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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 μmol L^{-1}) and inorganic monomeric Al (Ali) concentrations (27 μmol L^{-1}) were observed in acidic (pH 4.0) stream water at Lysina in the 1990s and these concentrations decreased to 32 μmol L^{-1} (Alt) and 13 μmol 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 (Alo) and particulate (Alp) fractions increased in the 2000s at Lysina. In contrast to Lysina, marked increases of Alt 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 Alp fraction, which increased more than 3-fold in stream water and up to 8-fold in soil water in the A horizon. Increase of Alp coincided with dissolved organic carbon (DOC) increases. Acidification recovery may have increased the content of colloidal Al though the coagulation of monomeric Al.

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. Ca^{2+}, Mg^{2+}) 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 SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+} and Mg^+ concentrations in the 1990s due to decreases in emissions of SO_2 and NO_x and associated decreases in acidic deposition [11]. Total mean annual deposition

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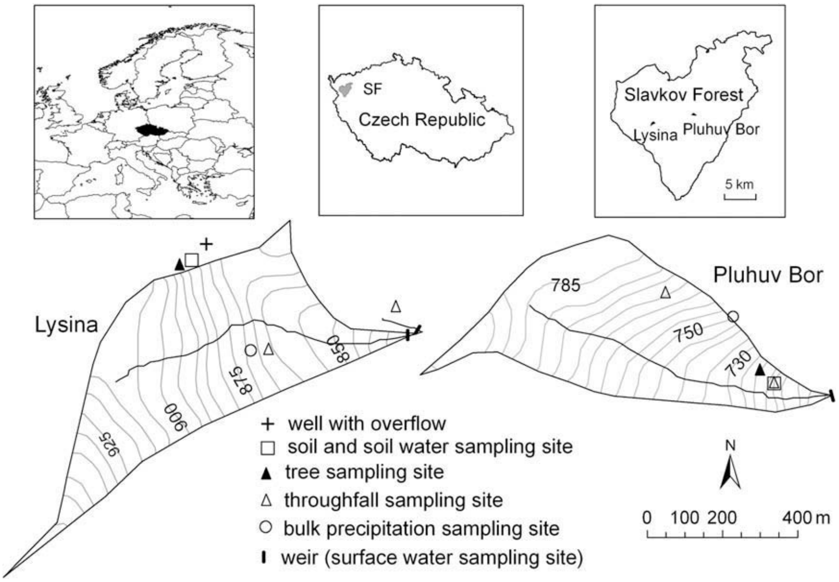

Fig. 1. Upper panels: map of Europe with the Czech Republic in black. Map of the Czech Republic, showing the Slavkov Forest (SF, 610 km^2). Map of the Slavkov Forest, showing the two study catchments 7 km apart. Lower parts: topographic maps of the Lysina and Pluhův Bor catchments, showing the catchment boundaries, the major stream channels and the major sampling locations. Contour interval of the maps is 5 m. 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.

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 μmol L^{-1} 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 four 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 cm^2 or 2000 cm^2), 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 h 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