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Seasonal variation of water extractable aluminium forms in acidified forest organic soils under different vegetation cover

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Abstract The Jizera Mountains area is affected by natural and anthropogenic acidification processes. The effect of acidification is reflected by presence of elevated amount of different Al forms in soil horizons. Changes of water extractable forms of Al (total Al_{H_2O}, species: $Al(X)^{1+}$, $Al(Y)^{2+}$ and Al^{3+}) and other soil characteristics (e.g. DOC, pH) were investigated in forest soils from April to October 2008. Seasonal changes of Al forms were identified in organic F and H soil horizons. No significant effect of the soil type on Al forms was documented. Nevertheless, influence of vegetation cover (beech and spruce forest, clear-cut area) on $Al(X)^{1+}$, $Al(Y)^{2+}$ forms was proved. The results show that binding and mobility of Al forms are controlled mostly by pH and dissolved organic carbon (DOC).

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Keywords Acidification · Aluminium speciation · Forest soil · Seasonal variation · Vegetation cover

Abbreviations

A	Organomineral (humic) horizon
Al_{H_2O}	Total amount of water extractable Al
ANOVA	Analysis of variance
B	Subsurface mineral horizons (cambic or spodic)
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
et PZ	Entic Podzols
F	Fermentation surface organic horizon
H	Humified surface organic horizon
H.G.	Homogeneous groups
dy CM	Dystric Cambisols
ha PZ	Haplic Podzols
HPLC/IC	High performance liquid chromatography equipped with ionic column
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
LMMOA	Low molecular mass organic acids
LSD	Least significant difference
pH_{H_2O}	Active soil reaction in soil suspension with water
pH_{KCl}	Exchangeable soil reaction in soil extract with KCl
WRB	World Reference Base for Soil Resources

Introduction

Acidification is a soil degradation process that is important for the forest soils worldwide (e.g. Krug and Frink 1983; Moldan and Schnoor 1992; Likens et al. 1996). The Jizera Mountains (north part of the Czech Republic) represent an area strongly affected by acidification processes due to high precipitation, naturally acid bedrock (granite), high sulphuric and nitric deposition and improper forest management (spruce forests) (Mládková et al. 2004; Borůvka et al. 2005; Drábek et al. 2007).

Acidification leads to Al mobilization (e.g. Mulder and Stein 1994; Norton and Veselý 2003). Long term Al exposure causes shoot growth inhibition, nutrition (Ca, Mg, P) and water deficiency, and also other physiological stresses due to phytohormone imbalances (e.g. Horst 1995; Puhe and Ulrich 2001). However, recent field study by Nygaard and de Wit (2004) documented that Al had surprisingly low influence on spruce roots and tree health. This phenomenon might be caused by "root protection mechanism" (Jones et al. 2001) where potentially rhizotoxic Al is bound to root exudates—mainly organic acids such as citric and oxalic. Nevertheless, water-soluble Al forms express a certain degree of actual Al stress for ecosystem (e.g. Lundström and Giesler 1995; Puhe and Ulrich 2001; Drábek et al. 2005). The content of Al in water extract or soil solution comes from dissolving amorphous Al (hydro)oxides or soluble Al-organic complexes; main controlling mechanisms are pH and soil organic matter (e.g. Mulder and Stein 1994; Berggren and Mulder 1995; Lofts et al. 2001; Scheel et al. 2007).

Seasonal changes influence trees, ground flora, soil chemistry and biological processes in forest ecosystems. Seasonality shows its affect already on weeks to months scale. Main seasonal processes are growth and population dynamics (Puhe and Ulrich 2001). Soil biological activity and dissolved organic matter (DOM) change during the year; also enzymatic activity increases through the growing season (spring and summer) (Kaiser et al. 2002; Boerner et al. 2005; Niemi et al. 2007). Seasonal changes in the concentration of dissolved organic carbon (DOC) and DOM are influenced by litter fall inputs and soil organic matter content (e.g. Kalbitz et al. 2000). Production of organic acids in soils together with anion atmospheric deposition control seasonal variations of soil solution acidity. Consequently, this influence is expressed by DOC amount in stream waters (Chapman et al. 2008). Stream waters are an indicator of soil conditions and reflect seasonal variation of many soil characteristic (e.g. DOC, pH, cation and anion content) (Likens and Bormann 1995; Dawson et al. 2008; Chapman et al. 2008). Soil biochemical factors (microbial enzymes and total activity) correlate with some chemical properties, e.g. NH_4^+ and NO_3^- contents, in beech and spruce forest soils (Rastin et al. 1988, 1990). Turpault et al. (2007) observed changes in the content of Al forms during season and increased biological activity in soils (March and June). Variations of exchangeable Al due to complexation of Al with organic root exudates and lower Al content were determined in the rhizosphere interface between June and March. Turpault et al. (2007, 2008) described increased exchangeable Al amounts during June in consequence of lower Al fixation by soil clay minerals in bulk soil fraction. Degradation of soil organic matter was referred as another factor controlling Al chemistry (Turpault et al. 2007). Amount of "free" Al (prevailing Al^{3+} and $Al(OH)^{2+}$) was higher during spring and summer and Al correlated with weather conditions (precipitation and temperature). Lange et al. (2006) have reported that high DOC production and sea salt input, caused by wind storms, were major driving forces of Al variations in soil water in forested catchments in Norway. These authors claimed that Al chemistry and availability was influenced at first by cation exchange reactions caused by sea salt. Secondly, great influence was also ascribed to complexation ability of DOC. Aluminium content was also affected by microbial nitrification and pH decreasing (Umemura et al. 2003). Generally, composition of soil solution is influenced mostly by the biological activity of soil biota, season and actual weather (mainly temperature and precipitation) (Vestin et al. 2008).

The aims of this work are (i) to describe seasonal variation of water-extractable Al species, and (ii) to determine principal factors controlling Al behaviour under different soil vegetation cover.

