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Long-term changes in aluminum fractions of drainage waters in two forest catchments with contrasting lithology

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Abstract

Aluminum (Al) chemistry was studied in soils and waters of two catchments covered by spruce (*Picea abies*) monocultures in the Czech Republic that represent geochemical end-members of terrestrial and aquatic sensitivity to acidic deposition. The acid-sensitive Lysina catchment, underlain by granite, was compared to the acid-resistant Pluhův Bor catchment on serpentine. Organically-bound Al was the largest pool of reactive soil Al at both sites. Very high median total Al (Alt) concentrations ($40 \mu\text{mol L}^{-1}$) and inorganic monomeric Al (Ali) concentrations ($27 \mu\text{mol L}^{-1}$) were observed in acidic (pH 4.0) stream water at Lysina in the 1990s and these concentrations decreased to $32 \mu\text{mol L}^{-1}$ (Alt) and $13 \mu\text{mol L}^{-1}$ (Ali) in the 2000s. The potentially toxic Ali fraction decreased in response to long-term decreases in acidic deposition, but Ali remained the largest fraction. However, the organic monomeric

(Al_o) and particulate (Al_p) fractions increased in the 2000s at Lysina. In contrast to Lysina, marked increases of Al_t concentrations in circum-neutral waters at Pluhův Bor were observed in the 2000s in comparison with the 1990s. These increases were entirely due to the Al_p fraction, which increased more than 3-fold in stream water and up to 8-fold in soil water in the A horizon. Increase of Al_p coincided with dissolved organic carbon (DOC) increases. Acidification recovery may have increased the content of colloidal Al though the coagulation of monomeric Al.

Keywords: Acidic deposition; Aluminum speciation; Stream water; Soil water; Water quality

1. Introduction

Aluminum (Al) is largely associated with aluminosilicate minerals and, in that form, is generally unavailable for biogeochemical reactions. Anthropogenic activities influence lithospheric cycling of Al to allow more rapid flux into the biosphere [1]. Elevated inputs of strong acids to sites with low supply rates of base cations may result in elevated concentrations of Al in drainage waters [2,3]. Such conditions may be toxic to forest vegetation [4] or downstream aquatic organisms [5]. In particular, there is concern that acidification of soil by acidic deposition, coinciding with the resulting depletion of labile pools of nutrient cations (e.g. Ca²⁺, Mg²⁺) and enhanced leaching of Al from soil may contribute to forest dieback [3,6,7]. Furthermore, dry deposition of acidic substances onto the canopy of coniferous spruce trees substantially increases acid inputs to the soil in comparison to the canopy of deciduous beech [8]. Another important factor controlling the effects of acidic deposition on water quality is the bedrock type [9,10].

Very few studies have been conducted that consider long-term changes in the fractions of aqueous Al. Different forms of aqueous Al have different toxicity levels for forest biota, with inorganic monomeric Al (Alⁱ) generally considered the most toxic [2]. Thus, changes in acid inputs may affect the health of forest and aquatic ecosystems by altering the total Al concentrations in drainage waters, fractions of Al, or both. The objectives of this study were to: 1) compare and contrast the biogeochemical patterns of Al in two forest catchments in the Czech Republic with different lithologies that can serve as end-members of catchment sensitivity to acidic deposition; and 2) evaluate long-term changes in the speciation of Al in drainage waters from these catchments in response to decreases in acidic deposition.

2. Site description

The study sites are located in the Slavkov Forest (Slavkovský les), about 120 km west of Prague (Fig. 1). Major geologic formations of the petrologically diverse Slavkov Forest were shown in [9]. Streams in the Slavkov Forest have experienced marked declines of SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺ and Mg²⁺ concentrations in the 1990s due to decreases in emissions of SO₂ and NO_x and associated decreases in acidic deposition [11]. Total mean annual deposition of sulfur to the Lysina catchment was 77 mmol m⁻² yr⁻¹ in 1991-1997 [10] and only 23 mmol m⁻² yr⁻¹ in 2003-2007 (the periods of our measurements of aluminum fractions). The two catchments we studied are situated 7 km apart, within a large Norway spruce (*Picea abies*) forest on a plateau in the Slavkov Forest. The catchments, Lysina and Pluhův Bor [9,10], have similar mean annual air temperature (5°C vs. 6°C), atmospheric deposition, mean altitude (884 m vs. 774 m), area (27.3 ha vs. 21.6 ha) and vegetation cover, but contrasting bedrock (leucogranite vs. serpentine) and soils (Podzol vs. Eutric Magnesic Cambisol). Both sites belong to the Czech GEOMON network of fourteen small forest catchments [12].

Moreover, Lysina is one of two Czech sites within the international network of forest sites comprising the International Cooperative Program – Integrated Monitoring (ICP IM) network, organized under the Economic Commission of the United Nations [13].

The Al chemistry of streams and soil waters of the root zone at Lysina has been previously reported [14,15]. In the early 1990s, runoff from Lysina was acidic and high in Al concentrations [2]. Long-term changes in Al concentrations have been simulated by the MAGIC model in both catchments [10]. A combination of a MAGIC model with a model that predicts short-term transient changes in hydrochemistry during hydrologic events (pBDM) showed that Al mobilization was highly variable at Lysina due to historic changes in acidic inputs [16]. Recovery of the organic soil horizons from acidification and further acidification of deeper mineral soil until 2025 was predicted at Lysina using the SAFE model [17]. The Pluhův Bor catchment has exhibited extremely rapid decreases in sulfate concentrations ($25 \mu\text{mol L}^{-1}\text{yr}^{-1}$ in the 1990s) in stream water [11,18].

