Laboratory Assay of Aluminium Transport through Intact Soil Sample under Controlled Conditions

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Abstract: Aluminium (Al) mobilisation in the forest soils is a serious problem due to the soil acidification. The rate and magnitude of leaching of Al and other elements and compounds from soils can be examined by means of percolation experiments. Aluminium elutriation was studied under laboratory conditions using undisturbed samples of forest topsoil from the Paličník area in the Jizera Mountains (Czech Republic), which originated under two different vegetation covers: European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst). Ponding infiltration was performed using three subsequently applied solutions. KCl solution was used to simulate the soil solution. Solutions with sulphates and nitrates addition (of two different pH values) were used to simulate acid rainfall. Passing liquid phase was analysed with respect to Al content and aluminium speciation. Differences were found in Al content and transport between different soils under spruce and beech covers. The soil sample under the spruce forest (SF sample) had a higher initial Al content than the soil sample under the beech forest (BF sample). As a result, the aluminium leaching from the spruce soil sample and the final content of water-extractable Al in the soil (Al content after the leaching experiment) were higher compared to the beech soil sample. This suggests that Al mobility and potential toxicity in the beech forest are grater than those in the spruce monoculture when studied in the acidification endangered areas.

Keywords: aluminium transport; forest soils; forest type; percolation experiment; soil acidification

Considerable attention has been focused on the studies on aluminium mobilisation in forest soils in relation to soil acidification. The basic causes of forest soils acidification in the mountainous areas are the acid parent rocks, unfavourable vegetation, high precipitation, and acid deposition. Soil acidification leads to the leaching of basic cations from the sorption complex and decrease of pH. Additional effects of this process are the acceleration of silicates weathering and Al conversion from solid phase to mobile (potentially toxic) phase (Richter 1986; Borůvka *et al.* 2005; Hofmeister *et al.* 2008). Aluminosilicate weathering can be physical and chemical, where the silicate hydrolysis being the main weathering process. Some of Al ions are released into the soil solution and some are built into the newly developing secondary minerals (Borůvka *et al.* 2005). In addition to the mineral weathering processes, Al is present in soils in various forms. Moreover, Al speciation

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and forms are strongly modified by soil organic matter (Drábek *et al.* 2005). The following forms can be found: inorganic, ionic, and organic. The soil pH is the controlling factor for the inorganic Al distribution. Al^{3+} is considered to be a major toxic Al form (Sposito1996; Pierzynski *et al.* 2000). Toxic forms of Al belong among the factors negatively affecting the forest ecosystems in the mountainous areas. It is assumed that deciduous trees contribute less to the soil acidification than coniferous trees. On the localities already affected by acidification, deciduous trees are able to grow relatively easily compared to coniferous trees (Pierzynski *et al.* 2000; Hofmeister *et al.* 2008). Augusto and Ranger (2001) reported that deciduous trees can reduce the soil acidity through increasing pH by 0.7 grades.

The rate and magnitude of Al and other elements and compounds leaching from soils can be examined by means of percolation experiments. Leaching and batch experiments were used by e.g. Guo *et al.* (2006) and Bohan *et al.* (1997, 1998). Solutions acidified via mineral acids (H_2SO_4, HNO_3, HCl) up to approximately 3.5 pH are usually used as leaching media. Guo *et al.* (2006) concluded that strongly organically bound Al is the main source of aqueous Al, whereas exchangeable Al plays an important role in regulating Al solubility during soil acidification. Soil organic carbon and soil water pH are considered as the key factors in Al release determination. Different behaviour of Al in soils with various forest covers has not yet been examined into details.

In this study it was assumed that the soil liquid phase composition depends on both the soil (properties and composition) and precipitation (composition and amount). The main goal of this work was to evaluate the impact of vegetation cover on water flux and Al mobility in the surface horizons of forest soils. A percolation experiment was performed to analyse the solutions passing through the undisturbed soil samples taken mainly from the organic horizons originated under spruce and beech forests.