Materials and methods

Study area

The study was carried out on the locality Paličník in the Jizera Mountains (Fig. 1). The altitude of studied plots ranged from 635 to 680 m and annual precipitation was approximately 1,705 mm. Vegetation cover is formed mainly by acidophilic beechwood (beech forest, *Fagus sylvatica* L.) and spruce monoculture (spruce forest, *Picea abies* [L.] Karst.) with dominance of *Calamagrostis arundinacea* and *Calamagrostis villosa* in herbal layer; clear-cut area is predominantly covered by *Calamagrostis villosa*. Soils developed from medium-grained porphyric granite to granodiorite of the upper carbon age. The soils were classified according to the World Reference Base for Soil Resources (WRB 2006). Prevailing soil types were Entic and Haplic Podzols (et PZ, ha PZ) accompanied by Dystric Cambisols (dy CM).

Soil samples

Soil samples were collected on three adjacent areas covered with beech forest, spruce forest and clear-cut area (Fig. 1). Sampling was done monthly in the period from April to October 2008, except the clear-cut area where the samples were collected every other month only. Each time, three new soil pits were dug on each area, two pits closer to the opposite edges, one close to the centre of the area. Following this rule, the particular place for each pit was selected randomly. The distance between the pits was at least 20 m in all cases.

Soil samples were collected from all horizons with sufficient thickness. In all cases, samples were collected from surface fermentation (F) and humified (H) organic horizons and subsurface B horizons (cambic or spodic). Where possible, samples from the surface organomineral (humic, A) were also collected. In total, 54 soil pits were described and sampled during the sampling period and 208 samples were collected.

Soil analysis

Soil samples were thoughtfully collected during sampling process to represent actual soil conditions as closely as possible. The collected samples were immediately treated and analysed in the laboratory. Each sample was thoroughly mixed and then divided into two parts—first part was analysed under "raw" conditions representing actual soil moisture. All stones, roots and undecomposed organic material

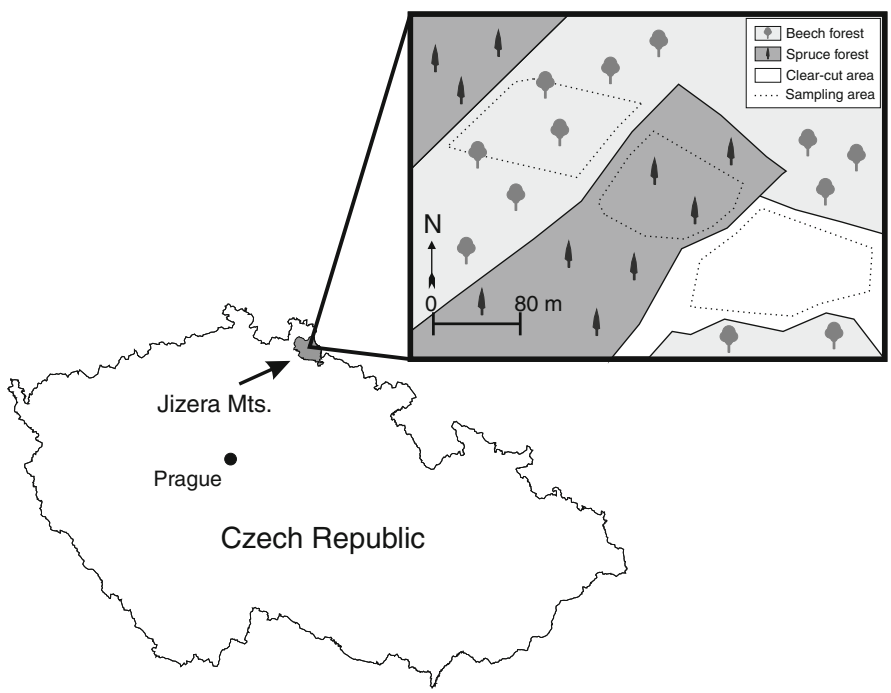

Fig. 1 Sampling sites of the studied areas shown on the map of the Czech Republic

were removed prior sample analyses. The method using fresh unsieved soil samples was adopted from works of Jones and Willett (2006) and Chantigny et al. (2008). Soil moisture content was determined by drying of soil samples to constant weight. Fresh samples were extracted by deionised water (ratio soil/water 1:10 w/v, 24 h extraction on a reciprocal shaker at stable laboratory temperature). The suspensions were then centrifuged at 4,000 rpm for 15 min; finally, extracts were filtrated through 0.45 μm nylon membrane filter (Cronus Membrane Filter Nylon, GB). In these aqueous extracts we have determined:

1. Major inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}). These anions were determined by means of ion-exchange chromatography with suppressed conductivity. The ion chromatograph ICS 90 (Dionex, USA) equipped with IonPac AS14A (Dionex, USA) guard and analytical columns was used. The eluent composition was 8.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ and flow rate was set to 1 mL min^{-1}. To suppress eluent conductivity the AMMS 300—4 mm suppressor (Dionex, USA) and 25 mM H_2SO_4 reagent was used. The eluent conductivity was even further suppressed by carbon removal device CRD 300—4 mm (Dionex, USA) and 0.2 M NaOH solution.
2. Total amount of Al (Al_{H_2O}). This was done by means of inductively coupled plasma-optical emission spectrometer (ICP-OES, An iCAP 6500 Radial ICP Emission spectrometer; Thermo Scientific, GB) under standard conditions.
3. The Al speciation was carried out under controlled stable temperature 25°C by means of high performance liquid chromatography equipped with ionic column (HPLC/IC) technique. The instrument consisted of GP50 gradient pump, Thermostated column compartment TCC 100 and PC Pneumatic controller for post column derivatization (Dionex, USA), UV/VIS detector Deltachrom UVD200 (Watrex, Prague, Czech Republic) and automated sampler Triathlon (Sparks Ltd., Netherlands). The IC column used was an Alltech cation R (USA), with the use of an old column as a guard column. The mobile phase used was 100 mM Na_2SO_4 (pH 2.40) in 7.5 mM H_2SO_4. For post-column derivatization, an agent 3×10^{-4} M tiron in 1 M ammonium acetate (pH 7.05) was used. Detection of created Al-tiron complexes was done at 310 nm. This chromatographic method enables separation of Al forms into three different groups mainly according to their charge (Drábek et al. 2005). These groups are assigned as follows: $Al(X)^{1+}$ {$Al(OH_2^+)$, $Al(SO_4)^+$, AlF_2^+, $Al(org.)^{\leq 1+}$, etc.}; $Al(Y)^{2+}$ {$Al(OH)^{2+}$, $(AlF)^{2+}$, etc.} and Al^{3+} {Al^{3+} and transformed hydroxyl Al polymers}.
4. Content of DOC was done by a modified wet dichromate oxidation method according to Yakovchenko and Sikora (1998) and Zbíral (2004). Generally, DOC is oxidized by dichromate-sulphate solution in preheated (140°C) temperature controlled oven for 20 min. This DOC digestion causes dichromate consumption; this dichromate consumption is determined spectrophotometrically at 340 nm (Hewlett Packard 8453 UV/VIS spectrophotometer, USA). Pure glucose (p.a.) was used as calibration standard for model digestion. Used concentrations were 0, 5, 10, 20, 30, 40 and 50 mg C L^{-1}.

