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Distribution of aluminium fractions in acid forest soils: influence of vegetation changes

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This study examines aluminium as a potentially phytotoxic element in acidic forest soils. Concentrations of Al forms in soils are generally controlled by soil chemical conditions, such as pH, organic matter, base cation contents, etc. Moreover, soil conditions are influenced by the vegetation cover. This study analyzed the distribution of Al forms in soils after changes in vegetation. HPLC/IC was used for the separation of three Al fractions in two soil extracts according to their charge. An aqueous extract (Al_{H2O}) simulated the natural soil conditions and bioavailable Al fractions. Potentially available Al form was represented by a 0.5 M KCl extract (Al_{KCl}). We demonstrated that the vegetation type influences the concentrations of different Al fractions, mainly in the surface organic horizons. Differences were more common in the KCl extract. The trivalent fraction was less influenced by vegetation changes than the mono- and divalent fractions. Afforestation increased the concentrations of Al_{KCl} and $Al_{H2O.}$ In contrast, grass expansion after deforestation led to significantly decreased concentrations of Al_{KCl} and Al_{H2O}. Concentrations of Al_{H2O} in organic horizons were higher in spruce forest than in beech forest. A long-term effect of liming on soil pH and concentrations of potentially toxic Al fractions was not apparent. The results provide information on the variations of Al fractions distributions following vegetation type changes and indicate the existence of some natural mechanisms controlling Al toxicity. Furthermore, the results can be used in the management of forested areas endangered by soil acidification.

Keywords: Aluminium Fractionation, Forest Soil, Afforestation, Deforestation, HPLC/IC

Introduction

Aluminium is one of the more abundant elements in soils, making up approximately 7% of its inorganic matter (Sposito 1996). Primary and secondary aluminosilicates are the main sources of Al in soils. Aluminium is mobilized by chemical or biochemical weathering and creates different dissolved ion fractions, which depend on the pH of the soil solution (Pierzynski et al. 2000). Mineral weathering of aluminosilicates is very slow, but the presence of organic compounds leads to higher weathering rates and to the formation of soluble Al complexes with organic molecules (Pohlman & McColl 1988, Van Hees et al. 2001, Fritsch et al. 2009). Therefore, Al occurs in soils and soil waters in many forms or fractions. The fractions of dissolved Al determine its potential bioavailability and toxicity. Toxicity to plants decreases qualitatively in the order: Al_{13} (not in a form of phosphates or silicates), Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$. Aluminium bound with organic complexes has been found to be nontoxic (Sposito 1996). Therefore, the complexation of Al by natural organic ligands is important for regulating concentrations of the highly toxic Al^{3+} ion in acid soils and natural waters (Wesselink et al. 1996, Collignon et al. 2012).

A significant change in the biogeochemical cycling of Al has resulted from the man-made acidification of the environment (Exley 2003). Past extensive acid deposition (Kopáček & Vesely 2005) of strong acids (sulfuric or nitric), has accelerated the release of Al from aluminosilicates and secondary Al soil phases. Higher sulfate content affects soil acidity and transforms hydroxylated Al fractions to Al^{3+} (Norton & Vesely 2003, Shaw & Hendry 2009, Jones et al. 2011). A strong negative correlation between the concentration of exchangeable Al in soils and the level of SO_4^{2-} deposition in the O horizon were demonstrated by Lawrence et al. (2015). Additionally, strong acid anions increase the release of Al-organic complexes in spodic soil horizons (Zeysset et al. 1999). Soil waters of anthropogenically acidified areas thus have a higher content of ionic and toxic Al forms. This situation is typical of the northern parts of the Czech Republic (Sucharova et al. 2011). Mountainous forests in the top parts of the mountains were damaged directly by acid rain and SO_2 fumigation in the past. Large-scale forest dieback, followed by grass expansion, has occurred. Damage to soils by anthropogenic acidification is related to a low content of base cations, a very acidic character of soils, and abundant mobile Al forms (Borg & Sundbom 2014). These conditions have made forest recovery difficult, including at present. Amelioration by forest liming has been attempted in these areas. Our previous studies (Mládková et al. 2004, Boruvka et al. 2005) reported that the distribution of

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Al forms in soils is controlled by pH. The pH value can be conditioned by the natural presence of Ca or Mg carbonate minerals, or it can be regulated by adding limestone. Organic matter plays a role in Al distribution by providing sorption and binding sites (Norton & Vesely 2003).

At altitudes below approximately 800 m a.s.l., natural forest cover in the Czech Republic consists of beech (*Fagus sylvatica* L.) or mixed beech-spruce (*Picea abies* [L.] Karst.) forests. In the past, these natural forests were widely transformed into spruce monocultures, which also can accelerate acidification processes (Augusto et al. 2002, De Schrijver et al. 2007).