MATERIALS AND METHODS

Elements elutriation was studied under laboratory conditions by means of a percolation experiment using forest soil samples from the Paličník area (altitude 650 m a.s.l.) in the Jizera Mountains (Czech Republic) with different vegetations, European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst.) with sporadic grass (*Calamagrotis villosa* Chaix., *Calamagrotis arundinacea* (L.) Roth and *Avenella flexunosa* (L.) Trin.) occurrence. The age of forest was 170 and 90 years, the stocking was 0.8 and 0.9, and the average tree distance was 10 and 8 m in the beech and spruce forests, respectively. The tested soils were classified as Dystric Cambisol under the beech cover and Entic Podzol under the spruce cover. Undisturbed samples were taken from the surface horizons using a plastic cylinder (15 cm high, 10.5 cm in diameter) (Figure 1) in August 2008. The samples were taken in minimal distance of 3 m from the tree stem at a grass free location. The samples included the organic horizons (F – partly decomposed organic material, H – the totally decomposed organic material with a potential mineral addition) and the A – organo-mineral horizon. The thickness of each horizon was approximately the same in both samples (F – 3 cm, H – 6 cm, A – 3 cm).

Figure 1. Sampling of BF (left) and SF (right) samples (BF – beech forest; SF – spruce forest)

The sums of depths of the F, H, and A horizons in the soil profiles studied were 14 and 13 cm in Dystric Cambisol and Entic Podzol, respectively. The depths of the characteristic mineral horizons in Dystric Cambisol were: 20 and 30 cm of the Bw_1 and Bw_2 horizons, respectively, and the substrate. The depths of the characteristic mineral horizons in Entic Podzol were: 1.5, 8 and 10 cm of the E, Bws and Bw horizons, respectively, and the substrate.

The experiments were carried out on both soils under the same boundary conditions. Ponding infiltration with a ponding depth of 1 cm was performed. Three different solutions of the same volumes (1500 cm^3) were subsequently applied. A low-concentration 0.02M KCl solution with pH of 6.4 was used as the leaching medium for the first infiltration sequence. It was followed by leaching solution containing sulphates (10 mg/kg as Na_2SO_4) and nitrates (10 mg/kg as KNO_3) with pH of 5.2 and then of 4.0. KCl was added to simulate the soil solution ionic strength. Sulphate and nitrate solutions were applied to simulate acid precipitation.

The cumulative infiltration and cumulative outflow from the bottom part of the soil samples were measured. The water regime inside the samples was monitored during the experiment using three microtensiometers at the depths of 3, 6, and 9 cm. The passing liquid phase was analysed to evaluate Al content and speciation. The measured species were $Al(X)^+$ ($Al(OH)_2^+$, $Al(SO_4)^+$, AlF_2^+, $Alorg^{\leq 1+}$), $Al(Y)^{2+}$ ($Al(OH)^{2+}$, AlF^{2+}) and Al^{3+}. The total Al content in the solution was measured using the ICPOES method. The Al speciation was determined by means of HPLC/IC (Drábek *et al.* 2005).

The water and Al mass balances were evaluated. The gross amounts of the total and various Al forms were calculated using the measured volumes and concentrations of the discharged solutes. The final contents of various Al forms remaining in the soil samples were also determined. The soil samples were divided into four layers and were air dried. 1 g of the dry soil and 10 cm^3 of demineralised water were used to determine the remaining water-extractable Al content and speciation using the same analytical techniques as described above. The sums of the aluminium contents in the solute and soil were used to calculate the Al contents per mass unite of dry soil for both the beech and spruce soil samples.