All analyte contents and soil characteristics determined on fresh samples were recalculated to dry soil mass.

The second part of each soil sample was air dried and sieved through 2 mm sieves. Active and exchangeable pH (pH_{H_2O} and pH_{KCl}) were determined potentiometrically (pH meter inoLab pH Level 1 WTW, Germany); ratio soil/water or 0.2 M KCl was 1:10 w/v. Remaining part of each soil sample was archived.

Statistical analysis

The effect of horizons, soil unit, vegetation type, and sampling month was assessed using multifactor analysis of variance (ANOVA). This approach was used as the factors affect the soil conditions together and their effect can be mutually enhanced or eliminated. Mutual relationships between soil characteristics were analysed using simple correlation and regression. Factor analysis enabled presenting of all the mutual relationships between determined soil properties at the same time. Analyzing the whole data set instead of individual characteristics corresponds better to the real situation in soil. All statistical

analyses were performed using Statgraphics XV Centurion and Statistica 9.

Results and discussion

General description of results

The contents of water-extractable Al forms (Al_{H_2O}, $Al(X)^{1+}$, $Al(Y)^{2+}$, Al^{3+}) were significantly different between surface organic horizons (F, H) and organo-mineral (A) and mineral (B) horizons ($p < 0.001$). The organic horizons were therefore further analyzed separately from other horizons. Higher contents of Al species were determined in organic horizons than in the A and B horizons (Fig. 2). The same results were reported also by Giesler et al. (2000), Drábek et al. (2005) and Dlouhá et al. (2009). Markewitz and Richter (1998) reported accumulation of Al in forest floor due to higher biological DOC and Al inputs (mainly litter accumulation and degradation) to these horizons. Litter fall is considered as the major external Al input (69%) into forest floor under coniferous trees, complemented by precipitation; however, mass balance of Al fluxes indicated that the primary Al sink even in the organic horizons is mineral weathering (Rustad and Cronan 1995).

Table 1 summarises basic statistical parameters of soil properties for organic horizons group (horizons F and H), Table 2 for organomineral and mineral horizons (A and B). Both organic types of horizons were acid, pH_{H_2O} in soil ranged from 3.17 to 5.10, and pH_{KCl} values ranged from 2.55 to 3.88 (Table 1). The A and B horizons were less acid than the organic ones (pH_{H_2O} 3.51–4.51; pH_{KCl} 2.77–4.12). In the organic horizons, DOC strongly correlated with $Al(X)^{1+}$ ($r = 0.752$, $p < 0.001$) and $Al(Y)^{2+}$ ($r = 0.803$; $p < 0.001$) (Fig. 3). Species $Al(X)^{1+}$ and $Al(Y)^{2+}$ can contain organic forms, as for example Al ions bound on LMMOAs and/or humic substances. van Hees et al. (2001) modelling behaviour of Al with low molecular mass organic acids (LMMOA) and humic substances predicted that the major part of Al in acid soil solution was organically complexed by humic substances and by LMMOAs. In accordance with this, we determined particular organic acids (formic, acetic and oxalic) using ion-exchange chromatography in the forest floor samples from the same area collected in 2009 (data being prepared for publication). We suppose that Al species are complexed with these organic acids, as it was reported e.g. by McColl and Pohlman (1986) or van Hees et al. (1996, 2000) and also suggested by Drábek et al. (2005). Nevertheless, Strobel (2001)

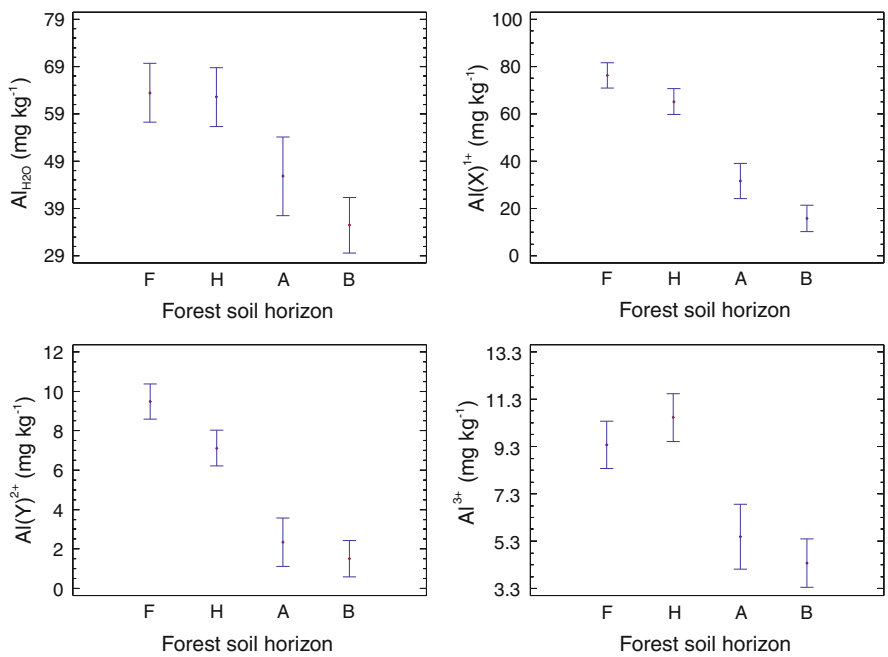

Fig. 2 Mean and 95% LSD intervals of water-extractable Al species from forest soils for the whole sampling period, and all soil vegetation covers and soil types (mg kg^{-1})

