleys. Pluhův Bor is almost entirely forested with a 100–120 year old Norway spruce stand mixed with Scots pine (*Pinus sylvestris*) at higher elevations (Table 1).

Methods and materials

The catchments have been monitored since 1989 (Lysina), and 1991 (Pluhův Bor). Bulk precipitation was collected bi-weekly using two continuously-open collectors in a clearing within the forest at Lysina catchment. Throughfall was collected monthly on square, 15 × 15 m plots containing five collectors: one in the center and one at each corner. The plots were located randomly in representative forest stands, two plots at Lysina and one at Pluhův Bor.

Nine zero-tension lysimeters, similar to the design used by Driscoll et al. (1988), were installed in two pits in each catchment in June 1993. Lysimeters were inserted just beneath the organic horizon and beneath A (at Pluhův Bor) or E horizons (at Lysina) in each pit. One pair of lysimeters was installed below the A horizon in one pit at Pluhův Bor. The lysimeters were rounded rectangular polyethylene containers 15 cm long by 9 cm wide and 4 cm high (area 132 cm^2). The lysimeters were filled with acid-washed silica sand, and drain into polyethylene containers situated in the back-filled soil pit. Soil water was collected continuously in the containers, and sampled at monthly intervals beginning in June 1994 using a sampling tube. All lysimeters were sampled and analyzed separately. The catchment outflow was monitored using V-notch weirs and water-level recorders. Streamwater was collected weekly for chemical analysis using the procedures outlined in the Table 3. Total Al (Al_T), monomeric Al (Al_m) and organic monomeric Al (Al_o) fractions were determined in water. Particulate Al (Al_p) was calculated as $Al_T - Al_m$, and inorganic monomeric Al (Al_i) was calculated as $Al_m - Al_o$. Bulk precipitation and throughfall concentrations were multiplied by water quantities of individual samples to determine annual fluxes. Streamwater fluxes for individual solutes were computed using annual discharge-weighted average solute concentrations and annual water flux.

Soils were sampled at nine locations at Lysina and at four locations at Pluhův Bor. Soil masses were estimated by excavating five 0.5 m^2 pits by the method described in Huntington et al. (1988). This technique entailed collection of the Oi plus Oe (litter and fermented layers) horizons as a single sample, and then the Oa (humus) horizon. The mineral soils were then collected at ten centimeter intervals from the surface of the mineral soil until the C horizon was reached. All soils were weighed in the field. Subsamples were taken from each layer and from each visible horizon (E, A, B_1, B_2 and C) with adequate thickness. The samples were then air dried, weighed and passed through either a 5-mm sieve (organic soil) or a 2-mm sieve (mineral soil). Sand and silt were separated from clays by gravimetric sedimentation. Clays were removed by pipetting and centrifugation, repeated at least six times until the majority of clay particles were removed.

Soil analyses were conducted using air dried samples, and the results reported on an oven-dried basis (105 °C; Table 3). Cation exchange capacity (CEC) was computed as the sum of exchangeable Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+ and Al^{3+}. Base saturation was determined as the fraction of CEC associated with basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+). Soil organic matter content was estimated by loss-on-ignition. Element pools were computed using oven-dry soil mass (<5 mm for organic and <2 mm for mineral) and average element concentrations.

Table 3. Methods and reagents, used in the analysis of samples from Lysina and Pluhův Bor (soil analyses after Thomas 1982; spruce tissue analyses after Sherman & Fahey 1994; water analyses after Paukert 1993, Al fractions after McAvoy et al. 1992).

Analyte	Equipment	Reagent	Procedure
Soil analysis			
pH	Potentiometric, glass combination electrode	H_2O	
Total C	Elemental analyzer		Combustion (1020 °C)
Loss on ignition	Muffle furnace		Combustion (550 °C)
Exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}	Atomic absorption spectrophotometer	1 M NH_4Cl	Mechanical vacuum extractor
Exchangeable acidity, Al^{3+}, H^{+}	Titration (0.1 M NaOH, 1 M HCl)	1 M KCl	Mechanical vacuum extractor
Spruce tissue analysis			
Total C, N	Elemental analyzer		Combustion (1020 °C)
Total Ca, Mg, Na, K, Al, Ni	Inductively coupled plasma spectrometry	Conc. HNO_3 + 30% H_2O_2, then 10% HCl + 10% HNO_3	Combustion
Water analysis			
pH	Potentiometric, glass combination electrode		
Cl^{-}, SO_4^{2-}, NO_3^{-}	Ion exchange chromatography		
Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al_T, Si	Inductively coupled plasma spectrometry		
NH_4^{+}	Indophenol blue colorimetry		
ANC	Titration (0.1 M HCl with Gran plot analysis		
DOC	Ultraviolet-enhanced persulfate oxidation, CO_2 detection by spectrophotometry		
Al_m, Al_o	Pyrocatechol violet colorimetry		

Spruce tissue was obtained from four representative trees within each catchment in July 1994. Whole branches were collected from the upper, middle, and lower canopy. Twigs and foliage, bark and bole wood, and roots and soil rhizosphere were separated after air-drying. Samples were dried at 70 °C and ground. The samples for the ICP spectrometry were dry-ashed; the ash was dissolved in concentrated HNO_3 plus 30% H_2O_2 and then in 10% HCl plus 10% HNO_3.

Results

Soil properties

The overall thickness of the regolith was slightly greater at Lysina (1–5 m) than at Pluhův Bor (0.5–4 m) (Hylský 1960; Krám 1989). The mean depth of the upper mineral soil (to the C horizon) was somewhat greater at Pluhův Bor (0.7 m) than at Lysina (0.5 m) (Table 4). Mass of the forest floor was twice as large at Pluhův Bor than at Lysina (Table 5). The soils at Pluhův Bor had a higher content of clay and silt (clay: 0.4–1.8%, silt: 32–43%) than at Lysina (clay: 0.2–0.6%, silt: 24–33%). Also, the mass of clay and silt in the upper 40 cm of mineral soil were greater at Pluhův Bor (clay: 5 kg m^{-2}, silt 110 kg m^{-2}) than at Lysina (clay: 0.6 kg m^{-2}, silt 60 kg m^{-2}).

Soil organic matter (SOM) and total C concentrations in the mineral soil were distinctly different at the two sites (Tables 4 and 5). The soils at Lysina had typical patterns of SOM and C for podzolic soils (low concentrations of SOM and C in the albic (E) horizon, higher concentrations in the spodic B horizon, and lower concentrations in the C horizon). In contrast, the soil at Pluhův Bor exhibited a steady decline in SOM and C with increasing depth.

The serpentinite catchment exhibited a high base saturation (BS), increasing with depth, reaching essentially 100% in the C horizon (Table 4). In contrast, the granitic catchment showed low concentrations of exchangeable basic cations and BS decreased with depth. Soil pH was similar in the forest floor at the two sites, but values in the mineral soil followed the patterns in BS. Soil pH increased with depth to near-neutral values at Pluhův Bor, while pH remained extremely acidic throughout the profile at Lysina. Patterns in CEC at Lysina were consistent with the SOM and C content of the mineral soil. The BS of soils at Lysina decreased from 37% in the litter layer to <5% in the lower mineral soil. In contrast, Al saturation increased from 28% in the litter to 91% in the C horizon. Overall, Al occupied 78% of all exchange sites at Lysina, and the solum BS was only 7% (Table 5). The increase in CEC with depth in the mineral soil at Pluhův Bor contrasts with the pattern of decreasing SOM content, but is consistent with the increasing pH and clay content. The increase of BS with depth was largely attributable to Mg, as the Mg saturation increased from 25% in the Oi + Oe horizon to 57% in the Oa horizon, and then again from 68% in the A horizon to 96% in the C horizon

Table 4. Mean values of soil properties at the two study sites.