Many combinations of effects exist in the natural soil environment, and the final Al distribution is controlled by many factors. Drábek et al. (2003) and Brandtberg & Simonsson (2003) showed marked differences in Al fractions distribution among soils of cropland, grassland, and forest, and also between different forest types. The aim of this research is to study the relationships between the dissolved or potentially soluble Al fraction distribution and land-use changes (afforestation, deforestation, amelioration). The main hypothesis is that land-use change impacts the Al fraction distribution in soil. The second hypothesis is that the effect of acid soil amelioration results in a long-term decrease of dissolved Al concentrations in soil.

Methods

This paper reports findings from three separate projects on aluminium fractionation in soils. These projects were located in two mountainous areas in the north of the Czech Republic (Fig. 1), where soil acidification has been observed and studied (Drábek et al. 2007, Dlouhá et al. 2009, Bradová et al. 2015). The altitude of the Jizera Mountains ranges between 400 and 1100 m a.s.l., and the altitude of Giant Mountains ranges between 400 and 1600 m. In both areas, the average annual precipitation is between 1200 and 1300 mm, and the average annual temperature is 4-7 °C. Precipitation and temperature are naturally altitude-dependent. The Jizera Mts. are underlaid by homogenous granite, while the Giant Mts. geology is more variable. At higher elevation, the bedrock is of the same granite massif as in the Jizera Mts. At lower elevation, the bedrock consists of gneiss, schist, and phyllites.

The afforestation study (1) in the Giant Mts. (Fig. 1) focused on the comparison among meadow, afforested meadow (50-year-old Norway spruce, and an old-growth Norway spruce forest. All sampling areas are on gneiss bedrock, and single variants are in close vicinity. In each vegetation cover variant, soil pits were dug (4, 4, and 3, respectively), and soil samples were collected (described in detail by Dlouhá et al. 2009).

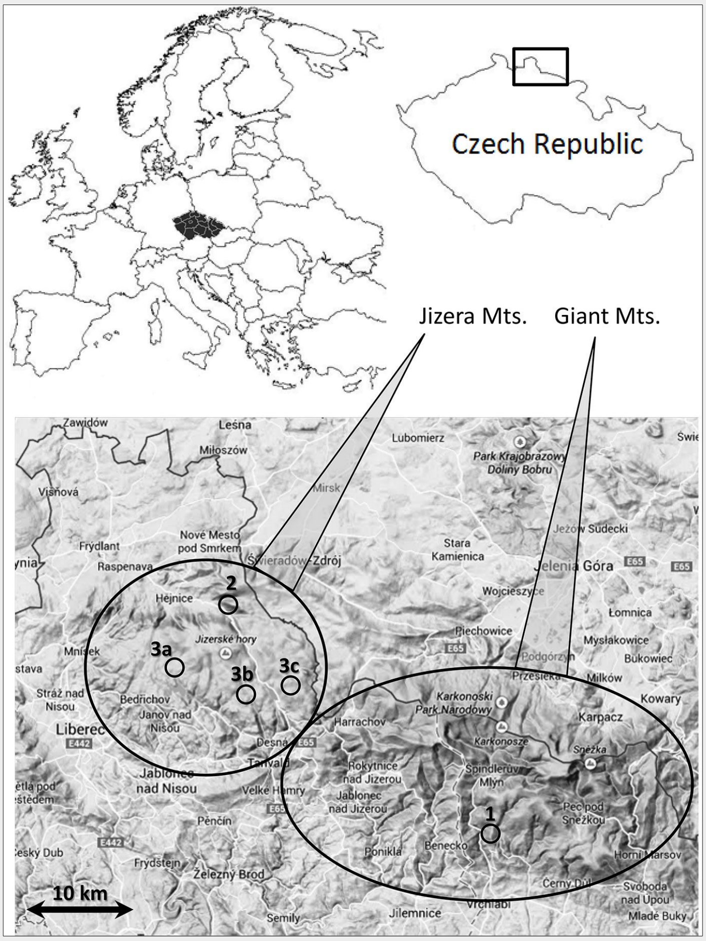

Fig. 1 - Sampling sites localization. (1): afforestation study; (2): forest type study; (3a, b, c): deforestation and liming study.

The study on forest type change (2) obtained results from two long-term monitoring plots in the Jizera Mts. (630-680 m a.s.l. – Fig. 1), described in detail by Bradová et al. 2015. The first plot is covered by an old-growth beech forest, typical for that location, and the second one is covered by a 100-year-old Norway spruce forest, which had artificially replaced a beech forest. Sampling occurred monthly from April to October during the years 2008-2011 (three soil pits per forest type in each month).