Table 1 Basic statistical parameters of soil properties for organic soil horizons F and H

	Al_{H_2O} (mg kg^{-1})	$Al(X)^{1+}$ (mg kg^{-1})	$Al(Y)^{2+}$ (mg kg^{-1})	Al^{3+} (mg kg^{-1})	NO_3^- (mg kg^{-1})	SO_4^{2-} (mg kg^{-1})	Cl^- (mg kg^{-1})	DOC (mg kg^{-1})	pH_{H_2O} (mg kg^{-1})	pH_{KCl} (mg kg^{-1})	Moisture (g g^{-1})
Count	107	102	102	102	105	105	105	105	138	138	106
Average	62.1	68.9	8.60	9.44	194	121	61.0	1430	3.85	3.09	0.53
Median	61.5	65.2	8.23	8.32	143	112	44.4	1259	3.82	3.10	0.54
Standard deviation	27.1	28.7	5.11	6.02	194	59.2	88.3	909	0.27	0.30	0.11
Minimum	0.00[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]	23.2	2.22	44.0	3.17	2.55	0.28
Maximum	135	150	25.3	26.3	1016	353	800	4149	5.10	3.88	0.88
Range	135	150	25.3	26.3	1016	329	798	4105	1.93	1.33	0.60

Recalculations to dry sample weight

[a] Under determination limit of the used analytical methods

Table 2 Basic statistical parameters of soil properties for organo-mineral and mineral soil horizons A and B

	Al_{H_2O} (mg kg^{-1})	$Al(X)^{1+}$ (mg kg^{-1})	$Al(Y)^{2+}$ (mg kg^{-1})	Al^{3+} (mg kg^{-1})	NO_3^- (mg kg^{-1})	SO_4^{2-} (mg kg^{-1})	Cl^- (mg kg^{-1})	DOC (mg kg^{-1})	pH_{H_2O} (mg kg^{-1})	pH_{KCl} (mg kg^{-1})	Moisture (g g^{-1})
Count	97	77	77	77	97	97	97	98	94	94	99
Average	38.7	20.7	2.21	4.01	55.5	159	28.6	366	4.08	3.53	0.30
Median	33.4	20.7	2.12	3.22	40.9	140	17.5	310	4.16	3.66	0.28
Standard deviation	26.3	17.6	2.00	3.29	56.7	102	51.4	401	0.26	0.38	0.08
Minimum	1.57	0.00[a]	0.00[a]	0.00[a]	0.00[a]	17.8	0.00[a]	0.00[a]	3.51	2.77	0.18
Maximum	116	70.5	8.10	13.8	342	476	405	3244	4.51	4.12	0.69
Range	114	70.5	8.10	13.8	342	458	405	3244	1.00	1.35	0.51

Recalculations to dry sample weight

[a] Under determination limit of the used analytical methods

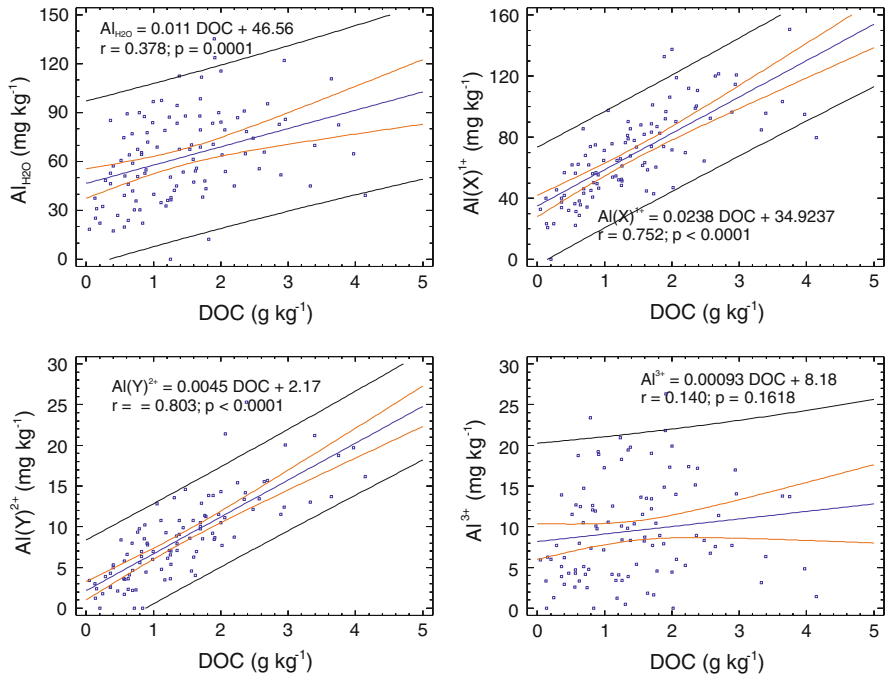

Fig. 3 Regression analysis for Al_{H_2O} and Al species in organic horizons (F, H) under different vegetation covers (mg kg^{-1}, g kg^{-1}; 102 samples)

showed that LMMOAs constitute a maximum of 10% of total DOC in forest soils under different vegetation cover. Al^{3+} species is not correlated to DOC ($p = 0.162$) as it is not bound on organic substances; it is formed only by Al^{3+} and transformed hydroxyl Al polymers (Drábek et al. 2005). The correlation between Al_{H_2O} measured by means of ICP-OES and DOC was weaker than the correlation between DOC and $Al(X)^{1+}$ and $Al(Y)^{2+}$ species. The ICP-OES method determines the sum of Al species in the solution, including Al^{3+}, which might be the reason of weaker relationship.

$Al(X)^{1+}$ species correlated also with both pH_{H_2O} ($r = -0.490$, $p < 0.001$) and pH_{KCl} ($r = -0.590$, $p < 0.001$). Moreover, pH values showed relationship with DOC (pH_{H_2O}: $r = -0.334$, $p < 0.001$; pH_{KCl}: $r = -0.537$, $p < 0.001$). This is in agreement with the results of Tipping and Woof (1990) who calculated increasing DOC mobility by more than 50% when pH increased by about 0.5. Negative correlation of pH with DOC and Al forms is shown also by the results of factor analysis (Fig. 4). The influence of soil organic acids to pH and soil acidity was published in many works, for example Pohlman and McColl (1988) and van Hees et al. (2001).