3. Methods

Soil pools were estimated by excavating 0.5 m^2 pits (four at Lysina, one at Pluhův Bor) in June 1993 by the method described in Huntington et al. [19]. This technique entailed collection of the L (litter) and F (fermented) horizons as a single sample, and then the H (humus) horizon. The mineral soils were then collected in 10-cm intervals from the surface of the mineral soil. Tissue samples of Norway spruce were obtained in July 1994 from 4 trees which were felled at different altitudes of the catchments. One whole branch was collected from the upper, middle, and lower canopy, and twigs and foliage were separated after air-drying. A disk of bole wood was sawn from the lowest part of the felled tree. After air drying,

bark and wood were separated from each disk. Roots and soil rhizosphere were separated after air-drying. Fine (<2 mm) and medium (2-5 mm) roots were separated according to the size in diameter. There was enough sample for separate analyses of these roots sizes only at Lysina [20,9]. Bulk precipitation and throughfall have been collected at several sites (Fig. 1) monthly since the beginning of 1990s [10]. Stream water discharge have been monitored continuously using V-notch weirs and mechanical water level recorders since September 1989 at Lysina and since November 1991 at Pluhův Bor [21]. Stream water was collected weekly for chemical analysis at both sites in the same time frame as the discharge measurements. Soil water has been sampled by several zero-tension lysimeters within each catchment at monthly intervals. Six lysimeters have been sampled since 1990 or 1994 at Lysina and five lysimeters since 1994 at Pluhův Bor. The lysimeters were rounded rectangular polyethylene containers (132 cm² or 2000 cm²), filled with acid-washed silica sand, draining into polyethylene containers situated below ground. Lysimeters drained soil water below the organic (O) horizon and the uppermost mineral soils (A or E horizon). In addition, a well with overflow (ground water), and a very small stream (seep water) with a V-notch weir situated immediately north from the main stream were sampled at Lysina at monthly intervals (Fig. 1).

Exchangeable Al was determined by extracting 2.5 g of soil with 50 mL of 1 M KCl for 12 hours using a mechanical vacuum extractor. The KCl extract was titrated with 0.1 M NaOH to a phenolphthalein endpoint and the exchangeable Al was determined by back-titrating the solution with 0.1 M HCl to the phenolphthalein endpoint after the addition of 1 M KF [22]. A pyrophosphate extraction was used to remove exchangeable and organically bound Al, while an acid-oxalate extraction was used to remove amorphous Al-oxides in addition to exchangeable and organically-bound Al. The acid-oxalate (0.2 M (NH₄)₂C₂O₄ + 0.23 M

H₂C₂O₄) extractable Al was collected using a mechanical vacuum extractor under dark conditions for 17 hours [23]. Na-pyrophosphate (0.1 M Na₄P₂O₇) extractable Al was collected using a reciprocating shaker for 17 hours, followed by centrifugation after addition of Superfloc flocculant [23]. The pyrophosphate and acid-oxalate extractable Al fractions were determined by direct-current plasma emission spectroscopy (DCP) at Syracuse University. The litter and spruce samples were dried at 70°C, ground and dry-ashed. The ash was dissolved in concentrated HNO₃ plus 30% H₂O₂ and then in 10% HNO₃. Total Al concentrations of the litter (L+F) horizons and the spruce tissues were analyzed by inductively-coupled plasma emission spectroscopy (ICP) at Cornell University. Sieved mineral soil was crushed and powdered in an agate mill. The prepared powder was dissolved in a mixture of H₂SO₄, HNO₃, and HF at 200°C and analyzed by flame atomic absorption spectrophotometry (flame AAS) at the Czech Geological Survey [20].

Water samples were neither acidified nor filtered in the field. Samples for determination of total concentrations of cations were acidified in the laboratory with ultra-pure HNO₃, diluted with distilled water, 1:1 V/V, 1 mL of acid to 100 mL of sample (resulting sample pH <2). Concentrations of total Al (Al_t) in water were determined by flame AAS (concentrations above 7.3 μmol L⁻¹) or graphite furnace AAS (concentrations below 7.3 μmol L⁻¹) in the Central Laboratories of the Czech Geological Survey. Samples for Al fractionation were not acidified. Modified methods of the original Al fractionation procedure of Driscoll [24] were used. Total monomeric Al (Al_m) and organic monomeric Al (Al_o) were measured by the pyrocatechol violet colorimetry method [25,26,27]. The Al_o was separated using a strong cation exchange resin Dowex 50 W in mixed H⁺ (98%) and Na⁺ (2%) form [24]. This method of separation utilizes charge exclusion by ion exchange. Inorganic monomeric Al (Al_i) was calculated as the difference between Al_m and Al_o. Acid-soluble Al, assumed to be mainly in

the particulate form (Alp) was calculated as the difference between Alt and Alm. Part of the Alp fraction is undoubtedly formed by colloids and strong organic complexes. The method of Røgeberg and Henriksen [25], modified by LaZerte et al. [26], was used in 1991-1994 at the Czech Geological Survey by J. Hruška and again in the 2000s. The latest measurements were performed by J. Kaňa at the Hydrobiological Institute of Czech Academy of Sciences in 2003-2006 and back at Czech Geological Survey in 2006-2007 (by M. Půlkrábková and J. Hruška). A similar method, but with a flow-injection analyzer [27], was used in 1993-1997 at Syracuse University (by P. Krám). Comparisons showed good agreement between the two similar Al fractionation methods and between the three chemical laboratories.