The deforestation and amelioration study (3) was conducted in the higher parts of the Jizera Mts. (800-900 m a.s.l. – Fig. 1), where the forest died in the 1980s due to acid rain, and the resulting change in the lighting conditions led to the expansion of the grass. For several decades, a large area was covered by grasses (*Calamagrostis villosa* [Chaix] J. F. Gmel., *Deschampsia flexuosa* [L.] Drejer) and was difficult to reforest. Liming was used to counter the effects of soil acidification from acid rain. Our study compared soil conditions of the soils still covered by grass (control), those covered by grass with amelioration by dolomitic limestone (once, 2 t ha^{-1}) 25 years before sample collection (limed), and those covered by more than 40-year-old Norway spruce native forest (forest). Results represent the analysis of 9 soil pits in each variant (3 isolated plots – 3a, b, and c in Fig. 1), where all 3 variants are in close proximity and sampled by 3 soil pits each.

Soil sampling was very similar in all studies. Soil pits, approximately 50 × 50 cm, were excavated for soil description and sample collection. Soils were classified by IUSS Working Group (2015), mostly as Cambisols or Podzols. Samples from all sufficiently thick horizons were collected. In most cases, surface organic horizons (F: fermentation horizons; H: humified horizons), organomineral humic horizons (A), eluvial albic horizons (Ep), spodic horizons (Bspod), cambic horizons (Bv), and substrate horizons (C) were present. Samples were air dried and sieved to <2 mm, and basic soil characteristics were determined. Active and exchangeable pH (pH_{H_2O} and pH_{KCl}, respectively) were determined potentiometrically by ion-selective electrode. Ca (Ca_{AR}) and Mg (Mg_{AR}) were determined after soil digestion with aqua regia by atomic absorption spectroscopy (AAS – Varian SpectrAA-200®, VARIAN, Australia). Effective cation exchange capacity (eCEC) of mineral horizons was determined by the Mehlich method with unbuffered 0.1 M $BaCl_2$ extraction solution (Podlešáková et al. 1992). Cation exchange capacity (CEC) was determined by the Bower method, with Na^+ as an index ion (Heese 1998); Na in the extract solution was determined by AAS.

A method of Al fractionation in deionized water and 0.5 M KCl extract by HPLC/IC was used (Drábek et al. 2005). This method enables Al fractions to be separated into three different groups according to their charge: $Al(X)^{1+}$ [*i.e.*, $Al(OH)_2^+$, $Al(SO_4)^+$, AlF_2^+, $Al(oxalate)^+$, $Al(H\text{-}citrate)^+$, etc.]; $Al(Y)^{2+}$ [$Al(OH)^{2+}$, $(AlF)^{2+}$, etc.]; and Al^{3+} (Al^{3+} and transformed hydroxyl Al polymers). However, $Al(X)^{1+}$ fractions co-elute with $Al(Z)^{so}$ fractions, where Z represents mainly organic ligands. The sum of the fractions in aqueous extracts is designated Al_{H2O}, and that of the KCl extracts is Al_{KCl}. A modified methodology of Al fractionation was used in the study on forest type change (2). This study also focused on the distribution of dissolved organic carbon (DOC – Tejnecký et al. 2010), and the sample processing was adjusted to apply to DOC measurements (Jones & Willett 2006). Fresh, unsieved soil samples were used, and only the aqueous extract was analyzed. Therefore, the concentrations of all studied Al fractions are lower than those from the other studies.

Statistical analysis, one-way analysis of variance, *t*-test, and paired *t*-test were performed using STATISTICA® v. 9.1 software (StatSoft Inc., Tulsa, OK, USA).

Results

All presented graphs (Figs. 2 to 5) show that KCl extracts had approximately 10 times more Al than deionized water. The relative distribution of the studied fractions also differs between extracts. The dominant fraction in KCl is Al^{3+} and in the water extract it is $Al(X)^{1+}$.

Generally, all presented studies were located in mountainous areas with acidic bedrock, representing areas strongly affected by soil acidification. The prevailing soil types in these areas are dystric Cambisols in the lower parts, and Podzols in the upper parts of the mountains. The differences in Al fraction distribution in the soil profiles of both these soil types are presented in Fig. 2 and Tab. S1 (Supplementary material).

Afforestation effect

Basic soil characteristics of meadow, young (50 years old) forest on former meadow, and native forest soils are shown in Tab. 1. There are clear differences among these three plots according to the described soil type. Cambisol was found in the meadow and young forest plots, whereas, on the original forest plot, Podzol with very well-defined diagnostic horizons was recognized. The strong-acid character of forest soil compared to other plots is also apparent. Cation exchange capacity is generally associated with organic matter in soils, and it decreases from organic to mineral soil horizons. Spodic horizons are enriched by organic compounds, and CEC follows this trend. The statistical comparison of vegetation cover variants in the sampled soil horizons is shown in Tab. 2.