RESULTS AND DISCUSSION

The infiltration and outflow solution fluxes are shown in Figure 2. Cumulative infiltrations and outflows are shown in Figure 3. It is obvious that the infiltration and outflow solution fluxes were significantly higher in the spruce forest samples than those in the beech forest samples. It was shown by Kodešová *et al.* (2007) that the spruce forest organic matter samples are less compact compared to the composition of the organic material in the organic horizon under the grass. As a result, the spruce samples had a lower retention ability and a higher saturated hydraulic conductivity than were those of the grass sample. Similarly in our study, the SF samples demonstrated a lower retention ability and a higher saturated hydraulic conductivity than were those of the BF samples. However, in both cases the wetting front proceeded through the

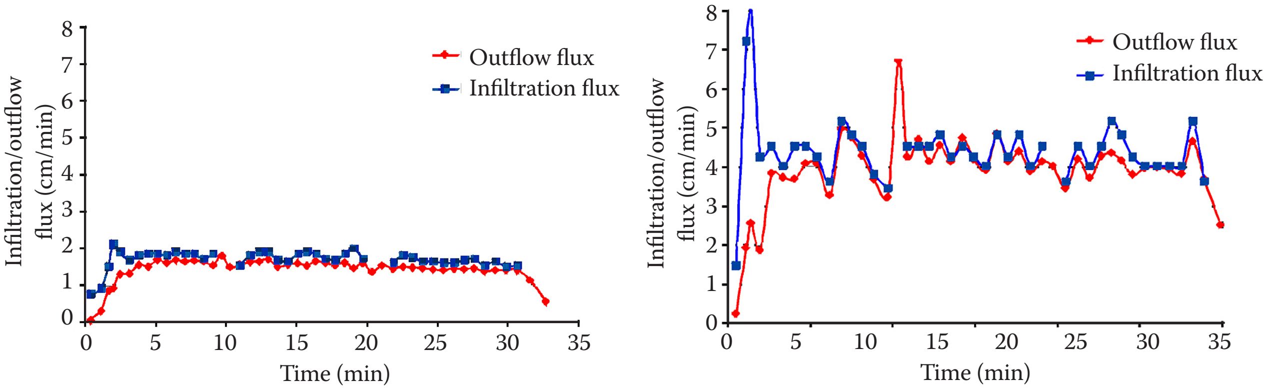

Figure 2. Solution infiltration and outflow rates measured for BF (left) and SF (right) samples; the scales of the time axes are different (BF – beech forest; SF – spruce forest)

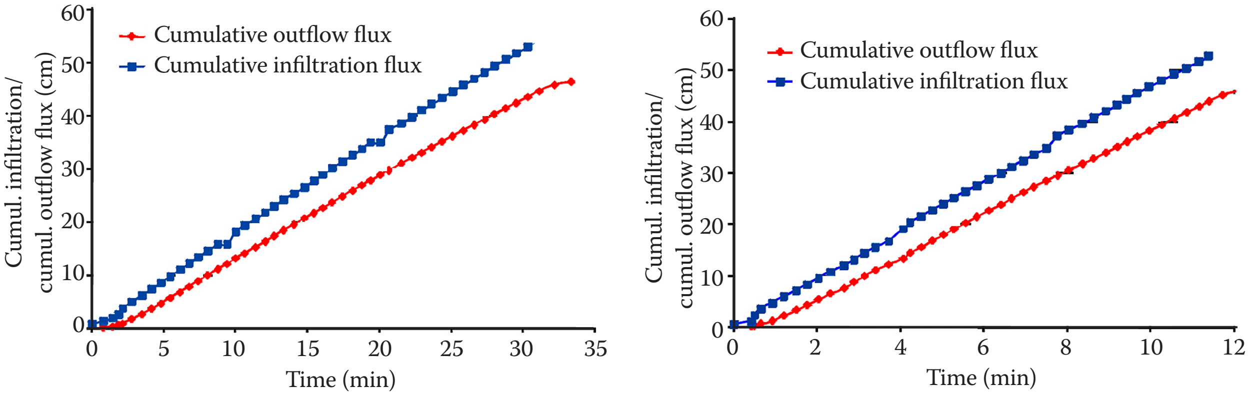

Figure 3. Cumulative infiltration and outflow measured for BF (left) and SF (right) samples; the scales of the time axes are different (BF – beech forest; SF – spruce forest)