Horizon	Thickness	Concentration													
		Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3+}	H^+	CEC	Exch. acidity	Exch. bases	BS	SOM	Total C	Clay	pH_w
	cm	mmolc kg^{-1}									%	mass%			
Lysina															
Oi + Oe	2.8	45.8	8.6	1.1	10.3	48.8	62.8	177	112	65.8	37.4	81.1	42.9	ND	3.7
Oa	3.9	25.8	6.1	0.71	5.9	96.5	70.8	206	167	38.5	18.1	58.4	31.9	ND	3.5
E	16.7	1.1	0.32	0.18	0.94	27.8	9.7	40.0	37.5	2.5	6.6	2.9	1.4	0.55	3.9
B	31.9	2.4	0.48	0.21	1.2	82.7	12.5	99.5	95.2	4.3	4.1	7.6	3.6	0.19	4.0
C	ND	0.78	0.13	0.14	0.63	34.1	1.7	37.4	35.7	1.7	4.5	3.9	0.67	0.38	4.5
Pluhův Bor															
Oi + Oe	4.0	50.9	59.5	0.93	6.9	46.9	70.9	236	118	118	47.9	74.2	38.3	ND	3.8
Oa	2.1	38.1	198.0	1.1	7.6	45.0	55.9	346	101	245	48.6	55.6	29.8	ND	4.0
A	13.1	3.9	70.1	0.18	0.66	22.0	5.4	103	28.2	75	69.2	5.5	1.9	0.39	5.0
B	60.0	4.4	113.0	0.17	0.81	15.1	3.0	136	18.0	118	77.3	4.3	2.3	1.43	5.8
C	ND	5.2	157.0	0.22	1.2	0.62	0.0	163	0.62	162	99.6	3.3	0.21	1.79	6.7

ND – not determined
CEC – cation exchange capacity
BS – base saturation
SOM – soil organic matter
pH_w – soil pH in water

Table 5. Fine soil mass (<2 mm: mineral soil, <5 mm: organic soil), and pools of exchangeable cations, soil organic matter (SOM), total carbon, and clay at the study sites.

Horizon	Mass/area	Pools											
		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	H^{+}	CEC	Exch. acidity	Exch. bases	SOM	Total C	Clay
	kg m^{-2}	mmol$_C$ m^{-2}									kg m^{-2}		
Lysina													
Oi + Oe	2.3	105	19.8	2.5	23.6	112	144	410	257	150	1.9	1.0	ND
Oa	11.5	297	69.7	8.2	67.7	1110	814	2370	1920	440	6.7	3.7	ND
0–10 cm	62.2	114	25.5	72.4	83.0	2020	613	2920	2830	300	2.8	1.7	0.23
10–20 cm	52.4	76	17.0	60.8	61.5	2410	452	3080	2870	220	2.0	0.8	0.17
20–30 cm	52.1	96	19.4	63.7	63.8	2730	667	3640	3400	240	2.3	1.7	0.12
30–40 cm	55.8	85	14.3	67.9	58.8	3010	257	3490	3270	230	3.1	1.0	0.11
40–43 (to C)	26.2	57	8.7	46.3	34.7	1250	45	1440	1300	150	1.4	0.4	0.09
Forest floor	13.8	402	89.5	10.7	91.3	1220	958	2780	2180	590	8.6	4.7	ND
Mineral soil (0–40 cm)	223	370	76.2	265	267	10200	1990	13100	12200	980	10.1	5.2	0.63
Pluhův Bor													
Oi + Oe	3.1	158	184	2.9	21.3	145	220	730	365	370	2.3	1.2	ND
Oa	4.1	156	812	4.4	31.0	185	229	1420	414	1000	2.3	1.2	ND
0–10 cm	39.7	95	245	13.4	41.1	2870	0	3260	2870	390	3.2	1.4	0.42
10–20 cm	68.2	93	935	21.3	23.0	1950	77	3100	2030	1070	2.3	0.8	0.98
20–30 cm	88.5	298	3030	23.7	15.0	550	0	3910	550	3360	2.2	0.2	1.65
30–40 cm	84.3	413	4810	21.1	11.9	103	0	5360	103	5260	2.1	0.1	1.53
Forest floor	7.2	314	996	7.3	52.3	330	449	2150	779	1370	4.6	2.4	ND
Mineral soil (0–40 cm)	281	899	9020	79.5	91.0	5470	77	15600	5550	10100	9.8	2.6	4.58

ND – not determined
CEC – cation exchange capacity

(Table 4). Overall, exchangeable Mg accounted for 58% of CEC, and the solum BS was 65% (Table 5). The forest floor at Pluhův Bor contained more than ten times the exchangeable Mg than Lysina, even though the soil mass was about one-half that at Lysina. The mineral soil Mg pool at Pluhův Bor was 120 times larger than at Lysina.

Concentrations and pools of exchangeable Mg increased with increasing depth in the mineral soil with about 80% of the soil exchangeable Mg found below 20 cm at Pluhův Bor (Tables 4, 5). Concentrations and pools of the other exchangeable basic cations were considerably lower than Mg. Exchangeable Ca pools were low in the 0 to 20 cm layer of the mineral soil, relative to values in the forest floor and in the lower mineral soil. Pools of K were greatest in the upper mineral soil layer, and decreased slightly with increasing depth in the mineral soil. The pools of Na were low in the forest floor, and higher and uniform in the mineral soil at Pluhův Bor.

Exchangeable Ca was the principal basic cation associated with the soil exchange complex at Lysina (Table 4). More than half of the exchangeable Ca at Lysina was found in the forest floor (Table 5). Pools of exchangeable Mg were higher, while the exchangeable K and Na pools were lower, in the forest floor than in the upper mineral soil at Lysina.

Precipitation chemistry

Bulk precipitation to the study catchments contributed large inputs of NH_4^+, NO_3^-, H^+ and SO_4^{2-} (Table 6). Sodium and calcium were the major basic cations in precipitation inputs. Throughfall fluxes were greater than bulk precipitation inputs for all solutes except NH_4^+ at Lysina and except NH_4^+, NO_3^-, and Na^+ at Pluhův Bor. Throughfall flux was dominated by SO_4^{2-}, H^+, NO_3^-, and K^+ (Table 6). The very high throughfall fluxes of SO_4^{2-} reflect the high loading of atmospheric sulfur to the region.

Soil solutions

Major solutes in the soil water at Lysina were dissolved organic carbon (DOC), H^+, SO_4^{2-} and dissolved Si; at Pluhův Bor DOC, Mg^{2+}, SO_4^{2-} and dissolved Si were predominant (Table 7). At Lysina, acidic throughfall (pH 3.8) below the spruce canopy was further acidified by organic acids leached from the O horizon, resulting in a low pH (3.6) of soil water in the O and E horizons. Soil waters were strongly acidic and exhibited little temporal variation in pH values, ranging from 3.52 to 3.77 in the O horizon and from 3.42 to 3.75 in the E horizon. In contrast, the acidic throughfall (pH 3.9) at Pluhův Bor was neutralized by the upper soil as reflected in the increased soil solution pH in the O (4.6) and A horizons (5.4). Soil water pH at Pluhův Bor exhibited

Table 6. Annual volume-weighted ion concentrations and mass fluxes in bulk precipitation, throughfall and streamwater measured at the Lysina (LYS) and Pluhův Bor (PLB) catchments for the water year 1993 (Nov. 1992–Oct. 1993).

Parameter	Concentration (μmol L^{-1})					Fluxes (mmol m^{-2} yr^{-1})				
	LYS	LYS	PLB	LYS	PLB	LYS	LYS	PLB	LYS	PLB
	Bulk	Throughfall		Streamwater		Bulk	Throughfall		Streamwater	
Water (mm)						1016	699	583	406	221
pH	4.40	3.81	3.90	3.97	7.01					
H^+	39.8	156	127	107	0.15	40.0	109	74.0	44.8	0.0
Ca^{2+}	7.4	49.2	31.4	86.0	44.7	7.6	34.4	18.3	34.9	9.9
Mg^{2+}	2.2	14.6	28.9	28.3	687	2.2	10.2	16.9	11.5	152
Na^+	11.2	23.6	14.5	89.7	49.5	11.3	16.5	8.5	36.4	11.0
K^+	1.7	80.8	46.2	24.5	5.4	1.7	56.7	27.0	9.9	1.2
Al_T	1.9	6.7	4.6	53.3	6.6	1.9	4.7	2.7	21.7	1.5
NH_4^+	51.0	52.2	25.8	2.2	0.6	51.8	36.4	15.0	0.9	0.1
NO_3^-	42.3	85.2	49.2	32.6	36.2	43.0	59.3	28.7	13.2	8.0
SO_4^{2-}	31.7	171	130	211	444	32.2	119	75.7	85.5	98.2
Cl^-	12.2	41.0	29.0	39.0	66.5	12.4	28.5	16.9	15.8	14.7
ANC	ND	ND	ND	−128	438	ND	ND	ND	−52.1	97.0
DOC	ND	ND	ND	1360	1030	ND	ND	ND	552	228
H_4SiO_4	ND	3.2	2.6	224	324	ND	2.2	1.5	75.8	59.7

ND – not determined
ANC – acid neutralizing capacity
DOC – dissolved organic carbon

Table 7. Arithmetic average and standard deviation (in parentheses) of annual ion concentrations in soil solutions at the study sites for May 1994 to April 1995.