In factor analysis, three major factors accounting for 67.66% of the variability in the original dataset

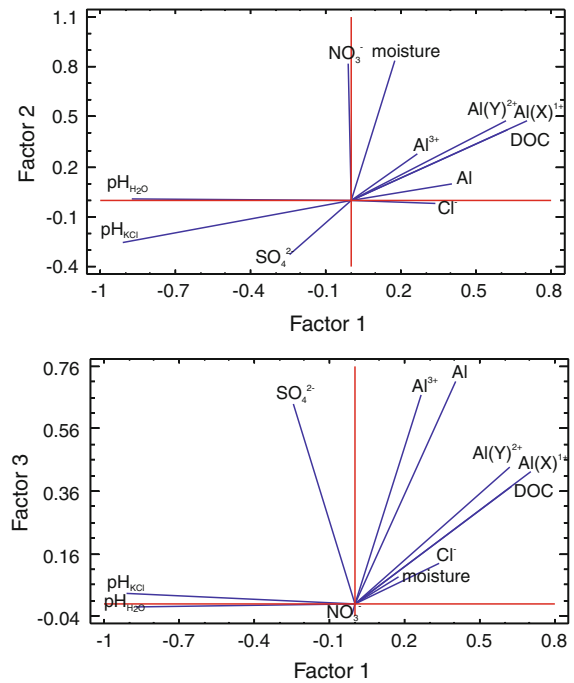

Fig. 4 Factor analysis for all soil samples (organic, organo-mineral and mineral horizons); three factors account for 67.66% of the variability in the original data

were selected (Fig. 4). The first factor shows a significant relationship between Al forms and DOC and a negative correlation of Al forms and both pHs

(pH_{H_2O}, pH_{KCl}). Similarly, Walker et al. (1990) showed that solubility of Al was increased when the pH was decreasing. The second factor describes a strong relationship between the content of NO_3^- in water extract and determined soil moisture. The relationship between NO_3^- content and actual dry or wet conditions is described for example by Prechtel et al. (2000) and Umemura et al. (2003). The third factor highlights correlation of Al_{H_2O} and Al^{3+} with the concentration of SO_4^{2-}. Sulphate dynamics plays an important role in Al behaviour. Higher sulphate content affects soil acidity and transforms hydroxylated Al species to Al^{3+} (Norton and Veselý 2003).

The contributions of various factors, namely soil unit, horizon, locality and sampling period, to the variation of soil properties were assessed by means of analysis of variance. All measured Al species in the organic horizons were significantly influenced by the sampling month (Table 3). The content of $Al(X)^{1+}$ and $Al(Y)^{2+}$ species in the organic horizons was influenced by the type of horizon (F vs. H) and vegetation cover. The effect of vegetation cover on the content and behaviour of Al forms in soils was reported also by Herbert and Bertsch (1995) and Dlouhá et al. (2009). Soil classification unit did not show any significant effect on measured Al species in the organic horizons; however, it influenced significantly the pH values (Table 4). Nevertheless, the effect of horizon, vegetation cover, and sampling month was more pronounced than the effect of soil unit and, moreover, it influenced also the content of DOC and SO_4^{2-}. DOC content in spruce forest soils (1,905 ± 147 mg DOC kg^{-1}) differed significantly from its content in soils under beech forest (902 ± 166 mg DOC kg^{-1}) and clear-cut area (1,121 ± 154 mg DOC kg^{-1}). The NO_3^- content was influenced

Table 3 Multifactor ANOVA of water-extractable Al species of organic soil horizons

Factor	Al_{H_2O}		$Al(X)^{1+}$		$Al(Y)^{2+}$		Al^{3+}	
	F test	*p*	F test	*p*	F test	*p*	F test	*p*
Soil type[a]	1.23	0.3032	0.71	0.5488	1	0.3966	0.56	0.6397
Horizon[b]	0.03	0.8674	6.29	**0.0139**	8.97	**0.0036**	1.92	0.1689
Vegetation cover[c]	1.72	0.1839	11.05	**<0.001**	10.18	**<0.001**	2.87	0.0619
Month[d]	4.24	**<0.001**	2.75	**0.017**	2.95	**0.0113**	15	**<0.001**

[a] et PZ, dy PZ, ha CM

[b] F, H

[c] Beech and spruce forest, clear-cut area

[d] April–October

Bold indicates significant differences at 0.05 confidence level

Table 4 Multifactor ANOVA of other determined parameters of organic soil horizons

Factor	NO_3^-		SO_4^{2-}		DOC		pH_{H_2O}		pH_{KCl}	
	F test	*p*	F test	*p*	F test	*p*	F test	*p*	F test	*p*
Soil type[a]	1.56	0.2052	0.32	0.811	0.42	0.7373	4.13	**0.0085**	4.02	**0.0097**
Horizon[b]	1.09	0.2999	5.15	**0.0255**	18.91	**<0.001**	7.5	**0.0074**	23.08	**<0.001**
Vegetation cover[c]	17.77	**<0.001**	6.04	**0.0034**	17.52	**<0.001**	43.99	**<0.001**	105.1	**<0.001**
Month[d]	1.93	0.0846	3.74	**0.0023**	7.84	**<0.001**	10.06	**<0.001**	2.89	**0.0126**

[a] et PZ, ha PZ, dy CM

[b] F, H

[c] Beech and spruce forest, clear-cut area

[d] April–October

Bold indicates significant differences at 0.05 confidence level

significantly only by the vegetation cover. The effect of these factors in the organomineral and mineral horizons was less pronounced.

Seasonal variability

As it was mentioned above, the sampling period was identified as the factor significantly affecting all the measured Al species (Table 3), as well as other soil chemical parameters—DOC, SO_4^{2-}, pH_{H_2O}, pH_{KCl} (Table 4). Only the amount of NO_3^- was not changed significantly during the monitored period.