The NCSS 2001 statistical software was used for data evaluation. The Kruskal-Wallis One-Way ANOVA procedure was used for estimation of differences between the two groups (samples from 1991-1997s vs. samples from 2003-2007), with significance at a p-level of 0.05, 0.01 and 0.001.

4. Results and discussion

Silica dominates the elemental composition of the leucogranite at Lysina, while alumina (Al_2O_3) is the second most abundant (1.4 mol kg^{-1} ; [9]). Ultramafic serpentine bedrock at Pluhův Bor is composed predominantly of Mg-silicates with very low (0.1 mol kg^{-1}) concentrations of alumina [28].

Soil pH (0.1 M CaCl_2) was low in the litter layers (L+F) at the two sites (Lysina: pH 2.9, Pluhův Bor: pH 3.1), slightly different in the humus layer H (Lysina: pH 2.8, Pluhův Bor: pH 3.4) and distinctly different in the upper mineral soil horizons (Lysina: mean pH 3.1-3.8,

Pluhův Bor: mean pH 4.1-4.9). Soil pH increased with depth up to a value of 4.1 in the C horizon at Lysina and 5.8 in the C horizon at Pluhův Bor [20]. The base saturation of soils at Pluhův Bor systematically increased from 49% in the H horizon to almost 100% in the C horizon, and this pattern was largely attributable to exchangeable Mg. In contrast, the catchment at Lysina showed low base saturation; it decreased with depth from 18% in the H horizon to less than 5% in the lower mineral horizons [9].

The total oxalate-extractable Al pools were slightly greater than the pyrophosphate-extractable pools, both of which were much greater than the exchangeable Al (Table 1). This pattern suggests that organically-bound Al is the dominant reactive pool of Al in forest floor and mineral soil at both sites with exception of the L+F horizon at Lysina (Table 2). It appears that amorphous Al is less dominant reactive pool at both sites, it prevails only in the L+F horizon at Lysina. Total pools of reactive Al, as represented by oxalate extractable Al, were only 5% (Lysina) or 2% (Pluhův Bor) of the total Al in the upper 40 cm of the mineral soil (Table 1). However, the pools of reactive Al were 98% (Lysina) or 87% (Pluhův Bor) of the total Al in the litter horizons. Crystalline Al pools were negligible in the L+F horizon and vast in the mineral soil, but are mostly unavailable for chemical reactions with soil water (Table 2).

Aluminum concentrations were elevated in fine roots (90 mmol kg^{-1}) and medium roots (33 mmol kg^{-1}) from the upper mineral soil at Lysina. The mean concentration of Al in the mix of fine and medium roots from the upper mineral soil at Pluhův Bor was lower (16 mmol kg^{-1}). The lowest concentrations of Al were measured in bole wood (Lysina: $0.33 \text{ mmol kg}^{-1}$, Pluhův Bor: $0.35 \text{ mmol kg}^{-1}$). Estimated pools of total Al in above-ground biomass were similar (0.02 mol m^{-2}) at both sites [20]. Pools of total Al in the litter (L+F) horizons (Table

1) were approximately one order of magnitude higher than pools in above-ground biomass. Symptoms of yellowing of older needles and canopy thinning of spruce stands at Lysina may be linked with the very low Mg content of foliage [9] and high Al content in soils, fine roots, and soil water [29].

Distinct patterns were evident in drainage water Al fractions at the two sites. Statistically significant ($p < 0.001$) increases in Alt concentrations were observed at Pluhův Bor in the 2000s (Fig. 2). Very high median Alt concentrations were observed, particularly at Pluhův Bor in the 2000s. The largest median concentrations were recorded in A horizon ($130 \mu\text{mol L}^{-1}$) and O horizon ($100 \mu\text{mol L}^{-1}$) soil solutions. Median stream water Alt at Pluhův Bor in the 2000s was $15 \mu\text{mol L}^{-1}$. Particulate Al was the dominant fraction of Alt in all drainage waters and both study periods at Pluhův Bor (Fig. 2, Table 3). Concentrations of stream water Alp at Pluhův Bor were highly variable, especially in the 2000s (Fig. 3). Higher values were usually recorded during elevated discharge (Table 4). Relative changes in median values of Al fractions in organic-horizon soil solutions at Pluhův Bor between the 1990s and the 2000s were as follows: Alp from 56% in the 1990s to 85% in the 2000s (56-85%), Alo 29-13%, Ali 15-2%. The median values of Al fractions in soil solutions draining the uppermost mineral horizon (A) at Pluhův Bor changed as follows: Alp from 65% in the 1990s to 91% in the 2000s (65-91%), Alo 22-9%, Ali 13-0.2%. In contrast to Pluhův Bor, all statistically significant changes of Alt in drainage waters at Lysina were decreases ($p < 0.001$ for stream water, $p < 0.05$ for seep water, $p < 0.01$ for ground water and soil water from the E horizon, Fig. 2). The median concentration of Alt in stream water decreased from $40 \mu\text{mol L}^{-1}$ in the 1990s to $32 \mu\text{mol L}^{-1}$ in the 2000s. Concentrations of Alt in Lysina soil solutions were lower than at Pluhův Bor (Fig. 2), and Ali was the dominant fraction only in the 1990s, as the fractionation shifted to Alp in the 2000s (O horizon: Alp from 18% in the 1990s to 48% in the 2000s (18-

48%), Alo 32-29%, Ali 51-22%; E horizon: Alp 10-59%, Alo 24-24%, Ali 66-17%). All increases in Alp in soil waters from both horizons at both sites were very large and statistically significant. Changes in Alo were usually not statistically significant. All decreases in Ali were large and showed different levels of statistical significance (Table 3). Stream waters at Lysina and Pluhův Bor were evaluated also with respect of discharge (Table 4). The largest decline of Ali at Lysina occurred during high flow events (floods), the largest increase of Alo occurred during elevated flow, and increase of Alp was usually significant. The largest increase of Alp at Pluhův Bor occurred during elevated flow conditions, the lowest during base flow, and all Alp increases were statistically highly significant.