	Lysina O horizon	Pluhův Bor O horizon	Lysina E horizon	Pluhův Bor A horizon
Parameter	μmol L^{-1}			
pH (units)	3.62 (0.07)	4.70 (0.48)	3.55 (0.10)	5.38 (0.27)
H^+	240 (36)	32 (25)	290 (62)	4.9 (2.4)
Ca^{2+}	39 (10)	88 (71)	28 (7)	24 (7)
Mg^{2+}	9.1 (2.1)	690 (330)	8.2 (1.8)	700 (320)
Na^+	39 (9)	69 (24)	33 (7)	65 (22)
K^+	52 (39)	120 (130)	71 (9)	19 (15)
Al_T	33 (9)	45 (21)	18 (4)	25 (10)
NH_4^+	22 (21)	77 (77)	13 (8)	10 (18)
NO_3^-	71 (43)	95 (160)	110 (42)	90 (150)
SO_4^{2-}	150 (63)	600 (240)	160 (34)	580 (270)
Cl^-	48 (13)	150 (96)	43 (11)	130 (97)
ANC	−270 (99)	45 (79)	−340 (72)	85 (34)
DOC	2700 (1500)	7300 (5100)	1700 (670)	2900 (1400)
H_4SiO_4	140 (59)	260 (160)	110 (47)	270 (99)

greater temporal variability, ranging from 4.17 to 5.71 in the O horizon and 4.97 to 6.12 in the A horizon. Hydrogen ion was the dominant cation in soil water at Lysina, but contributed little to the cationic equivalence of soil water at Pluhův Bor. Sulfate was the major anion in soil water at both sites. There were no significant trends in SO_4^{2-} concentrations with depth in either site, but average concentrations of SO_4^{2-} were about four times higher at Pluhův Bor than at Lysina. Chloride concentrations showed little pattern with depth at both sites, and were about three times higher at Pluhův Bor. Values of acid neutralizing capacity (ANC) were highly negative in soil solutions at Lysina and generally positive at Pluhův Bor. Concentrations of DOC were high in forest floor leachate (especially at Pluhův Bor), but decreased markedly with depth in the mineral soil at both sites.

Magnesium, the dominant cation at Pluhův Bor, exhibited concentrations between 330 and 1500 μmol L^{-1} in O horizon solutions and between 300 and 1700 μmol L^{-1} in A horizon solutions. In contrast, concentrations of Mg^{2+} at Lysina were low (5-13.5 μmol L^{-1}). Concentrations of Mg^{2+} did not exhibit large differences between horizons at either site. Soil water concentrations of Ca^{2+} at Pluhův Bor decreased with depth, from a mean value of 88 μmol L^{-1} in the forest floor to 24 μmol L^{-1} in the upper mineral soil. At Lysina, Ca^{2+} also decreased with depth, but less dramatically than at Pluhův Bor. At Pluhův Bor, K^+ concentrations were high in O horizon (120 μmol L^{-1}), and decreased to low values in A horizon (19 μmol L^{-1}). Concentrations of K^+ in soil water at Lysina were relatively constant with depth. Sodium exhibited little variation with depth at either site.

Elevated concentrations of Al_T were observed in O horizon soil solutions, especially at Pluhův Bor. The particulate fraction Al_p was the dominant fraction of Al_T at Pluhův Bor (O horizon: Al_p 43%, Al_o 37%, Al_i 20%; A horizon: Al_p 59%, Al_o 29%, Al_i 12%). In contrast, lower Al_T concentrations were observed at Lysina, but Al_i was the dominant Al fraction (O horizon: Al_p 11%, Al_o 22%, Al_i 67%; E horizon: Al_p 6%, Al_o 32%, Al_i 62%). Concentrations of Si were high in the forest floor, especially at Pluhův Bor, and remained elevated in the upper mineral soil.

Streamwater patterns

Different weathering reactions (Krám & Hruška 1994) in the granite and serpentinite catchments were strongly reflected in the composition of the runoff waters (Table 6). Streamwater draining the Lysina catchment was relatively dilute, showing low concentrations of basic cations (Ca^{2+} 86 μmol L^{-1}; Mg^{2+} 28 μmol L^{-1}; Na^+ 90 μmol L^{-1}; K^+ 25 μmol L^{-1}). In contrast, streamwater at Pluhův Bor showed higher ionic strength, largely due to elevated concentrations of Mg^{2+} (Ca^{2+} 45 μmol L^{-1}; Mg^{2+} 690 μmol L^{-1}; Na^+ 50 μmol L^{-1}; K^+ 5.4 μmol L^{-1}). Indeed, with the exception of Mg^{2+}, concentrations of basic cations were higher at Lysina than at Pluhův Bor. Weathering of feldspars in the granitic catchment resulted in drainage water with relatively high proportions of dissolved Si, Na^+ and Ca^{2+}. At the serpentinite site, however, the relatively high weathering rate of antigorite contributed to the high concentrations of Mg^{2+} and Si, and low Na^+, Ca^{2+} and Al_T.

Sulfate was the dominant anion in streamwater at both sites (Table 6). Bicarbonate (HCO_3^-) was the second most important anion in drainage water at Pluhův Bor (see ANC), but was negligible at Lysina. At Lysina, stream pH varied between 3.8 and 4.4 and the ANC varied between -180 and -40 μmol L^{-1} in the 1993 water year. Streamwater at Lysina was characterized by unusually high concentrations of Al_T (21–81 μmol L^{-1}). In contrast, stream pH varied between 6.1 and 8.1, and ANC between 100 and 2400 μmol L^{-1} in the serpentinite catchment, and concentrations of Al_T were low (1–11 μmol L^{-1}). Dissolved organic C was a major solute at both sites. Organic anions (estimated by discrepancy in charge balance) comprised about 19% of total anionic charge at Lysina, and 7% at Pluhův Bor.

Temporal patterns in concentrations of basic cations occurred with variations in stream flow (Figure 2). Stream discharge was usually low at both sites during the summer, and increased during the late fall and spring. At the granitic site, concentrations of Na^+ decreased markedly with increasing stream flow (Na^+ (μmol L^{-1}) = -38*log [discharge (L s^{-1})] + 125, r^2 = 0.81). Concentrations of Ca^{2+} and Mg^{2+} showed a similar trend, but the relationships were not statistically significant (r^2 = 0.24 and 0.14 respectively). Concentrations of K^+ showed relatively steady concentrations over time, with no relationship with discharge. There was also no correlation between SO_4^{2-} and discharge at Lysina.

At Pluhův Bor, all basic cations and ANC showed a pattern of dilution with increases in discharge (Ca^{2+} (μmol L^{-1}) = -62*log [discharge (L s^{-1})] + 75, r^2 = 0.73; Mg^{2+} (μmol L^{-1}) = -200*log [discharge (L s^{-1})] + 832, r^2 = 0.67; Na^+ (μmol L^{-1}) = -15*log [discharge (L s^{-1})] + 58, r^2 = 0.45; K^+ (μmol L^{-1}) = -9.3*log [discharge (L s^{-1})] + 8.4, r^2 = 0.57); ANC (μmol L^{-1}) = -811*log [discharge (L s^{-1})] + 888, r^2 = 0.85). Sulfate concentrations at Pluhův Bor increased with increasing discharge (SO_4^{2-} (μmol L^{-1}) = 106*log [dicharge (L s^{-1})] + 427, r^2 = 0.75).

Over the study period (1990–93 water years at Lysina and 1992–93 water years at Pluhův Bor), there were marked decreases in the concentration of SO_4^{2-} in streamwater. At Lysina, concentrations of Ca^{2+} and Mg^{2+} were positively correlated with SO_4^{2-} (Ca^{2+}(μmol L^{-1}) = 0.36*SO_4^{2-}(μmol L^{-1}) + 26, r^2 = 0.72, n = 185; Mg^{2+} (μmol L^{-1}) = 0.11*SO_4^{2-} (μmol L^{-1}) +9.6, r^2 = 0.47, n = 185). No relationships were evident with Na^+ or K^+ and SO_4^{2-}. In contrast, at Pluhův Bor, concentrations of basic cations all showed strong (r^2 > 0.5, n = 76) inverse relationships with stream $SO_4^{2-}$and a strong positive correlation with ANC for Ca^{2+}, Mg^{2+} and K^+ ($r^2 > 0.6$, n = 76).