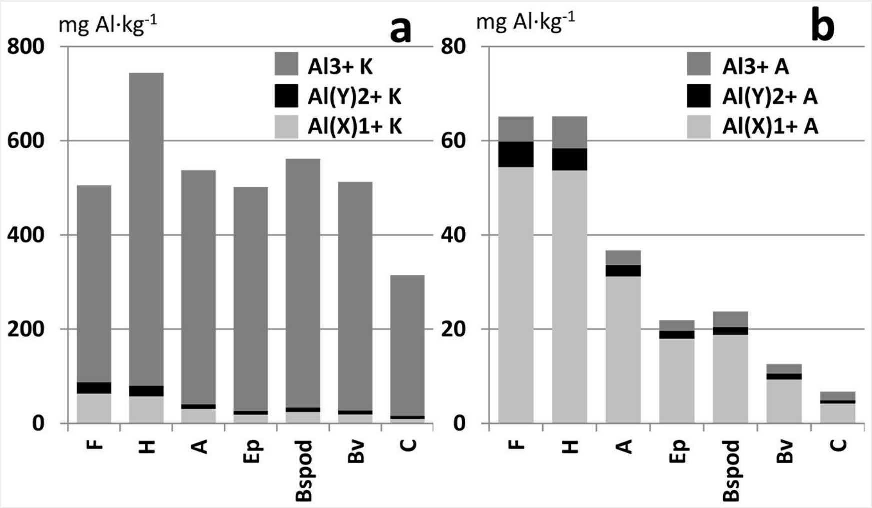

Fig. 2 - Distribution of Al fractions in soil horizons (a) in KCl extract, and (b) in aqueous extract). Average values of all samples from Jizera Mts. and Giant Mts.

The results of Al fractionation are shown in Fig. 3 and Tab. 2. Concentrations of $Al(X)^{1+}$ and Al^{3+} in the A horizon in both extracts are significantly higher for the 50-year-old forest soil than for the meadow. Concentrations of all Al fractions in aqueous extract are higher in the mineral Bv horizon of forest soil than in the meadow. The highest amount of phytotoxic Al^{3+} in both extracts occurred in the spodic horizons. Concentrations of Al fractions in the KCl extract increased from young to old forest in the F horizon. The opposite trend was observed in the aqueous extract.

Forest type change

Tab. 3 shows the values of soil pH in the original beech forest and in the planted

Tab. 1 - Average values of basic soil characteristics for separate soil horizons. (M): scythed meadow in forest vicinity; (F 50): 50 years old forest planted on former meadow; (F): old growth forest.

Variant	Soil type	Horizon	pH_{H2O}	pH_{KCl}	CEC (mmol 100 g^{-1})
M	cambisol	A	4.79	3.38	26.13
		Bv	4.90	3.56	18.06
F50	cambisol	F	3.80	2.79	50.38
		A	3.83	2.91	24.13
		Bv	4.16	3.23	16.81
F	podzol	F	3.17	2.05	140.83
		H	3.11	2.01	92.00
		Ep	3.53	2.35	8.58
		Bspod	3.68	3.04	47.07

Tab. 2 - Results of *t*-test (*t*-values of the differences) comparing the distribution of basic soil characteristics and Al fractions (K: in KCl extract; A: in aqueous extract) in selected soil horizons of three vegetation cover types. (M): scythed meadow in forest vicinity; (F50): 50-year-old forest planted on former meadow; (F): old growth forest.

Variable	F horizon (F50 × F)		A horizon (M × F50)		Bv horizon (M × F50)	
	t	Prob	*t*	Prob	*t*	Prob
pH_{H2O}	8.13	<0.001	6.87	0.001	3.55	0.012
pH_{KCl}	8.90	<0.001	5.76	<0.001	2.43	0.051
CEC	-4.23	0.008	1.77	0.128	0.77	0.473
$Al(X)^{1+}K$	-4.72	0.005	-9.40	0.003	-2.76	0.070
$Al(Y)^{2+}K$	-4.77	0.005	1.46	0.240	-0.95	0.413
$Al^{3+}K$	-2.02	0.090	-4.09	0.026	-1.42	0.251
Al_{KCl}	-2.30	0.070	-4.19	0.025	-1.50	0.231
$Al(X)^{1+}A$	2.69	0.043	-6.70	0.007	-3.08	0.054
$Al(Y)^{2+}A$	0.29	0.781	-2.50	0.087	-4.42	0.022
$Al^{3+}A$	0.65	0.544	-5.37	0.013	-2.79	0.068
Al_{H2O}	2.36	0.065	-6.73	0.007	-3.57	0.038