Highest contents of all Al species determined by means of ICP-OES were observed in summer and late summer; the maximum amount of total water-extractable Al was measured in July and reached 81.3 mg kg^{-1} (Table 5). Also $Al(X)^{1+}$ and $Al(Y)^{2+}$ species showed maximum values in July, while Al^{3+} content increased in autumn months. This relates to the development of DOC in soils (Table 6). Decomposition processes due to higher microbial and fungal activity produce DOC in forest floor during summer and autumn (Rastin et al. 1990; Boerner et al. 2005). Chemical composition of this DOC enables binding metals on both aromatic and aliphatic DOC compounds (Kaiser et al. 2001, 2002). Major part of the $Al(X)^{1+}$ and $Al(Y)^{2+}$ species is supposed to be organically bound. The decline of DOC during late summer and autumn is thus followed by a decline particularly of $Al(X)^{1+}$ species and increase of Al^{3+} content (Fig. 5). A different situation is in the spring. Though the DOC content is the highest in April, Al species, including the $Al(X)^{1+}$ and $Al(Y)^{2+}$ and total Al_{H_2O}, are rather low in this month. Low contents of soluble Al forms in spring can be caused partially by runoff due to snow melting (Vestin et al. 2008). Nevertheless, the principal cause of lower content of water soluble Al forms can be ascribed to higher

Table 5 Seasonal variations of water-extractable Al species of soil organic horizons (mg kg^{-1}, F test, mean and 95% LSD interval)

Months	Al_{H_2O}			$Al(X)^{1+}$			$Al(Y)^{2+}$			Al^{3+}		
	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.
April	49.8	6.67	ab	64.0	6.76	a	9.23	1.19	bc	4.5	1.22	a
May	67.9	7.60	cd	53.6	7.54	a	5.89	1.33	a	5.7	1.22	ab
June	42.9	6.54	a	62.2	6.79	a	6.70	1.19	ab	6.2	1.36	ab
July	81.3	8.01	d	89.5	7.94	b	11.60	1.40	c	7.7	1.22	b
August	69.5	6.72	cd	62.2	6.88	a	6.35	1.21	a	11.7	1.24	c
September	65.1	8.34	bcd	65.2	8.29	a	7.85	1.46	ab	14.5	1.49	cd
October	57.3	6.84	abc	70.3	6.81	a	7.20	1.20	ab	16.2	1.43	d

H.G. homogeneous groups

Table 6 Seasonal variations of other determined parameters (NO_3^-, SO_4^{2-}, DOC, pH_{H_2O}, pH_{KCl}) of tested organic soil horizons (mg kg^{-1}, F test, mean and 95% LSD interval)

Months	NO_3^-			SO_4^{2-}			DOC			pH_{H_2O}			pH_{KCl}		
	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.	LS mean	LS sigma	H.G.
April	231	48.8	bc	104	14.9	ab	1949	180	d	3.94	0.04	d	3.03	0.04	b
May	186	55.3	abc	151	16.9	c	1008	205	ab	3.97	0.05	d	3.09	0.04	b
June	230	49.9	bc	104	15.3	ab	603	179	a	3.72	0.04	ab	2.90	0.04	a
July	284	59.8	c	124	18.3	bc	1694	216	cd	3.68	0.05	ab	3.00	0.05	b
August	102	49.1	a	145	15.0	c	1421	181	bc	3.83	0.04	c	2.99	0.04	ab
September	123	60.1	ab	107	18.4	abc	1430	225	bc	3.63	0.05	a	3.07	0.05	b
October	152	48.7	abc	74.3	14.9	a	1062	190	ab	3.77	0.04	bc	3.03	0.04	b

H.G. homogeneous groups

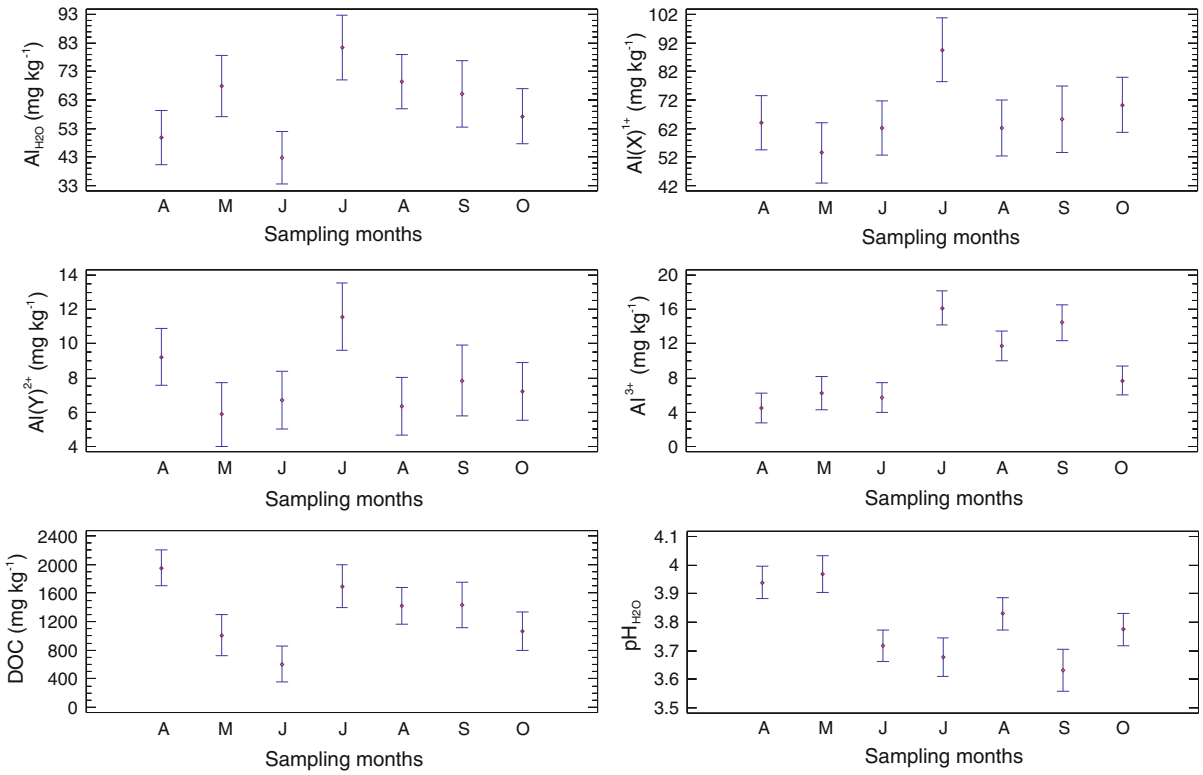

Fig. 5 Seasonal variation of water-extractable Al species, DOC and active pH (pH_{H_2O}) from forest organic (F and H) horizons with all vegetation covers (beech and spruce forest, clear-cut area) and soil types (et PZ, ha PZ, ha CM) (mg kg^{-1}; mean and 95% LSD intervals; 102 samples)