Tree tissue chemistry

Among the basic cations, Ca exhibited the highest concentrations in tree tissue at both sites (Table 8). The highest Ca concentrations were found in the bole bark at both sites. At Pluhův Bor, foliage and roots in mineral soil also had relatively high Ca concentrations. Concentrations of Mg in spruce tissues at Lysina were low. Foliar concentrations of Mg were extremely low, even lower than Mg concentrations in bark and branches. In contrast, the Mg concentrations in foliage, bark, branches and roots of the mineral soil were very high at Pluhův Bor. Concentrations of K were higher in all vegetation tissues at Lysina than at Pluhův Bor. At both sites, the highest K concentrations were found in the foliage. Concentrations of Na were very low in tree tissues at both sites. With the exception of bole wood, the Na concentrations were similar or slightly higher at Lysina. Aluminum concentrations were elevated in fine roots from the upper mineral soil at Lysina. Very high concentrations of Ni were observed in spruce tissues at Pluhův Bor, Ni was especially concentrated in the bole bark.

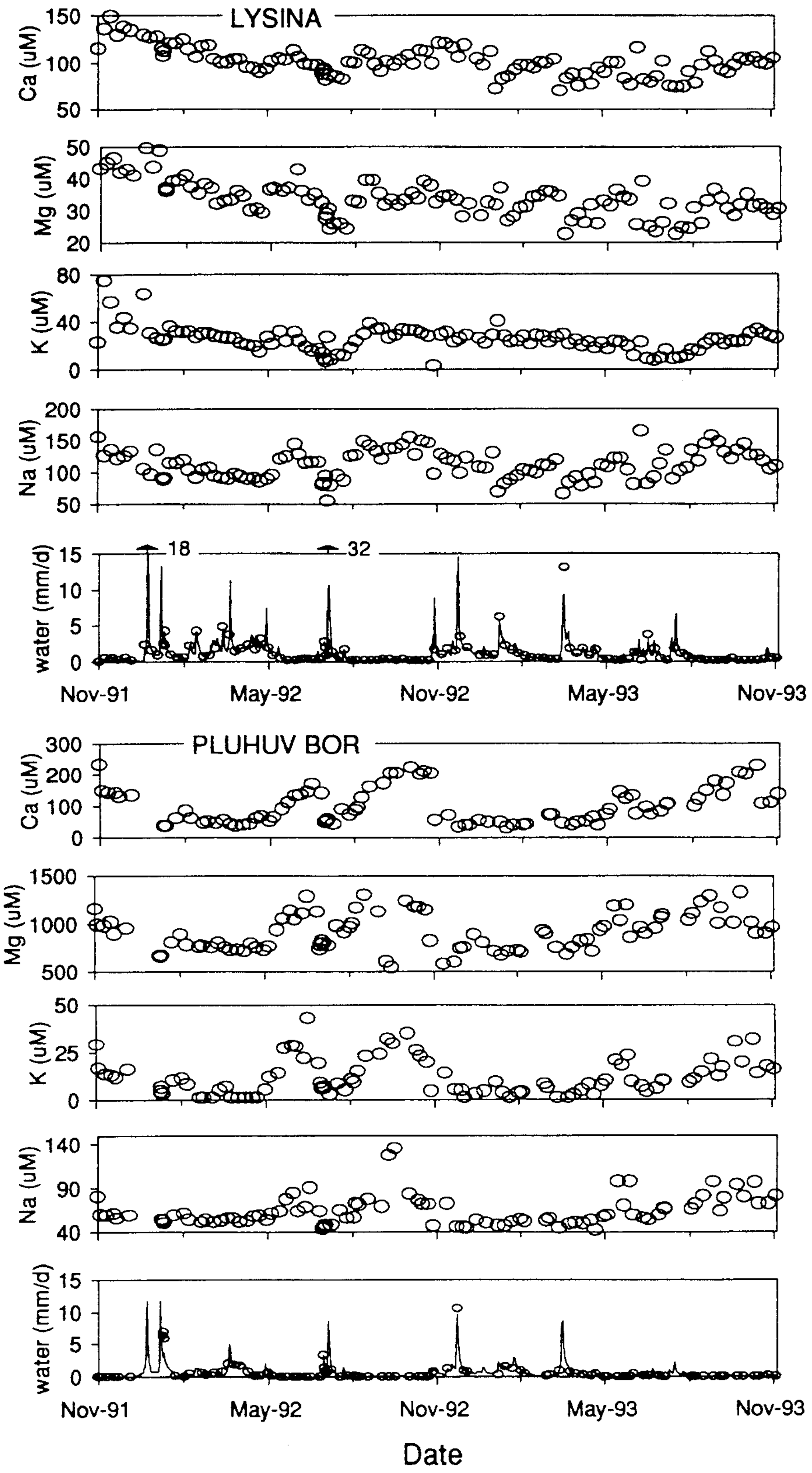

Figure 2. Temporal patterns in streamwater concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ (μmol L^{-1}), mean daily runoff (curve) and instantaneous runoff at the time of sampling (circle or arrow) (mm day^{-1}) at Lysina and Pluhův Bor in 1992–1993 water years.

Table 8. Mean total element concentration of Norway spruce tissues at Lysina and Pluhův Bor.

Spruce tissue	Ca	Mg	Na	K	Al	Ni	N	C
	mmol kg^{-1}							mass %
Lysina								
Foliage	70	13	1.2	141	2.1	0.03	960	49
Branches and twigs	87	20	2.5	81	8.0	0.05	360	43
Bole bark	180	29	0.9	84	3.7	0.06	480	48
Bole wood	16	4	0.1	4	0.33	0.007	100	49
Cones	4	6	1.2	40	1.8	0.03	420	51
Coarse roots (organic horizon)	41	7	0.8	19	1.8	0.01	530	57
Fine roots (organic horizon)	80	19	1.7	61	17	0.03	420	51
Medium roots (mineral horizon)	54	14	2.3	41	33	0.02	380	48
Fine roots (mineral horizon)	33	9	2.7	27	90	0.03	620	58
Pluhův Bor								
Foliage	160	110	1.2	84	2.5	0.20	860	48
Branches and twigs	92	41	0.7	46	5.4	0.17	640	56
Bole bark	210	62	0.4	51	2.2	0.34	360	49
Bole wood	13	8	0.4	3	0.35	0.012	93	48
Cones	5	16	1.0	28	1.8	0.19	390	52
Coarse roots (organic horizon)	36	14	0.9	13	2.6	0.05	380	45
Fine roots (organic horizon)	100	26	1.2	40	8	0.13	450	51
Medium + fine roots (min. hor.)	150	34	1.1	25	16	0.22	410	42

Discussion

Element cycling

Bulk precipitation is often an underestimate of total atmospheric deposition to forests in polluted areas. In areas of high S deposition the "net throughfall" of S (throughfall flux minus bulk precipitation flux) approximately equals the dry deposition of S to the forest ecosystems (Mayer & Ulrich 1974; Hultberg 1985; Lindberg & Garten 1988). Unfortunately, for other elements there is no reliable method to differentiate the plant-derived component of throughfall from the atmospheric component (Parker 1990). Moreover, some particulate deposition does not represent a true input to the ecosystem (e.g., local soil dust, plant debris and pollen; Likens et al. 1994). In Norway spruce ecosystems, investigators have reported both increases and decreases in throughfall pH values relative to bulk deposition (Farrell et al. 1994).