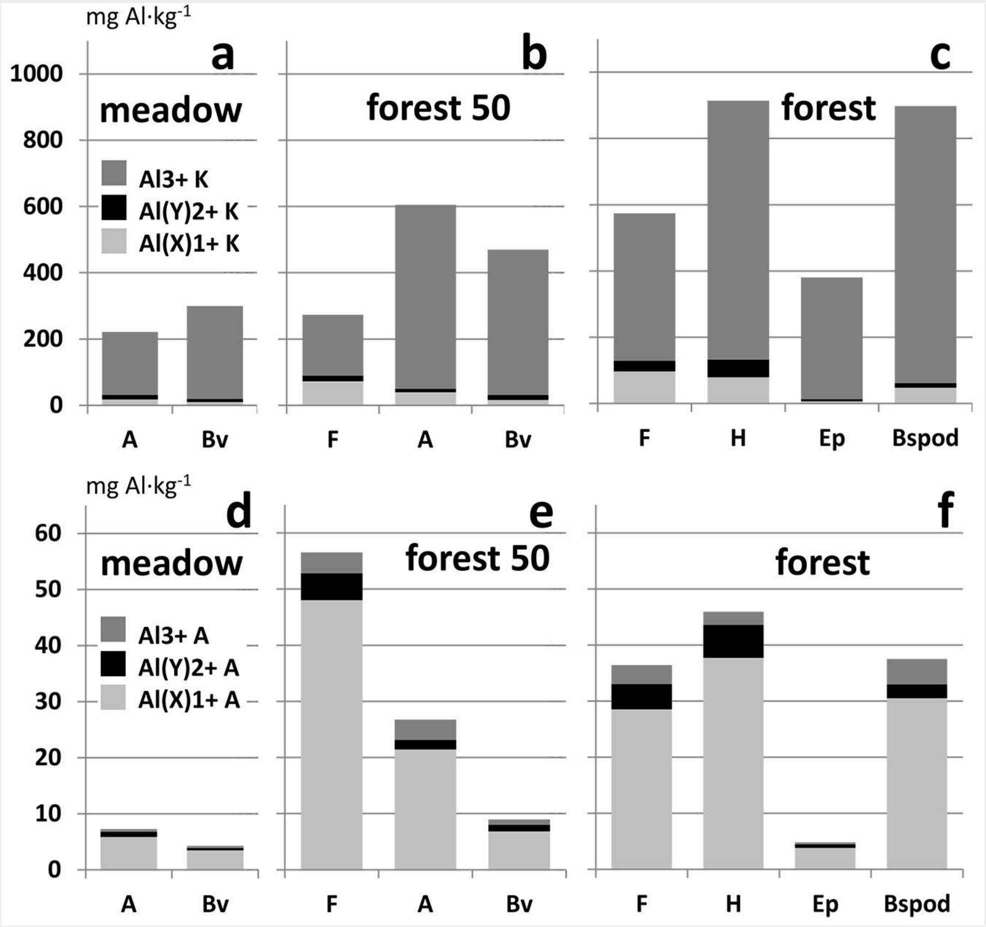

Fig. 3 - Distribution of Al fractions (a, b, c: in KCl extract; d, e, f: in aqueous extract) in soil horizons. Average values of samples from meadow. (a, d): scythed meadow in forest vicinity; (b, e): 50-year-old forest planted on former meadow; (c, f): old growth forest.

Tab. 3 - Average values of pH_{H2O} and pH_{KCl} in beech and spruce forest, by soil horizons.

Soil horizon	Beech forest		Spruce forest	
	pH_{H2O}	pH_{KCl}	pH_{H2O}	pH_{KCl}
F	4.18	3.33	3.84	2.87
H	4.14	3.5	3.78	2.96
A	4.17	3.58	3.89	3.19
B	4.27	3.78	4.11	3.77

Tab. 4 - Differences in the distribution of pH and Al fractions between beech and spruce forests for each soil horizon (results of pair *t*-test; *t*-values of the differences).