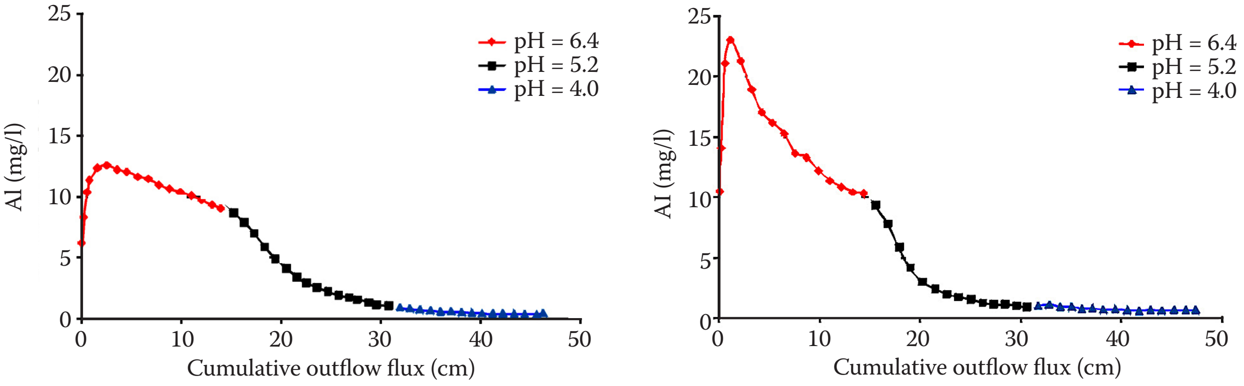

Figure 4. Concentrations of total Al measured for BF (left) and SF (right) samples (BF – beech forest; SF – spruce forest)

soil sample very quickly as was also indicated by tensiometers (not shown here).

It should be noticed that a temporal soil water repellency occurred at the beginning of the experiment performed on both samples. It was observed that the infiltration rates, which were initially low, first increased and then slightly decreased and subsequently oscillated around a constant value. The highest infiltration rates are expected at the infiltration beginning when the soil is not water-repellent. The water-repellence in soils was for instance described using the tension disk-permeameter by Lichner *et al.* (2007) and Orfánus *et al.* (2008). The water repellence may decrease

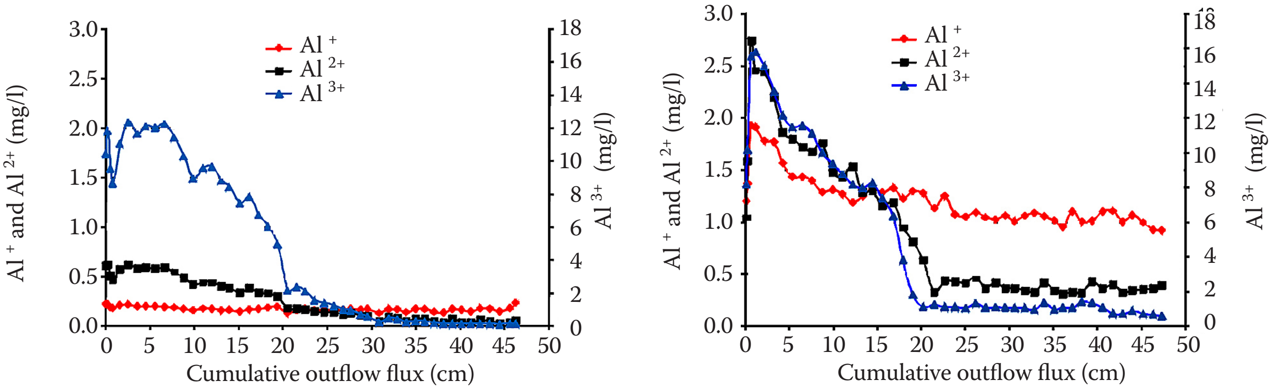

Figure 5. Concentrations of Al(X)$^+$, Al(Y)$^{2+}$ and Al^{3+} forms measured for BF (left) and SF (right) samples; separate scales are used for Al(X)$^+$ and Al(Y)$^{2+}$ (left axes) and for Al^{3+} (right axes) (BF – beech forest; SF – spruce forest)