Very high Al concentrations ($40 \mu\text{mol L}^{-1}$) and Ali ($27 \mu\text{mol L}^{-1}$) were observed in stream water at Lysina in the 1990s (Fig. 2, Table 3). These concentrations were among the highest values reported in the literature for surface waters [2]. The dominance of the Ali fraction in stream water decreased from the 1990s to the 2000s, but Ali remained the largest fraction. On the other hand, the fractions of Alo and Alp increased in the 2000s (Alp 14-27%, Alo 18-31%) while the fraction of Ali decreased (68-42%). All these changes were highly statistically significant (Table 3). Also, stream water Al fractions at Pluhův Bor changed significantly (Table 3) but the absolute values were very large only for the Alp fractions (Fig. 2). The Al fractions between the 1990s and 2000s changed as follows at Pluhův Bor: Alp 82-97%, Alo 12-2%, Ali 5-1%.

Long-term inputs of elevated acidity and sulfate from atmospheric deposition, coupled with a slow rate of base cation supply from weathering of the leucogranite, has resulted in highly acidic soil water and the mobilization of available soil Al pools to stream water at Lysina. More recently, decreases in acidic deposition have caused decreases in Ali and Al at Lysina.

In contrast, drainage water at Pluhův Bor showed the opposite patterns, with Alt increasing significantly between the 1990s and 2000s. Stream water Al at Pluhův Bor showed decreases in both Alo and Ali fractions, which together contributed 18% to Alt in the 1990s and only 3% of Alt in the 2000s. Therefore, the overwhelming fraction of Alt at Pluhův Bor was Alp. Our study suggests that the highly acidic drainage waters at Lysina have responded to decreases in acidic deposition by a very small increase of pH, and a large shift from Ali to other Al fractions. Waters with circum-neutral pH at Pluhův Bor, on the other hand, responded with a large mobilization of Al pools to the Alp fraction in water. Alp associated with mineral matter is relatively unavailable to participate in chemical and biological transformations.

Soil water pH at Lysina did not change significantly in the study period and was typically between 3.3-3.8. Soil water pH at Pluhuv Bor was also unchanged, varying mainly between pH 5.2 and 5.7. Concentrations of dissolved organic carbon (DOC) were high, typically between 2 and 10 mmol C L⁻¹ at Lysina and between 2 and 7 mmol C L⁻¹ at Pluhův Bor. Soil water DOC concentrations increased significantly at both catchments by 450 μmol C L⁻¹yr⁻¹ at Lysina and by 190 μmol C L⁻¹yr⁻¹ at Pluhův Bor between 1993-2007 [21].

In response to decreases in atmospheric S deposition of anthropogenic origin [10], stream water SO₄²⁻ decreased markedly in both catchments, by 30 μmol L⁻¹ yr⁻¹ in annual mean concentration at Pluhův Bor and 13 μmol L⁻¹ yr⁻¹ at Lysina [21]. Despite such pronounced decreases, stream water pH showed only a moderate (though statistically significant) increase, at a rate of 0.006 pH unit yr⁻¹ at Lysina (the annual discharge-weighted mean pH was around 4.0). Annual discharge-weighted mean pH at Pluhův Bor was around 7.5 and the pH increased at a rate of 0.02 pH unit yr⁻¹. The sum of base cation concentrations

($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) in stream water decreased less than sulfate (as 85% of μeq at Pluhův Bor and as 62% μeq at Lysina). Stream water concentrations of DOC were generally lower than values observed in soil water. Mean annual discharge-weighted stream water DOC averaged $1.6 \text{ mmol C L}^{-1}$ at Lysina and $1.7 \text{ mmol C L}^{-1}$ at Pluhův Bor. Between 1993 and 2007 the mean annual increase in DOC concentration was $35 \mu\text{mol C L}^{-1}\text{yr}^{-1}$ at Lysina and $36 \mu\text{mol C L}^{-1}\text{yr}^{-1}$ at Pluhův Bor. Daily mean, maximum and minimum air temperature values and daily precipitation quantity at the nearest stations of the Czech Hydrometeorological Institute and daily mean discharge values at Lysina and Pluhův Bor showed no statistically significant trends between 1993 and 2007. Therefore climatic factors could be ruled out as the reason for the observed changes of aquatic Al concentrations at Lysina and Pluhův Bor. These DOC increases were driven by decreases of ionic strength dominated by decline in concentrations of SO_4^{2-} , followed by Ca^{2+} and Mg^+ at Lysina and by decline of Mg^+ , followed by SO_4^{2-} and HCO_3^- at Pluhův Bor [21].