Variable	F horizon		H horizon		A horizon		B horizon	
	t	Prob	*t*	Prob	*t*	Prob	*t*	Prob
pH_{H2O}	10.97	<0.001	14.24	<0.001	7.67	<0.001	5.30	<0.001
pH_{KCl}	17.47	<0.001	23.80	<0.001	9.03	<0.001	1.25	0.218
$Al(X)^{1+}A$	-0.23	0.818	-6.13	<0.001	-3.11	0.006	-3.20	0.003
$Al(Y)^{2+}A$	-1.12	0.273	-2.69	0.012	-2.12	0.047	-3.32	0.003
$Al^{3+}A$	3.12	0.004	1.29	0.207	-0.83	0.417	-2.50	0.018
Al_{H2O}	1.28	0.211	-3.76	<0.001	-2.75	0.013	-4.20	<0.001

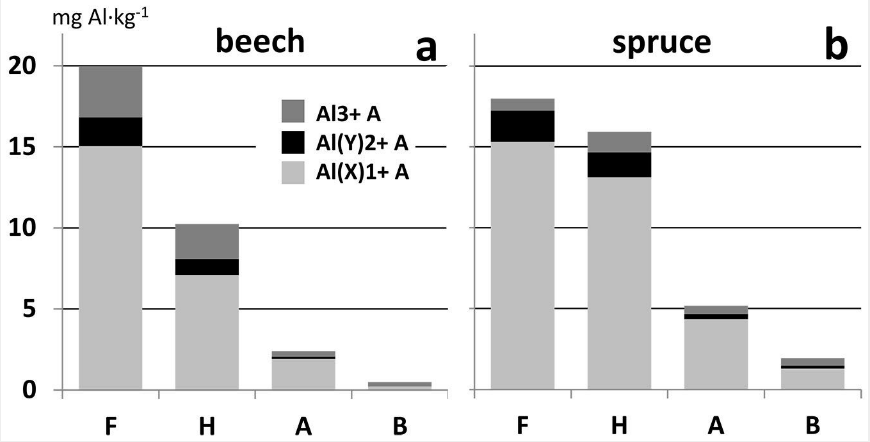

Fig. 4 - Distribution of Al fractions in aqueous extract in soil horizons. Average values of samples from beech (a) and spruce (b) forest.

spruce forest. A higher pH of surface horizons in the beech forest is evident, in comparison with spruce forest. Statistical differences are presented in Tab. 4.

Results of Al fractionation (Fig. 4, Tab. 4) show that the differences between beech and spruce forest soil exist in both organic and mineral horizons. Except for the F horizon, the sum of the Al fractions, and also $Al(X)^{1+}$ and $Al(Y)^{2+}$ fractions concentrations, are significantly higher in the spruce forest. The concentration of the Al^{3+} fraction in the organic F horizon is higher in the beech forest than in the spruce forest.

Deforestation and amelioration

The basic soil characteristics of long-term deforested area (grass-limed, grass-control) and surviving native forest plots are presented in Tab. 5. Analysis of variance (Tab. S2 in Supplementary material) shows that organic horizons are more affected than mineral horizons by land-use change. Forested soils are more acidic than grass-covered soils. The long-term liming effect resulted in higher Ca_{AR} concentrations in the organic horizons of the limed variant. Soil pH was not significantly changed 25 years after liming. Higher differences in soil pH were found between forest and grass-covered (control and limed) plots. Cation exchange capacity was similar for all land uses.

The results of Al fractionation and comparison of vegetation cover variants are shown in Fig. 5 and Tab. S2 (Supplementary material). Analysis of variance for the Al fractions showed that most of the differences occur in the surface organic horizons. These horizons in the surviving forest have the highest concentrations of most of the Al fractions. Almost no difference between the limed and control variant was found. A change of land use influenced the $Al(X)^{1+}$ and $Al(Y)^{2+}$ fraction distribution more than that of Al^{3+}.

Tab. 5 - Average values of basic soil characteristics in variants (grass-limed, grass-control, native forest) separately for soil horizons.

Variant	Horizon	pH_{H2O}	pH_{KCl}	Mg_{AR} ($Mg\ kg^{-1}$)	Ca_{AR} ($mg.kg^{-1}$)	ECEC ($mmol\ 100g^{-1}$)
Grass limed	F	4.33	3.57	1396	2282	26.75
	H	4.11	3.26	813	1292	22.90
	Ep	4.05	3.32	683	246	7.01
	Bspod	4.21	3.78	2794	376	8.01
	C	4.51	4.23	3634	429	3.34
Grass control	F	4.23	3.45	1034	986	24.14
	H	4.13	3.40	861	545	22.97
	Ep	4.12	3.49	1353	332	7.76
	Bspod	4.18	3.65	2692	372	10.65
	C	4.44	4.19	4042	470	3.44
Native forest	F	3.88	2.96	929	1408	24.75
	H	3.82	2.96	523	422	25.24
	Ep	3.70	3.28	1105	206	7.20
	Bspod	4.08	3.74	2895	299	8.74
	C	4.29	4.18	4295	447	3.84