pH_{H_2O} values in the spring months compared to the later months. Higher pH leads to lower Al dissolution and consequently lower absolute Al amount, though the proportion of $Al(X)^{1+}$ from the sum of $Al(X)^{1+}$, $Al(Y)^{2+}$ and Al^{3+} (determined by HPLC/IC) remains high (around 80%). As pH_{H_2O} declines starting in June, the Al amounts in the solution tend to increase. The negative correlation between pH_{H_2O} and Al^{3+} ($r = -0.327$; $p < 0.001$) and results of factor analysis support this statement. The speciation of the released Al is then controlled mainly by DOC. Decline of pH, higher productivity of LMMOA by biological activity in soils in summer months, and also pH decline through the influences of LMMOA was reported by Fox (1995).

Influence of vegetation cover

As it was shown above, the vegetation cover influence most monitored soil properties particularly in the organic horizons (Tables 3 and 4). The effect of vegetation cover on Al species, DOC and pH (pH_{H_2O}) in organic horizons is shown in Fig. 6. pH was the lowest under spruce forest, compared to beech forest and clear-cut area. The acidifying impact of spruce cover on soil (for example Matzner and Prenzel 1992; Mládková et al. 2006) is clearly apparent here. In the contrast, the DOC content was significantly highest under spruce.

Contents of mono- and divalent Al species were in significantly higher amount under spruce forest than on the clear-cut area and under the beech forest. In contrast, the highest content of trivalent, the most toxic Al form was found under beech forest, though the difference was not statistically significant. This phenomenon is caused most probably by lower DOC content under beech forest (Fig. 6). In other words, soil under spruce is more acid compared to soil under beech, but the production of complexing compounds of DOC is greater and therefore more Al is bound into less toxic forms. Under beech, the acidity is lower, but the content and metal-complexing ability of DOC is smaller. We can hypothesize that the

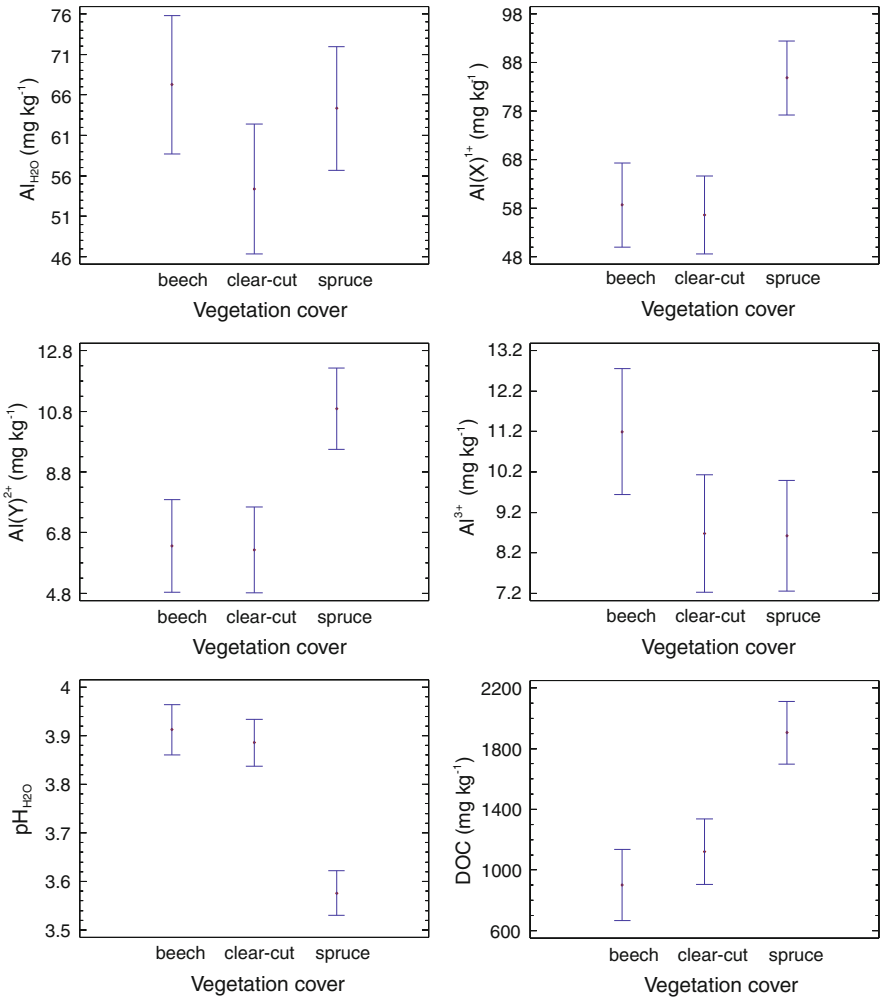

Fig. 6 Influence of vegetation cover (clear-cut area, beech and spruce forest) on Al species, DOC and pH_{H_2O} in forest organic horizons (mg kg^{-1}; mean and 95% LSD intervals; 102 samples)

actual toxicity of Al under spruce is smaller. Nevertheless, we have to take into account also the higher sensitivity of spruce and the level of potential toxicity represented by low base saturation and high Al saturation of soil sorption complex (data not shown).

Conclusion

Seasonal variation in Al contents and forms was studied for a particular time period (April–October 2008). Crucial factors affecting Al forms and their mobility during the monitored period were pH and DOC. Production of DOC in summer and following decline of its content in autumn control water-soluble Al speciation in soils strongly. The influence of soil type and vegetation cover on Al^{3+} content in soil was generally not significant. However, significantly different contents of $Al(X)^{1+}$ a $Al(Y)^{2+}$ species were observed in soils with different vegetation cover. Though soils under spruce forest are more acid compared to soils under beech forest, they have higher content of less toxic $Al(X)^{1+}$ and $Al(Y)^{2+}$ species and lower content of Al^{3+} thanks to complexing with DOC. The results confirm the positive effect of DOC in decreasing actual Al toxicity in forest soils.