A toxic limit for Ali of $2 \mu\text{mol L}^{-1}$ for fish has been reported [5,3]. Streams at Lysina and Pluhův Bor are too small [30] to support fish populations (e.g. annual mean minimum discharge at Pluhův Bor was 0.03 L s^{-1} and at Lysina 0.2 L s^{-1}). Reported effects of Ali on stream benthic macroinvertebrates were summarized by Herrmann [31]. Physiological problems usually occur above the Ali concentration interval $3.7\text{-}11.1 \mu\text{mol L}^{-1}$. Mayfly (*Ephemeroptera*) nymphs are reportedly the most sensitive to Ali [31]. Taxa richness of stream benthic macroinvertebrates declined clearly with increasing acidity of nine Czech stream waters [32] and probably also with increasing concentration of Ali. Unfortunately, toxicologically the most important Ali fraction was not measured at seven other study sites. The biodiversity of macroinvertebrates at Lysina with high Ali concentrations was very low (9 taxa). Macroinvertebrates biodiversity at Pluhův Bor with usually low Ali

concentrations in stream water (Table 3, Fig. 3) was 19 taxons which was slightly above the average for nine Czech streams (18 taxons). The most abundant macroinvertebrates at both sites were the needleflies (*Leuctridae*) and the non-biting midges (*Chironomidae*). Mayflies (*Ephemeroptera*) were absent from the stream at Lysina because they are acid- and Al-sensitive but they were frequently present at Pluhův Bor [32].

Long-term Ali decreases ($-0.26 \mu\text{mol L}^{-1} \text{yr}^{-1}$) were observed in stream water in the W6 catchment at Hubbard Brook, New Hampshire, USA, during 1982-2000. Significant decreases in Ali and Alo in soil waters collected from the mineral soil were also observed there. Moreover decreases of Ali and Alo in soil waters draining from organic soil horizons were observed but these were not statistically significant. The Alp fraction was not evaluated [33,34]. Concentrations of Alt, Ali and Alo decreased in lakes of the Northeastern USA, as described by Warby et al. [35], who concluded that a major effect of acidification recovery was a shift in the Al fractionation from more toxic Ali to less toxic Alo and Alp. That study suggested that surface waters responded to decreases in acidic deposition by increasing pH with a shift from Ali to Alo, whereas waters with moderate pH responded with a shift in Al fractionation to Alp. Between pH 5.5 and 6.7, Alp was the dominant fraction of lake water Al. Alp was the dominant fraction in all regions, except for the Adirondacks Mountains in New York, which had the lowest lake water pH. Alp increased by $0.4 \mu\text{mol L}^{-1}$ over the 15-year study period (1986 vs. 2001), resulting in 90% of Al in Central New England lake waters occurring in the Alp fraction [35]. This reported increase in Alp was much lower than the increase between 1991-1997 and 2003-2007 at Lysina ($2.8 \mu\text{mol L}^{-1}$) and Pluhův Bor ($10.4 \mu\text{mol L}^{-1}$) stream waters (Table 3). Unlike the USA study [35], there was no evidence of a long-term shift in Al fractionation from the more toxic Ali to less toxic Alo and Alp forms in the French river Vienne in the period 1994-2004 [36]. Their sampling points were 4

km (Peyrelevade) and 89 km (Royères) from the spring. The study period may not have been sufficiently long to detect changes in Al fractionation in the river Vienne.

Aqueous Al is largely derived from free soil/sediment pools (nonsilicate bound), including exchange from cation exchange sites, dissolution from amorphous mineral phases and/or decomposition/mineralization of organic forms [37]. The large increase in Al_{tot} at Pluhův Bor might be explained by dissolution of a secondary Al-bearing mineral containing SO_4^{2-} . The marked decline in SO_4 deposition and its concentrations in soil and stream water alters the equilibrium between mineral precipitation (perhaps as Al-hydroxosulfate) and its dissolution. When solute SO_4 concentrations decline, equilibrium is expected to shift toward greater mineral dissolution. Interactions with Al could alter biogeochemical cycling of DOC, P, Pb and other trace metals during acidification recovery of surface waters. Desorption, and subsequent mobilization of DOC may be facilitated by decreased Al_{li} . This mobilization of DOC could have important implications for ecosystems as DOC is important in the attenuation of light and can alter the clarity of waters [38]. Terrestrial DOC can be an important substrate for the food chain of aquatic ecosystems.

Acidification recovery could increase the content of colloidal Al, and hence Al_p in drainage waters, through increased coagulation of Al_m associated with increases in pH. During conditions of oversaturation, Al will hydrolyze, forming particulate Al oxyhydroxides. These materials would include microcrystalline hydroxide particles [37].

Marked increases in drainage water DOC at both catchments [21] might have resulted in an increase in the importance of complexes between Al and anions of organic acids.

Surprisingly, however, Al_o trends were inconsistent, and often statistically insignificant

(Table 3). Driscoll and Postek [2] observed that the extent of alumino-organic complexes decreased with increases in pH and decreases in concentrations of Ali. An alternative explanation is that the strength of some Al-organic complexes could be greater than the complex between pyrocatechol violet (used in the analytical procedure to determine Alo) and Al. Thus, some of the Al-organic complexes may not have been fully detected in the monomeric Al fractions. If so, these complexes would be included in the Alp fraction and therefore contribute to the observed increases in the operationally defined Alp fraction. This finding is supported by the observations from both catchments (21) where DOC increased by 65% in stream water and ca. 3 times in soilwater (O and E/A horizon respectively). Alp increased proportionally with DOC (Table 3) at Lysina, but at Pluhův Bor Alp increased to a greater extent than DOC. This pattern may suggest that other mechanisms played an important role in Al chemistry in the base-rich catchment.