Discussion

Firstly, the differences between Al distributions in the dominant soil types in this mountain area (Fig. 2, Tab. S1) are addressed. Podzol formation is directly controlled by Al transport in the soil profile, from the Ep horizon to spodic type horizons with or without organic matter (Lundström et al. 2000, Sauer et al. 2007). Relative Al depletion of the Ep horizon and relative Al enrichment of the Bspod horizon can be seen in Fig. 2. The high contents of all Al fractions in the surface organic horizons are probably due to the high sorption capacity of organic compounds and long-term accumulation of organic matter, especially in the H horizon (Niemtur et al. 2002). The cambic Bv horizon is characterized by braunification processes. Fe and Al are released from silicates *in situ* by this special type of weathering. The Bv horizon is relatively enriched with Al in contrast to substrate (C), but aluminium content is still lower than in the Bspod horizon, which is enriched with Al transported from the upper horizons (Fig. 2, Tab. S1). Different Al distributions in the Podzol and Cambisol soil profiles were also shown by Berggren (1992) and Maitat et al. (2000). These differences illustrate the importance of the study sites comparison according to soil horizon.

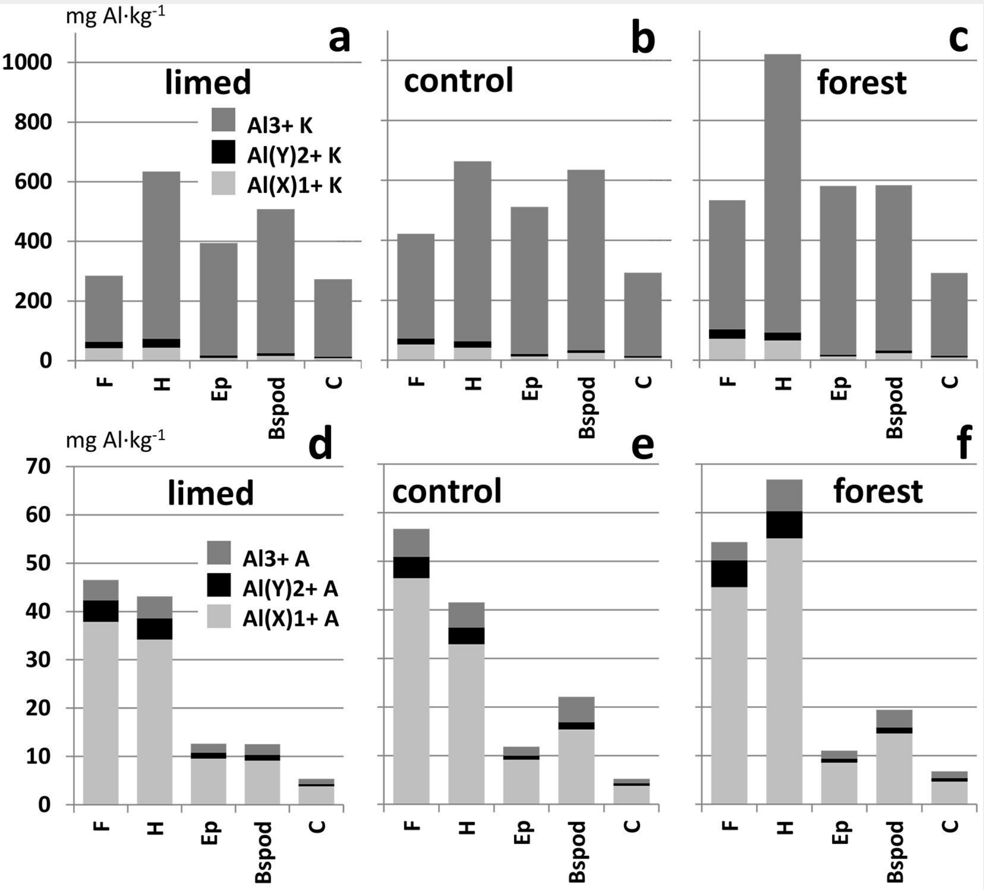

Fig. 5 - Distribution of Al fractions (a, b, c: in KCl extract; d, e, f: in aqueous extract) in soil horizons. Average values of samples from grass-limed (a, d), grass-control (b, e), and native forest (c, f).

Afforestation effect

Generally, long-term planting of spruce or other coniferous species leads to enhanced soil acidification and conditions conducive to the podzolization process (Brady & Weil 2008). Findings in line with this theory are documented in Tab. 1, which shows that the Podzol soil type was found only in old-growth forest. The increase of soil acidity leads to Al release in its mobile forms (Sposito 1996, Pierzynski et al. 2000). The results in Fig. 3 and Tab. 2 confirm that the afforestation of meadow leads to the release of monovalent and trivalent Al fractions, especially in the A horizon. A similar situation was documented by Adams et al. (2001) in New Zealand.