There is considerable uncertainty in the use of bulk precipitation and throughfall fluxes to estimate atmospheric inputs of basic cations. Throughfall fluxes of Ca, Mg, and K generally increase with the nutritional status of soils, thus reflecting the internal cycling and leaching from foliage. However, nutrient enrichment in throughfall, relative to bulk precipitation also reflects dry deposition to the forest ecosystem. For example, in a Norway spruce stand at Solling, Germany, about 70% of Ca throughfall flux was attributed to external sources (Matzner & Meiwes 1994). The enrichment of throughfall by internal cycling is especially characteristic of K^+ (Figure 3). The mean enrichment ratio of K^+ (the ratio of throughfall flux to bulk precipitation) for numerous forests throughout the world is approximately 13, compared to values of 4.0, 2.8 and 2.4 for Mg^{2+}, Ca^{2+}, and Na^+, respectively (Parker 1990). In our study, higher enrichment ratios for Ca^{2+} (4.5) and Na^+ (1.5) at Lysina compared to Pluhův Bor (Ca^{2+}: 2.4, Na^+: 0.8) (Table 6) were not consistent with the differences in Ca and Na concentrations in foliage (Table 8). Thus, it appears that throughfall enrichment of these elements is largely due to external sources. Marked differences in enrichment ratios for Mg^{2+} and K^+ were also evident between the two sites (Table 6, Figure 3). The enrichment ratio of K^+ was greater at Lysina (33) than at Pluhův Bor (16), while the ratio for Mg^{2+} was lower at Lysina (4.6) than at Pluhův Bor (7.7). These patterns were consistent with observed differences in foliage concentrations, suggesting that canopy leaching is a more important contributor to net throughfall for Mg^{2+} and K^+ than for Ca^{2+} and Na^+.

The net output of basic cations was estimated as the difference between element output via steamwater and element input via bulk precipitation (Table 6, Figure 3). Thus the input values do not consider the portion of dry deposition input of basic cations to the catchments not collected in bulk collectors. The net output from the catchments represents the net loss of cations by drainage water but does not consider the net accumulation of basic cations by forest vegetation. Thus, the net output values reflect only the balance between base cation production (via weathering, net cation exchange, and mineralization from SOM) and input by wet deposition and a portion of dry deposition collected in bulk precipitation. Basic cations, dissolved Si, and Al_T showed net production in the Lysina catchment. At Pluhův Bor, stream outputs of Mg^{2+} and dissolved Si were much higher than atmospheric inputs. Outputs of other basic cations (Ca^{2+}, Na^+, K^+) and Al_T at Pluhův Bor were similar to bulk precipitation inputs. The net output of Ca^{2+} was 27 mmol m^{-2} yr^{-1}, Mg^{2+} was 9.3 mmol m^{-2} yr^{-1}, Na^+ was 25 mmol m^{-2} yr^{-1}, K^+ was 8.2 mmol m^{-2} yr^{-1} at Lysina. At Pluhův Bor, the net output of Ca^{2+} was 2.3 mmol m^{-2} yr^{-1}, Mg^{2+} was 150 mmol m^{-2} yr^{-1}, Na^+ was -0.3 mmol m^{-2} yr^{-1}, K^+ was -0.5 mmol m^{-2} yr^{-1}. The total net output of basic cations for the Lysina catchment (106 $mmol_c$ m^{-2} yr^{-1}) was lower than the rate for Pluhův Bor (304 $mmol_c$ m^{-2} yr^{-1}) due to the lower weatherability of soil

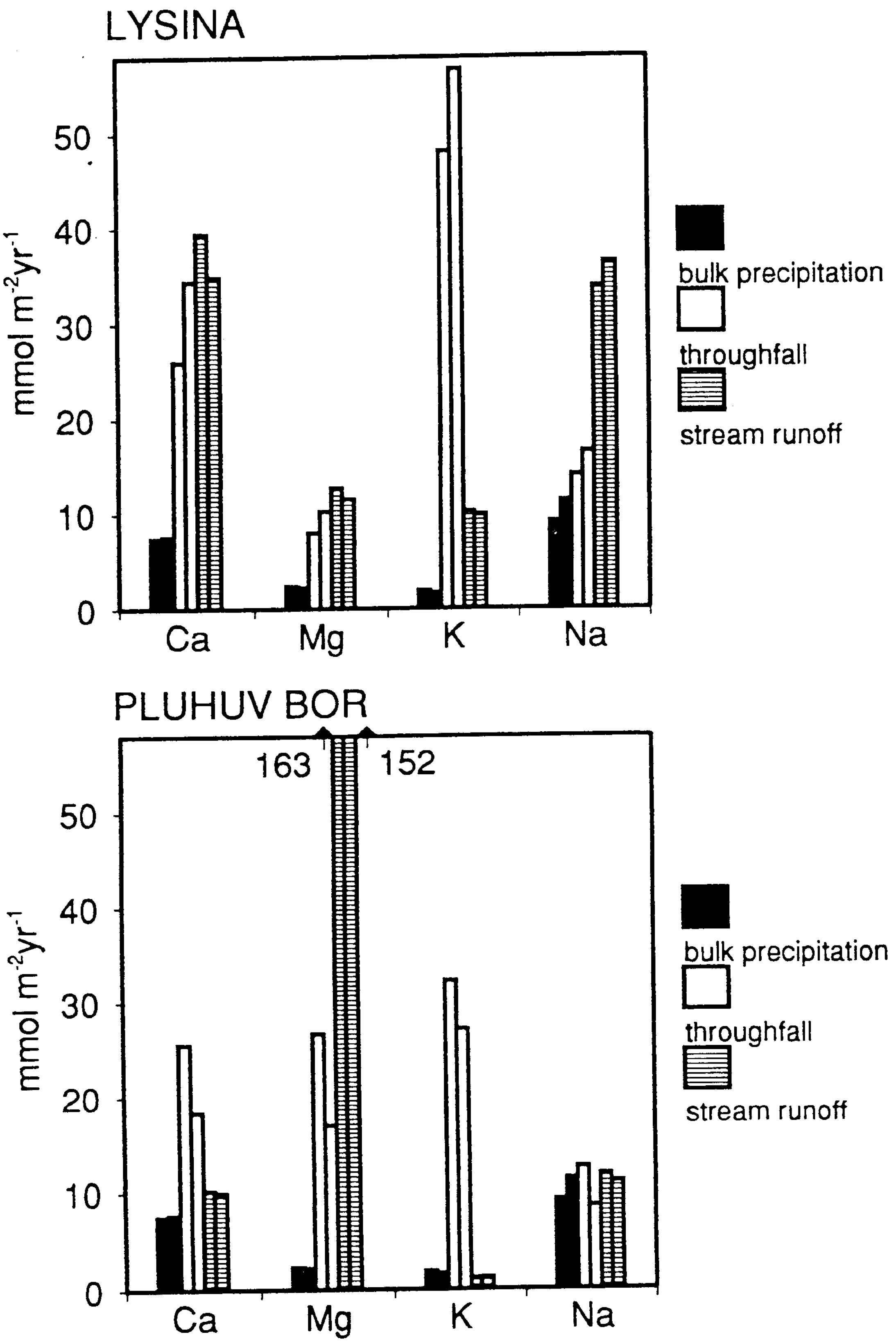

Figure 3. Annual fluxes of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} in 1992 (left columns; Krám & Hruška 1994) and 1993 (right columns) water years (November 1–October 31) in bulk precipitation, throughfall and streamwater at Lysina and Pluhův Bor.

minerals derived from granite. Cleaves et al. (1974) reported a similar value for net total cation supply at a serpentinite catchment in a less-polluted area (281 $\text{mmol}_c\ \text{m}^{-2}\ \text{yr}^{-1}$; Soldiers Delight, Maryland, USA).

Total deposition of S at Lysina (93 $\text{mmol m}^{-2}\ \text{yr}^{-1}$) and at Pluhův Bor (73 $\text{mmol m}^{-2}\ \text{yr}^{-1}$) was calculated according to the proportion of forested and open area of the catchment (Table 1) using throughfall and bulk precipitation fluxes (Table 6). Total input of SO_4^{2-} was similar to stream outflow of SO_4^{2-} at Lysina, suggesting that transport of SO_4^{2-} was approximately conservative (Table 6). Sulfur output was about one third higher than the input at Pluhův Bor suggesting export of previously stored S in the soil.

Soil processes

Strong relationships were evident between CEC and SOM for the Oa horizons of both sites (Lysina CEC ($\text{mmol}_c\ \text{kg}^{-1}$) = 0.18*SOM(%) + 11.39, $r^2 = 0.55$; Pluhův Bor CEC ($\text{mmol}_c\ \text{kg}^{-1}$) = 0.74*SOM(%) − 6.73, $r^2 = 0.53$), which is indicative of the role of SOM in regulating CEC. The mineral soil at Lysina showed a strong relationship between CEC and SOM (CEC ($\text{mmol}_c\ \text{kg}^{-1}$) = 0.75*SOM(%) + 0.09, $r^2 = 0.76$). In contrast, the mineral soil at Pluhův Bor did not exhibit a significant relationship between CEC and SOM. This pattern may be due to: (1) greater contribution of clays to CEC at lower depths; (2) higher pH at lower depth, resulting in greater CEC of SOM and clay.