Table 1. Aluminium balace in studied soil columns

Sample	Phase	Al_{tot}	Al^{+}	Al^{2+}	Al^{3+}
Beech	Al content in solute (mg)	17.85	0.63	0.92	16.30
	Al content in soil* (mg)	3.34	2.65	0.24	0.45
	sum of Al contents (mg)	21.19	3.28	1.16	16.75
	mass of the dry soil column (kg)			0.231	
	Al content per mass unite of dry soil (mg/kg)	91.58	14.16	5.01	72.41
Spruce	Al content in solute (mg)	22.77	4.70	3.39	14.69
	Al content in soil* (mg)	5.14	4.52	0.39	0.23
	sum of Al contents (mg)	27.91	9.22	3.78	14.92
	mass of the dry soil column (kg)			0.125	
	Al content per mass unite of dry soil (mg/kg)	223.84	73.91	30.32	119.68

*water-soluble form

the water infiltration and consequently decrease Al leaching when a low precipitation occurs. However, it may increase the runoff possibility.

The total Al concentrations in the discharged solutes are shown in Figure 4. The Al leaching behaviour was similar in both cases, but the values for SF sample were higher than those for BF sample. The concentration fluxes of various Al forms are shown in Figure 5. The speciation results of Al forms also showed similar trends in both samples. However, the concentrations of each Al form were different. The concentrations of $Al(X)^{+}$ forms were stable during the leaching, just a small decrease of the concentration with time was observed with SF sample. The behaviour of $Al(Y)^{2+}$ and Al^{3+} forms was very similar. A concentration decrease in time was observed with these two Al forms. The highest concentrations were observed with Al^{3+} form in both cases. This was caused by KCl addition, which might, even in a very low concentration, displace Al^{3+} from the sorption sites (Drábek *et al.* 2005). Significantly higher concentration values of $Al(X)^{+}$ and $Al(Y)^{2+}$ forms were obtained with the SF sample than with the BF sample. Interestingly, very similar Al^{3+} courses (though they were affected by different infiltration rates) and values were observed.

Table 2. Average water-soluble Al concentrations (mg/kg) that were obtained from 3 soil pits in Paličník area

Horizon	Beech	Spruce
F	87.17	87.59
H	51.78	102.15
A	17.79	65.98

Table 1 shows the Al balance in the soil columns studied. It is evident that the BF sample initially contained moderately larger aluminium amount than the SF sample. A considerably greater difference was obtained when Al content was expressed per mass unite of a dry soil. The resulting Al concentrations in Table 1 were compared with the average values of the water-soluble Al concentrations, which were obtained from 3 soil pits in the Paličník area (Table 2). The Al concentrations measured in the soil columns were considerably greater than the average values of the water-soluble Al concentrations. The main reasons are the displacement of Al^{3+} from the sorption sites using KCl solution, and the application of the considerably larger volumes of the extraction solutes in the soil columns in comparison to the water volumes used for the water-soluble Al concentration analysis. However, the Al concentration trends (Al content in the SF sample was larger than in the BF sample) were similar. It should be also mentioned that a large variability of the organic horizons depths and Al contents in different horizons was measured in both forests. Therefore, a variable Al leaching is expected if studied on new soil samples taken from each location. However, general difference in Al leaching between both locations would be the same. Similar trends were obtained also by other authors who examined the Jizera Mountains (Mládková *et al.* 2005; Pavlů *et al.* 2007). For example Pavlů *et al.* (2007) showed that beech forest soils had a significantly higher pH in the surface organic horizons and contained less Al than the spruce forest soils.

CONCLUSIONS

The undisturbed samples of surface soil layers from spruce forest showed a lower soil water retention ability and a higher saturated hydraulic conductivity than those from beech forest. As a result, a faster solution flux was observed in the SF sample as compared to the BF sample. A higher initial Al content was found in the SF sample in comparison to that in the BF sample. There was also an apparent difference in the amounts of Al leaching between the soils with beech or spruce covers. Higher concentrations of all Al forms were measured in the sample with the spruce cover. These results suggest that a higher Al leaching intensity can be expected in the soils with the spruce cover.

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