The concentration of monovalent and divalent Al fractions in the KCl extract increased significantly from young to old forest in the F horizon (Fig. 3, Tab. 2). This agrees with the soil pH decrease and cation exchange capacity increase (Drábek et al. 2005 – Tab. 1, Tab. 2). The opposite trend was seen in the aqueous extract. The concentration of the monovalent Al fraction decreased from young to old forest in the F horizon. This result may be explained by the difference between the aggrading humus layers of young forest and the mature humus layers of old forests. It has been suggested that leaf litter quality varies with tree age and has a huge impact on humus development (Inagaki et al. 2004, Descheemaeker et al. 2009). Ponge et al. (1998) suggested that a higher uptake of nutrients by trees during their phase of intense growth may lead to lower soil nutrient availability and decomposer activities. The decrease in biological activity may lead to lower litter decay rates, promoting the accumulation of organic materials (Trap et al. 2011). The aggrading humus layers of young forest have lower cation exchange capacity and do not bind Al as much as the mature humus layers in old forests.

Other authors (Drábek et al. 2003) found a huge difference in the relative distribution of Al fractions in KCl extracts between spruce and meadow. This was not confirmed in the present study.

Forest type change

Better soil conditions (pH, nutrient concentrations) of beech than spruce forest have been reported by several authors (Misson et al. 2001, Niemtur et al. 2002). The organic horizons of Norway spruce forest were found to be more acidic than those of beech forest (Tab. 3, Tab. 4). It could be supposed that higher concentrations of Al fractions will be found in spruce forest. The indirect relationship between the concentration of mobile Al forms and soil reaction is well known (Sposito 1996, Pierzynski et al. 2000). However, the results in Fig. 4 and Tab. 4 confirm this only partially. In the case of the F horizon and Al^{3+} fraction, the opposite trend was found. Tejnecký et al. (2010) showed higher dissolved organic carbon (DOC) content in spruce forest surface horizons than in beech forest. DOC is a significant ligand for Al complexation (Van Hees et al. 2000). These two facts have opposing effects on Al^{3+} concentration (Li & Johnson 2016). It is probable that the DOC effect plays a more important role than soil pH. Therefore, Al complexation with DOC would decrease Al^{3+} concentration in spruce more than it would in beech forest soils.

Deforestation and amelioration

Analysis of variance (Fig. 5, Tab. S2) for Al fractions showed that most of the differences occur in the surface organic horizons. Twenty-five years after limestone application, the difference between grass-limed and grass-control was not found. This result is not in contradiction with the decrease of Al concentration related to the short-time liming effect (Tyler & Olsson 2001, Boruvka et al. 2007 Huang et al. 2014). In contrast, both of these grass variants often have lower concentrations of Al fractions in comparison with native forest. Therefore, grass expansion could be considered as a natural regeneration mechanism of acidified soils. However, the toxic effect of aluminium, represented by Al^{3+} concentration in aqueous extract, is similar in all variants. Only the potential (KCl extract) risk of Al toxicity was higher in the native forest variant.

Conclusion

Vegetation cover change can influence the concentration of Al fractions, mainly in surface organic horizons. Differences were found to be more common in the KCl extracts and for $Al(X)^{1+}$ and $Al(X)^{2+}$ fractions than in aqueous extracts and the Al^{3+} fraction, respectively. Afforestation increased the concentration of Al_{KCl} and Al_{H2O}. An increase of Al fraction concentrations in the KCl extract from younger to older forests was observed in the F horizon. The opposite trend occurred in the aqueous extract. This could be explained by the fact that while forming the humus layer, Al is not bound as strongly as in the mature humus layer of old-growth spruce forests. Where natural beech forest was replaced by spruce, the concentration of Al_{H2O} increased, but concentration of Al^{3+} decreased in the F horizon. This seems to confirm that organic compounds in the soils of spruce forest can transform this toxic fraction. In contrast, grass expansion after deforestation led to a significant decrease in the concentrations of Al_{KCl} and Al_{H2O}. Acid soil liming increased the Ca concentration, but their long-term effects on soil pH and the concentrations of potentially toxic Al fractions were not apparent. With respect to the distribution of the most toxic Al fraction (Al^{3+} in aqueous extract), no significant long-term effect of deforestation and liming was observed.

These results could be used in the management of forested areas endangered by soil acidification. Limestone application can be recommended for younger forests preferentially, where Al toxicity is probable, or for utilization of natural mechanisms in damaged forest recovery.

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Supplementary Material

Tab. S1 - Distribution of Al fractions among soil horizons.

Tab. S2 - Results of ANOVA multiple range test

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