5. Conclusions

Organically-bound Al was the largest pool of reactive soil Al, while amorphous Al was less abundant in the organic horizons and upper 40 cm of mineral soils at Lysina and Pluhův Bor. Exchangeable soil Al pools formed a much smaller portion of the reactive Al. Pools of crystalline Al in the studied mineral soil were vast but mostly unavailable for chemical reactions with soil water. Very high median Alt concentrations ($40 \mu\text{mol L}^{-1}$) and Ali ($27 \mu\text{mol L}^{-1}$) were observed in the chronically acidic stream water at Lysina in the period of 1991-1997, concentrations that were among the highest values reported anywhere for surface waters. Median concentrations of these fractions in stream water decreased to $32 \mu\text{mol L}^{-1}$ (Alt) and $13 \mu\text{mol L}^{-1}$ (Ali) in the period of 2003-2007. The dominance of the potentially toxic Ali fraction in stream water decreased from the 1990s to 2000s due to recovery

following decreases in acidic deposition, but remained the largest fraction. On the other hand, the fractions of Alo and Alp increased in the 2000s at Lysina. The overwhelmingly dominant fraction of the Alt was the Alp fraction in the circum-neutral soil waters and stream waters at Pluhův Bor in both study periods. In contrast to Lysina, the marked increases of Alt concentrations in waters at Pluhův Bor were observed in the 2000s in comparison with the 1990s, and these increases were entirely associated with the Alp fraction.

Table of abbreviations

Alt total aluminum

Alm monomeric aluminum

Alo organic monomeric aluminum

Ali inorganic monomeric aluminum

DOC dissolved organic carbon

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Table 1

Measured pools of Al in fine soil (<2mm: mineral soil, <5mm: organic soil) at the two study sites.

Site Horizon	POOLS			Total Al
	Exchangeable Al	Pyrophosphate- extractable Al	Oxalate- extractable Al	
Unit	mol m ⁻²	mol m ⁻²	mol m ⁻²	mol m ⁻²
LYSINA CATCHMENT				
L+F horizon	0.04	0.09	0.16	0.163
H horizon	0.37	1.0	1.2	ND
Mineral soil 0-40 cm	3.39	15.0	20.0	439*
PLUHŮV BOR CATCHMENT				
L+F horizon	0.05	0.18	0.23	0.264
H horizon	0.06	0.43	0.44	ND
Mineral soil 0-40 cm	1.82	7.0	9.5	484*

* measured only on the very fine soil fraction (<0.5 mm), ND not determined

Table 2

Estimated pools of Al in fine soil at the two study sites.

Site Horizon Unit	POOLS		
	Organically-bound Al mol m ⁻²	Amorphous Al mol m ⁻²	Crystalline Al mol m ⁻²
LYSINA CATCHMENT			
L+F horizon	0.05	0.07	0.003
H horizon	0.63	0.20	ND
Mineral soil (0-40 cm)	11.6	5.0	419
PLUHŮV BOR CATCHMENT			
L+F horizon	0.13	0.05	0.034
H horizon	0.37	0.01	ND
Mineral soil (0-40 cm)	5.2	2.5	474

Three fractions were calculated from the values in Table 1 as follows:

organically bound Al = pyrophosphate Al - exchangeable Al

Amorphous Al = oxalate Al - pyrophosphate Al

Crystalline Al = total Al - oxalate Al

Table 3

Comparison of concentrations of Al fractions in water at the study sites during two time periods (1991-1997 vs. 2003-2007).

Compartment	Measured Al fraction, number of samples (n)	Statistical significance (p level)	Median concentration in 1990s ($\mu\text{mol L}^{-1}$)	Median concentration in 2000s ($\mu\text{mol L}^{-1}$)	Trend (up +, down -)
LYSINA CATCHMENT					
Soil water O horizon	Ali	<0.01	10.8	5.9	-
	Alo	NS	6.7	7.8	NS
	Alp	<0.001	3.7	12.8	+
	n		28	69	
Soil water E horizon	Ali	<0.001	16.3	2.9	-
	Alo	NS	6.0	4.1	NS
	Alp	<0.001	2.6	10.0	+
	n		27	61	
Ground water	Ali	<0.05	13.3	5.2	-
	Alo	<0.05	1.5	0.3	-
	Alp	NS	11.8	11.5	NS
	n		4	41	
Seep water	Ali	<0.05	27.8	13.7	-
	Alo	NS	2.8	3.0	NS
	Alp	<0.05	3.3	7.8	+
	n		10	37	
Stream water	Ali	<0.001	27.1	13.3	-
	Alo	<0.001	7.3	10.0	+
	Alp	<0.001	5.7	8.5	+
	n		209	296	
PLUHŮV BOR CATCHMENT					
Soil water O horizon	Ali	<0.01	5.2	2.0	-
	Alo	NS	10.2	13.2	NS
	Alp	<0.001	19.8	84.3	+
	n		10	18	
Soil water A horizon	Ali	<0.001	3.0	0.3	-
	Alo	<0.05	4.9	11.9	+
	Alp	<0.001	14.7	117.9	+
	n		12	69	
Stream water	Ali	<0.001	0.3	0	-
	Alo	<0.001	0.6	0.3	-
	Alp	<0.001	4.1	14.5	+
	n		104	269	

Table 4

Comparison of median concentrations of Al fractions in stream water at the study sites during two time periods (1991-1997 vs. 2003-2007) and three hydrologic situations [30]. Base flow was defined as instantaneous discharge during the sample collection below the long-term daily mean median flow Q_{med} . Elevated flow was defined as discharge between the median flow and the Q_{30d} (mean 30-day discharge value from the exceedance curves of daily discharges of individual years, represents the 30th highest daily discharge). Floods were defined as instantaneous discharge above the Q_{30d} . Long-term Q_{med} and Q_{30d} at Lysina were $7.7 \text{ L s}^{-1} \text{ km}^{-2}$ and $39.9 \text{ L s}^{-1} \text{ km}^{-2}$, long-term Q_{med} and Q_{30d} at Pluhův Bor were $2.3 \text{ L s}^{-1} \text{ km}^{-2}$ and $27.3 \text{ L s}^{-1} \text{ km}^{-2}$.