Soil chemical properties at the study sites clearly reflect the differences in lithology. Bedrock at Pluhův Bor contains approximately 35 times the Mg as the Lysina granite (Table 2). The exchangeable Mg pool in Pluhův Bor soils was 60 times the pool at Lysina, and exchangeable Mg concentrations were up to 1000 times greater (Tables 4, 5). In contrast, soil exchangeable K pools and concentrations were greater at Lysina, where the bedrock had a higher K content, than at Pluhův Bor. Interestingly, exchangeable concentrations and pools of Ca were greater at Pluhův Bor, despite the fact that Ca exists in only trace amounts in the bedrock. This may be due to retention of atmospherically-derived Ca within the soils at Pluhův Bor and differences in soil pH. In the acidic soils at Lysina, there is an abundance of Al. Since Al competes effectively with Ca for exchange sites, levels of exchangeable Ca were low. At Pluhův Bor, elevated soil pH limits Al concentrations in drainage waters. Thus, inputs of Ca may be retained in larger quantities at Pluhův Bor, despite the fact that there is little in bedrock.

Organic matter decomposition in the forest floor and immobilization of DOC in the upper mineral soil were evident from soil solution patterns in DOC (Table 7). Differences in DOC concentrations between the study catchments were possibly related to differences in microbial activity, which may be influenced by composition of microorganisms, nutrient content in litter, pH, and microclimate. There was an apparent decline in Ca^{2+} and K^+ soil solution concentration with depth at Pluhův Bor possibly reflecting uptake by forest vegetation. Dissolution of mineral soil pools of Ca and K was probably a minor input of these cations at Pluhův Bor since concentrations in parent material are very low. Surprisingly no pattern in soil solution concentrations of Mg^{2+} were observed with depth at either site. Absence of a trend of Na^+ with soil depth reflected its low importance in nutrient cycling.

Elevated Al concentrations in forest floor leachate could be the result of dissolution of minerals by naturally-occurring organic acids generated in the forest floor. Aluminum-bearing minerals occur in the forest floor because of physical processes as tree wind throw, frost heave, and upward movement of water (Lawrence et al. 1995; Geary & Driscoll 1996), bioturbation (burrowing), and vegetative cycling from the mineral soil (Lawrence et al. 1995; LaZerte & Scott 1996). Dissolution of Al in deeper mineral soil resulted in mean Al_T concentration of 120 μmol L^{-1} at 80 cm depth at Lysina (Krám et al. 1995). Soil solution Ca/Al_i molar ratios at Lysina were near the critical value of 1.0 reported for trees (Cronan & Grigal 1995) (O horizon: range 0.98–4.1, mean 2.1, median 1.5; E horizon: range 1.5–4.0, mean 2.6, median 2.5). The soil water at Lysina may already be toxic, because the critical value of the Ca/Al_i ratio for Norway spruce may be as high as 1.8 (Cronan & Grigal 1995); 36% of the soil water samples at Lysina had Ca/Al_i ratios below 1.8. The forest floor was the primary rooting layer at Lysina even though its Ca/Al_i ratio was often below critical value of 1.8 for Norway spruce because of its high concentration of nutrients (Table 4). In contrast, Pluhův Bor tended to have higher Ca/Al_i ratios in both horizons, with very few values below 3.0 (O hor.: 2.8–26.7, A hor. 4.5–35.4) and a relatively deep rooting layer, extending into the mineral soil. Sverdrup et al. (1994) proposed a critical value of 1.2 for the molar ratio $(Ca + Mg + K)/Al_i$. Soil waters were well above this critical value for this ratio (Lysina: O horizon: 3.2–6.6, E horizon 5.7–16.9; Pluhův Bor: O horizon 54–177, A horizon 144–665).

Tree nutrition

Values of the elemental composition of spruce tissues may be compared to results from the Fichtelgebirge in Germany, about 70 km west of the Slavkov Forest. The Mg content of needles of Norway spruce at Lysina (Table 8) was similar to sites exhibiting decline at Oberwarmensteinach (13 mmol kg^{-}), and lower than healthy sites at Wülfersreuth (33 mmol kg^{-1}) of the Fichtelgebirge (Schulze et al. 1989). These results reflect all age classes of needles composited and collected during the same month (July) in both mountains. The Ca content in foliage at Lysina was about 70% of values in Fichtelgebirge stands showing decline (100 mmol kg^{-1}) and only about

35% of the values reported for healthy trees. The N content of foliage at Lysina (960 mmol kg^{-1}) was slightly higher than values for both healthy and declining sites (800 mmol kg^{-1}) of Fichtelgebirge. The Al content in needles (needle age 0-4 years) at Fichtelgebirge was higher (2.5–8 mmol kg^{-1}) than in composite needle samples at Lysina (2.1 mmol kg^{-1}).

The composition of foliage and soil at Pluhův Bor were similar to values reported by Kaupenjohann & Wilcke (1995) at a serpentinite site at Zell in the Fichtelgebirge, Germany. The foliar content (current needles) were slightly lower for Mg (74 mmol kg^{-1}) and slightly higher for Ni (0.27 mmol kg^{-1}) for a 120-year old Norway spruce stand at Zell than at Pluhův Bor.

Foliar concentrations of basic cations and N at Lysina and Pluhův Bor are compared with deficiency and optimum concentrations and ratios proposed by several authors in Table 9. Magnesium in foliage was clearly deficient (40–50% of the critical values) at Lysina and K in foliage appeared to be deficient (70–85% of the critical values) at Pluhův Bor. In contrast, foliar Ca was in the upper optimum range and foliar Mg exceeded upper optimum by 90% at Pluhův Bor (Table 8).

The visible symptoms of needle-yellowing in the Fichtelgebirge spruce forests have been attributed to Mg deficiences caused by nutritional imbalances associated with elevated inputs of N from atmospheric deposition (Schulze et al. 1989). The similarities observed for the composition of needles at Lysina and Fichtelgebirge, and the root Al content suggest that the Al-induced base cation deficiency postulated for the Fichtelgebirge may be relevant at Lysina as well. There is not yet evidence of widespread decline of the relatively young and vigorous spruce forest at Lysina. However, the symptoms of yellowing of older needles and canopy thinning of old spruce stands may be linked with the unusually low Mg content of foliage and high Al content in soil solutions, and fine roots. The spruce forest at Lysina showed typical symptoms of decline by needle yellowing attributed to Mg deficiency (Moravčík 1995). Foliar chlorosis can be attributed to excessive removal of Mg from older needles to supply new needles. The chlorosis of foliage at Lysina might be characterized as "Type 1 Norway spruce decline" which is caused by Mg deficiency and possibly Ca and Zn deficiency (Innes 1993).

The forest at Pluhův Bor showed no visible symptoms of decline (e.g. apparent discoloration). Nevertheless, the annual increment of wood bole biomass of spruce was unusually low at Pluhův Bor, only about 35% of the increment observed at Lysina when comparing individual trees in approximately 120 year old stands. Foliar reddening of Norway spruce was found at some low elevation sites on Cambisols (brown forest soils) with high Mg and neutral pH in Germany. This nutrient imbalance, called "Type 3 Norway spruce decline", may be attributed to K deficiency (Innes 1993). Despite of the

Table 9. Range of foliage deficiency and optimum concentrations for Norway spruce in comparison with measured values (arithmetic average and standard deviation) at Lysina (n = 12) and Pluhův Bor (n = 12).

Element	Deficiency concentration[†,‡] (mass%)	**Deficiency concentration (mmol kg^{-1})**	Optimum concentration[§,‡] (mass%)	**Optimum concentration (mmol kg^{-1})**	**Concentration at Lysina (mmol kg^{-1})**	**Concentration at Pluhův Bor (mmol kg^{-1})**
N	<1–1.3	<710–930	1.7–2.4	1200–1700	960 (200)	860 (87)
K	<0.4–0.45	<100–120	0.5–1.3	130–330	141 (27)	84 (4)
Ca	<0.1–0.2	<25–50	0.03–0.68	8–170	70 (32)	160 (31)
Mg	<0.06–0.08	<25–33	0.07–0.14	29–58	13 (6)	110 (18)
N:K			1–3	3–8	7	10
N:Ca			2–7	5.7–20	14	5.4
N:Mg			8–30	14–52	74	8

[†] after Zech et al. 1985
[‡] after Zoettl et al. 1989
[§] after Innes 1993

low K concentrations only 3–4% of spruce needles at Pluhův Bor exhibited browning. Thus, Moravčík (1995) attributed this discoloration only to natural senescence of older needles. Magnesium and trace metal toxicity have been noted on serpentinite sites; high Mg saturation of the exchange complex can limit the availability of other nutrient cations, such as Ca and K (Roberts & Proctor 1992). However, the availability of Ca did not appear to be inhibited at Pluhův Bor (Table 9). Foliar concentration of Ni (0.2 mmol kg^{-1}) was about twice the critical level which could have a detrimental effect on spruce growth at Pluhův Bor (Innes 1993).

Depletion of basic cations

Elevated inputs of acidic deposition may facilitate the depletion of basic cations from forest soils, resulting in soil acidification and potentially altering the function of forest ecosystems. If inputs of strong acids, on an equivalence basis, exceed the rate of supply of basic cations through weathering, depletion of exchangeable cations may occur. If strong acid inputs exceed both weathering release and net exchange of basic cations, increases in the concentrations of H^+ and/or Al_T in drainage water will result. Assimilation of Ca, Mg and K by forest vegetation, which may be enhanced by from elevated inputs of atmospheric N, can also deplete soil pools of exchangeable basic cations on sites with slow weathering rates (Binkley & Richter 1987). There is evidence of depletion of available pools of basic cations from soil in regions impacted by acidic deposition. Bailey et al. (1996) concluded that about two-thirds of the net export of Ca at the Cone Pond watershed in New Hampshire, USA, was due to depletion of labile Ca pools. Likens et al. (1996) suggested that similar depletion of basic cations occurred at nearby Hubbard Brook.

Our observations of a strong positive relationship between concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} in streamwater at Lysina are suggestive of depletion of basic cations from the soil exchange complex due to SO_4^{2-} leaching. By 1993, soils in the Lysina catchment showed very low concentrations and pools of exchangeable basic cations. Thus, continued high inputs of H^+ and SO_4^{2-} from atmospheric deposition, coupled with a slow rate of basic cation supply from weathering, has resulted in highly acidic soil water and the mobilization of available soil Al. Indeed, Al concentrations in streamwater at Lysina are among the highest values reported in the literature (Hornung et al. 1990; Hruška & Krám 1994a, b; Driscoll & Postek 1995). Podzolization processes and vegetation uptake of nutrients undoubtedly also influence the leaching of basic cations from the soil at Lysina. Because the BS is very low in the mineral soil and sites of the soil exchanger are largely occupied by Al, there is little potential for further depletion. Recovery of exchangeable basic cation pools is likely to be slow because weathering release at Lysina is very slow, and basic cations compete poorly for exchange sites with Al, which currently occupies 78% of the available exchange sites.

In contrast to Lysina, Pluhův Bor soils showed large concentrations and pools of exchangeable Mg due to the weathering of the serpentinite. The BS of the mineral soil was high and soil pH was near neutral. This pool of exchangeable Mg provides a large buffer capacity against inputs of strong acids. Stream concentrations of basic cations at Pluhův Bor showed marked temporal variations associated with changes in discharge, but no dependence on concentrations of sulfate. The pattern of dilution of basic cations with increasing discharge suggests that temporal changes in hydrologic flowpaths are important in regulating changes in concentrations of basic cations. Under low-flow conditions, drainage water is largely derived from deeper flowpaths and basic cations are supplied from weatherable minerals. Under higher flow conditions, streamwater is increasingly derived from shallow flowpaths and has less contact with weatherable minerals. The inverse relationship between concentrations of Mg^{2+} and other basic cations and SO_4^{2-} is consistent with this change in hydrologic flowpaths. As concentrations of basic cations are not coupled with SO_4^{2-}, it seems likely that the geochemistry of Pluhův Bor has not been severely impacted by acidic deposition, despite the elevated inputs. In all streamwater samples, the Mg^{2+} concentration was higher than SO_4^{2-}. Only under the highest-flow conditions, when SO_4^{2-} concentrations were at a maximum, were the concentrations of Mg^{2+} and SO_4^{2-} nearly equal. Therefore, strong acid weathering of antigorite can not entirely explain the Mg losses. These patterns suggest that the dominant geochemical reaction in Pluhův Bor soils is bicarbonate weathering of antigorite. Thus, we hypothesize that changes in acidic deposition may affect the level of solute concentrations at Pluhův Bor, but should have little effect on stream pH and ANC.

Conclusions

The major conclusions of this comparative study are as follows:

1. Different effects of acidic atmospheric deposition can clearly be seen at the two contrasting catchments. The similar inputs of acidic deposition coincided with very different patterns in the biogeochemistry of basic cations at the sites.
2. Soils developed in the slow weathering granite catchment showed small pools of exchangeable basic cations, and low soil, soil solution, and stream pH. Weathering and exchange processes at Lysina were unable to neutralize the high inputs of atmospheric acidity, resulting in elevated

stream H^+ and Al_T concentrations. Visible symptoms of forest decline by needle yellowing was probably caused by Mg deficiency at Lysina.

3. The Pluhův Bor catchment, underlain with the faster weathering serpentinite, showed extremely large pools of exchangeable Mg but smaller pools of other basic cations. Exchangeable concentrations and pools of soil Ca were larger at Pluhův Bor, despite the fact that Ca was found only in trace amounts in the serpentinite. Interestingly, foliar Ca was in the upper optimum range in Norway spruce. Much of the Ca is probably returned to the soil via canopy leaching and litterfall. Slow tree growth appears to be caused by K deficiency, Mg oversupply and/or Ni toxicity at Pluhův Bor.

Acknowledgements

Support for this research was provided by the Czech Geol. Survey, the Grant Agency of the Czech Rep., an IBM Corp. Environmental Research Program Award, the Nat. Science Foundation, and Syracuse University. We are indebted to T. Pačes, J. Černý, D. Fottová, and B. Moldan for their support. We appreciate the technical help of Z. Dedek, V. Kmínek, J. Tůma, F. Veselovský, S. Petřík, P. Baresh, M. Aloi, A. Tanguay, R. Romanowicz, J. Ruiz, R. Womble, R. Geary, D. Long, and T. Fahey. Most of the water analyses were done by P. Pokorný, H. Vitková, L. Dempírová, and P. Foch. We thank four anonymous reviewers for helpful suggestions.

References

Anonymous (1993) Environmental Year-Book 1992 (In Czech). Ministry of Environment of the Czech Republic, Prague

Bailey SW, Hornbeck JW, Driscoll CT & Gaudette HE (1996) Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. Water Resour. Res. 32: 707–719

Baker JP & Schofield CL (1982) Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut. 18: 289–309

Binkley D & Richter D (1987) Nutrient cycles and H^+ budgets of forest ecosystems. Adv. in Ecol. Research 16: 1–51

Černý J (1993) Atmospheric deposition in the Krušné hory Mts. Preliminary results of throughfall measurements. Acta Universitatis Carolinae Geologica, Prague 37: 29–44

Chadwick MJ, Kuylenstierna JCI & Gough CA (1991) The Stockholm Environmental Institute map of relative sensitivity to acidic deposition in Europe. In: Hetteligh J-P, Downing RJ & de Smet PAM (Eds) Mapping Critical Loads for Europe (pp 49–57). CCE Tech. Rep. 1, Nat. Inst. of Public Health and Environ. Protection, Bilthoven, Netherlands

Cleaves ET, Fisher DW & Bricker OP (1974) Chemical weathering of serpentinite in the Eastern Piedmont of Maryland. Geol. Soc. Am. Bull. 85: 437–444

Creasey J, Edwards AC, Reid JM, MacLeod DA & Cresser MS (1986) The use of catchment studies for assessing chemical weathering rates in two contrasting upland areas in northeast

Scotland. In: Colman SM & Dethier DP (Eds) Rates of Chemical Weathering of Rocks and Minerals (pp 468–502). Academic Press, London

Cronan CS & Grigal DF (1995) Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. J. Environ. Qual. 24: 209–226

Driscoll CT, Fuller RD & Simone DM (1988) Longitudinal variations in trace metal concentrations in a northern forested ecosystem. J. Environ. Qual. 17: 101–107