Compartment	Measured Al fraction, number of samples (n)	Statistical significance (p level)	Median concentration in 1990s ($\mu\text{mol L}^{-1}$)	Median concentration in 2000s ($\mu\text{mol L}^{-1}$)	Trend (up +, down -)
LYSINA CATCHMENT – STREAM WATER					
Base flow	Ali	<0.001	23.9	12.6	-
	Alo	<0.001	5.5	7.0	+
	Alp	<0.001	4.6	6.3	+
	n		85	169	
Elevated flow	Ali	<0.001	31.9	14.5	-
	Alo	<0.001	8.4	12.2	+
	Alp	<0.001	7.1	11.1	+
	n		94	85	
Floods	Ali	<0.001	30.2	13.0	-
	Alo	<0.01	9.7	12.2	+
	Alp	NS	11.6	14.1	NS
	n		21	49	
PLUHŮV BOR CATCHMENT – STREAM WATER					
Base flow	Ali	<0.001	0.2	0	-
	Alo	<0.001	0.4	0.3	-
	Alp	<0.001	0.8	2.2	+
	n		40	134	
Elevated flow	Ali	<0.001	0.4	0	-
	Alo	<0.001	0.6	0.3	-
	Alp	<0.001	5.6	28.2	+
	n		54	105	
Floods	Ali	NS	0.3	0.1	NS
	Alo	NS	1.4	1.1	NS
	Alp	<0.001	8.3	28.3	+
	n		9	30	

Figure captions

Fig. 1. Upper panels: Map of Europe with the Czech Republic in black. Map of the Czech Republic, showing the Slavkov Forest (SF, 610 km²). Map of the Slavkov Forest, showing the two study catchments 7 km apart. Lower parts: Topographic maps of the Lysina and Pluhův Bor catchments, showing the catchment boundaries, the major stream channels and the major sampling locations. Contour interval of the maps is 5 meters. Two major brooks have variable length (with not stable location of their springs), streams could be ca. 200 m shorter than on the map during dry weather. The first northern tributary at Lysina is called seep water in this paper because its spring has fixed location even during dry weather.

Fig. 2. Comparison of Al concentrations in water at Lysina (left) and Pluhův Bor (right). Total Al contains the three individual fractions (Ali inorganic monomeric + Alo organic monomeric + Alp particulate). Two time periods were evaluated (1991-1997 vs. 2003-2007). Differences of total Al in stream water at Lysina, soil water O at Pluhův Bor, soil water A at Pluhův Bor and stream water at Pluhův Bor were statistically significant at level $p < 0.001$. Differences of total Al in soil water E at Lysina and ground water at Lysina were significant at level $p < 0.01$ and in seepage water at Lysina at level $p < 0.05$. Differences of total Al in soil water O at Lysina were statistically not significant. Statistical details about all individual Al fractions are in Tab. 1.

Fig. 3. Long-term patterns of concentrations of Al fractions in streamwater at Lysina (left) and Pluhův Bor (right). Three individual Al fractions are shown: Ali = inorganic monomeric, Alo = organic monomeric, Alp = Al particulate.

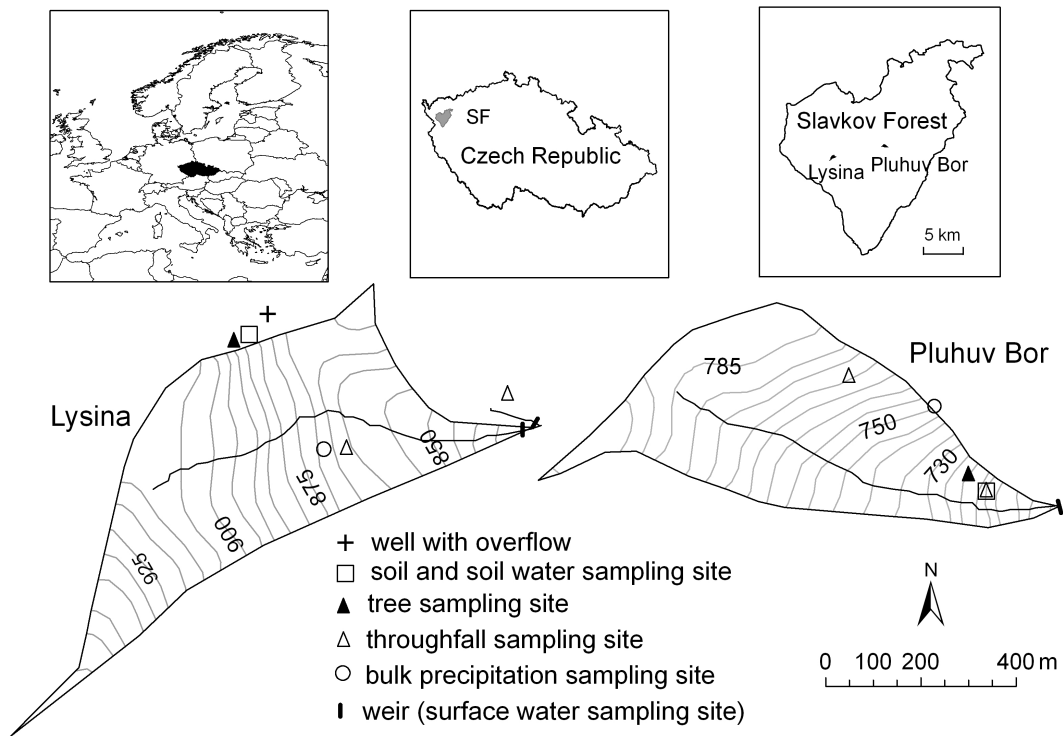


Fig. 1.