Driscoll CT & Postek KM (1995) The chemistry of aluminum in surface waters. In: Sposito G (Ed) The Environmental Chemistry of Aluminum, 2nd Edition (pp 363–418). CRC Press, Lewis Publishers, Boca Raton, Florida

Fanta J (1994) Forest ecosystem development on degraded and reclaimed sites. Ecol. Eng. 3: 1–3

Farrell EP, Cummins T, Collins JF, Beier C, Blanck K, Bredemeier M, de Visser PHB, Kreutzer K, Rasmussen L, Rothe A & Steinberg N (1994) A comparison of sites in the EXMAN project, with respect to atmospheric deposition and the chemical composition of the soil solution and foliage. Forest Ecol. and Manage. 68: 3–14

Federer CA, Hornbeck JW, Tritton LM, Martin CW, Pierce RS & Smith CT (1989) Long-term depletion of calcium and other nutrients in eastern U.S. forests. Envir. Manage. 13: 593–601

Fiala F (Ed) (1961) Final Report on Geologic Investigations of the Císařský (Slavkov) Forest in 1955–1960 (In Czech). Res. Report. Czech Geological Survey, Prague

Gasser UG & Dahlgren RA (1994) Solid-phase speciation and surface association of metals in serpentinitic soils. Soil Sci. 158: 409–420

Gasser UG, Juchler SJ & Sticher H (1994) Chemistry and speciation of soil water from serpentinitic soils: Importance of colloids in the trasport of Cr, Fe, Mg, and Ni. Soil Sci. 158: 314–322

Geary, RJ & Driscoll CT (1996) Forest soil solutions: Acid/base chemistry and response to calcite treatment. Biogeochem. 32: 53–78

Hornung M, Roda F & Langan SJ (1990) A Review of Small Catchment Studies in Western Europe Producing Hydrochemical Budgets. Air Pollution Research Report 28. Commission of the European Communities, Brussels

Hruška J & Krám P (1994a) Hydrochemical monitoring of a forested catchment with extremely high aluminum concentrations in runoff: The Lysina catchment, Czech Republic. Intl. Assoc. Hydrolog. Sci. Publ. 219: 357–368

Hruška J & Krám P (1994b) Aluminium chemistry of the root zone of forest soil affected by acid deposition at the Lysina catchment, Czech Republic. Ecol. Eng. 3: 5–16

Hultberg H (1985) Budgets of base cations, chloride, nitrogen and sulphur in the acid Lake Gårdsjön catchment, SW Sweden. Ecol. Bull. (Stockholm) 37: 133–157

Huntington TG, Ryan DF & Hamburg SP (1988) Estimating soil nitrogen and carbon pools in a northern hardwood forest ecosystem. Soil Sci. Soc. Am. J. 52: 1162–1167

Hylský R (1960) Map of Foundation Soils. Map Sheet M-33-62-C-d Lázně Kynžvart (In Czech). Res. Report, Geofond Archive, Prague

Innes JL (1993) Forest Health. Its Assessment and Status. CAB International, Wallingford, UK

Johnson NM, Driscoll CT, Eaton JS, Likens GE & McDowell WH (1981) "Acid rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochim. Cosmochim. Acta 45: 1421–1437

Kaupenjohann M & Wilcke W (1995) Heavy metal release from a serpentine soil using a pH-stat technique. Soil Sci. Soc. Am. J. 59: 1027–1031

Krám P (1989) Small Catchment Research in the Protected Region of Slavkov Forest (In Czech). Res. Report. Czech Geological Survey, Prague

Krám P & Hruška J (1994) Influence of bedrock geology on elemental fluxes in two forested catchments affected by high acidic deposition. Appl. Hydrogeol. 2/2: 50–58

Krám P, Hruška J, Driscoll CT & Johnson CE (1995) Biogeochemistry of aluminum in a forest catchment in the Czech Republic impacted by atmospheric inputs of strong acids. Water Air Soil Poll. 85: 1831–1836

Lawrence GB, David MB & Shortle WC (1995) A new mechanism for calcium loss in forest-floor soils. Nature 378: 162–165

LaZerte B & Scott L (1996) Soil water leachate from two forested catchments on the Precambrian Shield, Ontario. Canadian J. Forest Research 26: 1353–1365

Likens GE, Driscoll CT, Buso DC, Siccama TG, Johnson CE, Lovett GM, Ryan DF, Fahey T & Reiners WA (1994) The biogeochemistry of potassium at Hubbard Brook. Biogeochem. 25: 61–125

Likens GE & Bormann FH (1995) Biogeochemistry of Forested Ecosystem. 2nd edn. Springer-Verlag, New York

Likens GE, Driscoll CT & Buso DC (1996) Long-term effects of acid rain: Response and recovery of a forest ecosystem. Science 272: 244–246

Lindberg SE & Garten CT (1988) Sources of sulphur in forest canopy throughfall. Nature 336: 148–151

Matzner E & Meiwes KJ (1994) Long-term development of element fluxes with bulk precipitation and throughfall in two German forests. J. Environ. Qual. 23: 162–166

Mayer R & Ulrich B (1974) Conclusions on the filtering action of forests from ecosystem analyses. Oecol. Plant. 9: 157–168

McAvoy DC, Santore RC, Shosa JD & Driscoll CT (1992) Comparison between pyrocatechol violet and 8-hydroxyquinoline procedures for determining aluminum fractions. Soil Sci. Soc. Am. J. 56: 449–455

Moldan B & Schnoor J (1992) Czechoslovakia: examining a critically ill environment. Environ. Sci. Technol. 26: 14–21

Moravčík P & Černý M (1995) Forest die-back affected regions of Czech Republic. In: Černý J & Pačes T (Eds) Acidification of the Black Triangle Region (pp 11–22). Acid Reign '95? 5th Int. Conf. on Acidic Deposition Science and Policy. Göteborg, Sweden

Moravčík P (1995) Evaluation of Spruce Stands Status in the Pluhův Bor and Lysina Catchments, Slavkov Forest (In Czech). Res. Report. Institute for Forest Ecosystem Research, Davle nad Vltavou, Czech Republic

Pačes T (1983) Principles of Water Geochemistry (In Czech). Academia, Prague

Pačes T (1986) Weathering rates of gneiss and depletion of exchangeable cations in soils under environmental acidification. J. Geol. Soc., London 143: 673–677

Parker GG (1990) Evaluation of dry deposition, pollutant damage, and forest health with throughfall studies. In: Lucier AA & Haines SG (Eds) Mechanisms of Forest Response to Acidic Deposition (pp 10–61). Springer-Verlag, New York

Paukert T (Ed) (1993) Laboratory Handbook (In Czech). Internal Report. Czech Geological Survey, Prague

Roberts BA & Proctor J (Eds) (1992) The Ecology of Areas with Serpentinized Rocks. A World View. Geobotany 17. Kluwer Academic Publishers, Dordrecht

Schulze ED, Lange OL & Oren R (Eds) (1989) Forest Decline and Air Pollution. A Study of Spruce (*Picea abies*) on Acid Soils. Springer-Verlag, Berlin

Sherman RE & Fahey TJ (1994) The effects of acid deposition on the biogeochemical cycles of major nutrients in miniature red spruce ecosystems. Biogeochem. 24: 85–114

Sverdrup H, Warfvinge P & Nihlgård B (1994) Assessment of soil acidification effects on forest growth in Sweden. Water Air Soil Poll. 78: 1–36

Thomas GW (1982) Exchangeable cations. In: Page AL (Ed) Methods of Soil Analysis, Part 2 (pp 159–166). Agron. Soc. Amer. and Soil Sci. Soc. Amer., Madison, Wisconsin

Thorne JF, Anderson JE & Horiuchi KM (1988) Cation cycling in a base-poor and base-rich Northern Hardwood Forest ecosystem. J. Environ. Qual. 17: 95–101

Van Breemen N, Driscoll CT & Mulder J (1984) Acidic deposition and internal proton sources in acidification of soils and waters. Nature 307: 599–604

Zech W, Suttner T & Popp E (1985) Elemental analyses and physiological responses of forest trees in SO_2-polluted areas of NE-Bavaria. Water Air Soil Poll. 25: 175–183

Zoettl HW, Huettl RF, Fink S, Tomlinson GH & Wisniewski J (1989) Nutritional disturbances and histological changes in declining forests. Water Air Soil Poll. 48: 87–109