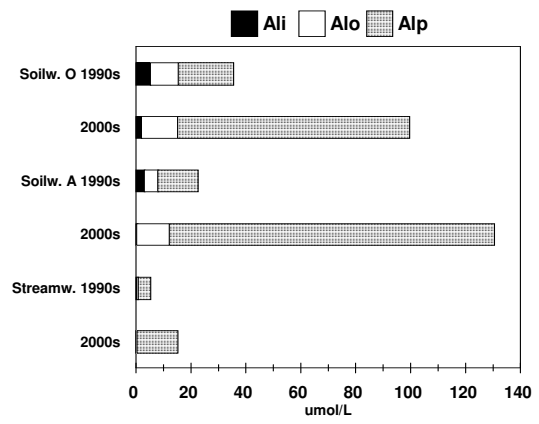
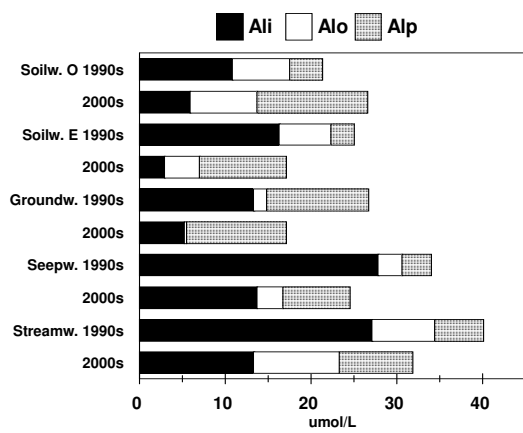


Fig. 2.

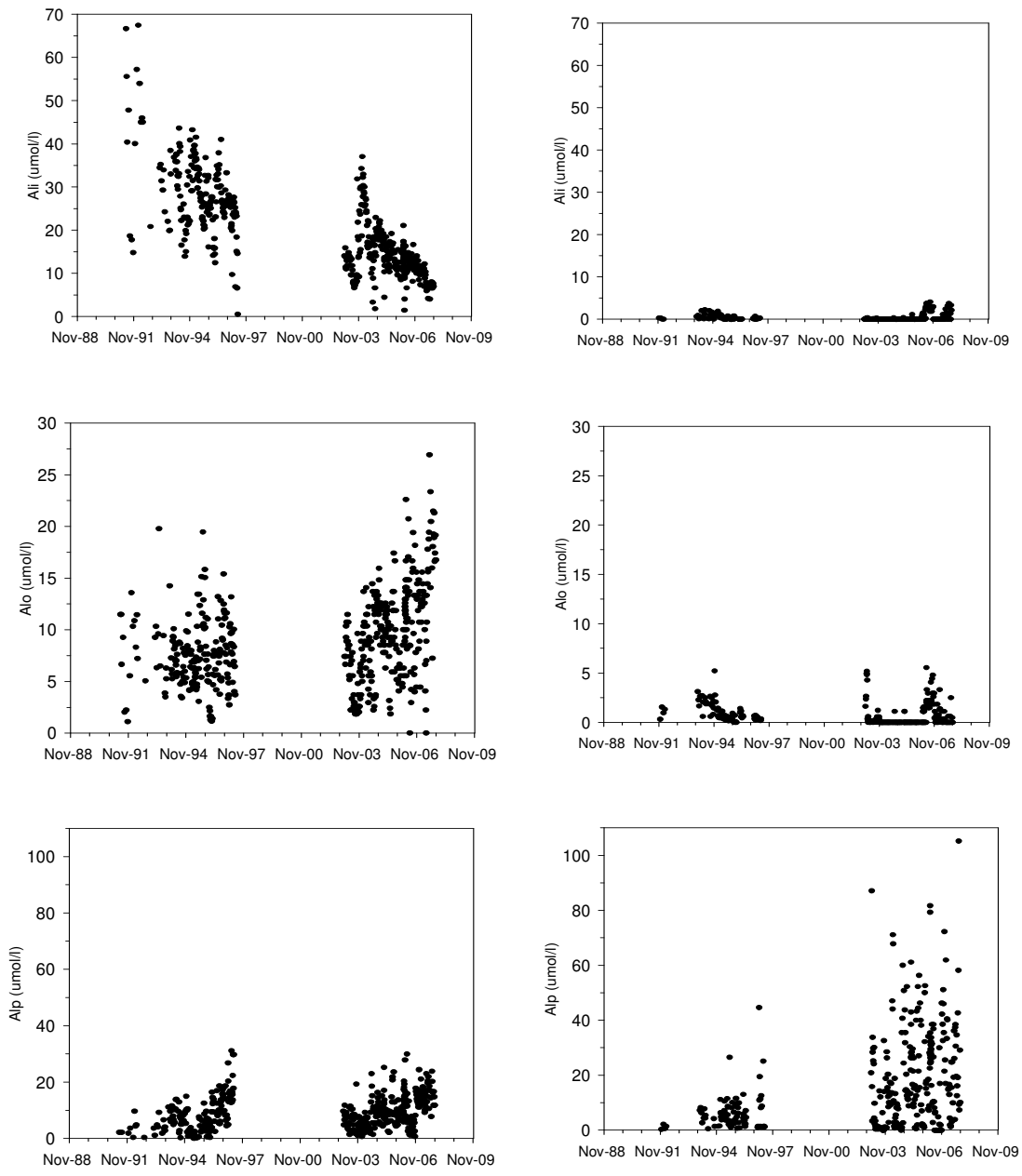


Fig. 3.