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References

Berggren D, Mulder J (1995) The role of organic matter in controlling aluminium solubility in acidic mineral horizons. Geochim Cosmochim Acta 59:4167–4180

Boerner REJ, Brinkman JA, Smith A (2005) Seasonal variations in enzyme activity and organic carbon in soil of a burned and unburned hardwood forest. Soil Biol Biochem 37(8):1419–1426

Borůvka L, Mládková L, Drábek O (2005) Factors controlling spatial distribution of soil acidification and Al forms in forest soils. J Inorg Biochem 99:1796–1806

Chantigny MH, Angers DA, Kaiser K, Kalbitz K (2008) Extraktion and charakterization of dissolved organic matter. In: Carter MR, Gregorich EG (eds) Soil sampling and methods of analysis, 2nd edn. Canadian Society of Soil Science, CRC Press, Boca Raton

Chapman PJ, Clark JM, Reynolds B, Adamson JK (2008) The influence of organic acids in relation to acid deposition in controlling the acidity of soil and stream waters on a seasonal basis. Environ Pollut 151:110–120

Dawson JJC, Soulsby C, Tetzlaff D, Hrachowitz M, Dunn SM, Malcolm IA (2008) Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. Biogeochemistry 90(1):93–113

Dlouhá Š, Borůvka L, Pavlů L, Tejnecký V, Drábek O (2009) Comparison of Al speciation and other soil characteristics between meadow, young forest and old forest stands. J Inorg Biochem 103:1459–1464

Drábek O, Mládková L, Borůvka L, Száková J, Nikodem A, Němeček K (2005) Comparison of water-soluble and exchangeable forms of Al in acid forest soils. J Inorg Biochem 99:1788–1795

Drábek O, Borůvka L, Pavlů L, Nikodem A, Pírková I, Vacek O (2007) Grass cover on forest clear-cut areas ameliorates some soil chemical properties. J Inorg Biochem 101(9): 1224–1233

Fox TR (1995) The influence of low-molecular weight organic acids on properties and processes in forest soils. In: McFee WW, Kelly JM (eds) Carbon forms and function in forest soil. Soil Science Society of America, Inc, Madison, USA

Giesler R, Ilversniemi H, Nyberg L, van Hees P, Starr M, Bishop K, Kareinen T, Lundström US (2000) Distribution and mobilization of Al, Fe, and Si in three podzolic soil profiles in relation to the humus layer. Geoderma 94:249–263

Herbert BE, Bertsch PM (1995) Characterization of dissolved and colloidal organic matter in soil solution: a review. In: McFee WW, Kelly JM (eds) Carbon forms and function in forest soil. Soil Science Society of America, Inc, Madison, USA

Horst WJ (1995) The role of the apoplast in aluminium toxicity and resistence of higher plants: a review. J Plant Nutr Soil Sci 158:419–428

Jones DL, Willett VB (2006) Experimental evaluation of methods to quantify dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) in soil. Soil Biol Biochem 38:991–999

Jones DL, Eldhuset T, de Wit HA, Swensen B (2001) Aluminium effects on organic acid mineralization in a Norway spruce forest soil. Soil Biol Biochem 33:1259–1267

Kaiser K, Guggenberger G, Haumaier L, Zech W (2001) Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of oldgrowth Scots pine (*Pinus sylvestris L.*) and European beech (*Fagus sylvatica L.*) stands in northeastern Bavaria, Germany. Biogeochemistry 55:103–143

Kaiser K, Guggenberger G, Haumaier L, Zech W (2002) The composition of dissolved organic matter in forest soil solutions: changes induced by seasons and passage through the mineral soil. Org Geochem 33:307–318

Kalbitz K, Solinger S, Park J-H, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci 165(4):277–304

Krug EC, Frink ChR (1983) Acid rain on acid soil: a new perspective. Science 221(4610):520–525

Lange H, Solberg S, Clarke N (2006) Aluminum dynamics in forest soil waters in Norway. Sci Total Environ 367: 942–957

Likens GE, Bormann EH (1995) Biogeochemistry of a forest 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(5259):244–246

Lofts S, Woof C, Tipping E, Clarke N, Mulder J (2001) Modelling pH buffering and aluminium solubility in European forest soils. Eur J Soil Sci 52:189–204

Lundström U, Giesler R (1995) Use of the aluminium species composition in soil solution as an indicator of acidification. Ecol Bull 44:114–122

Markewitz D, Richter DD (1998) The bio in aluminum and silicon geochemistry. Biogeochemistry 42:235–252

Matzner E, Prenzel J (1992) Acid deposition in the German solling area: effects on soil solution chemistry and Al mobilization. Water Air Soil Pollut 61:221–234

McColl JG, Pohlman AA (1986) Soluble organics and their chelating influence on aluminium and other metal dissolution in forest soils. Water Air Soil Pollut 31: 917–927

Mládková L, Borůvka L, Drábek O (2004) Distribution of aluminium among its mobilizable forms in soils of the Jizera mountains region. Plant Soil Environ 50:346–351

Mládková L, Borůvka L, Drábek O, Vašát R (2006) Factors influencing distribution of different Al forms in forest soils of the Jizerské hory Mts. J For Sci 52:87–92

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

Mulder J, Stein A (1994) The solubility of aluminum in acidic forest soils: long-term changes due to acid deposition. Geochim Cosmochim Acta 58(1):85–94

Niemi RM, Vepsäläinen M, Erkomaa K, Ilvesniemi H (2007) Microbial activity during summer in humus layers under *Pinus silvestris* and *Alnus incana*. For Ecol Manag 242: 314–323

Norton SA, Veselý J (2003) Acidification and acid rain. In: Lollar BS (ed) Environmental geochemistry, treatise on geochemistry, vol 9. Elsevier, Amsterdam

Nygaard PH, de Wit HA (2004) Effects of elevated soil solution Al concentrations on fine roots in a middle-aged spruce (*Picea abies* (L.) Karst.) stand. Plant Soil 265:131–140

Pohlman AA, McColl JG (1988) Soluble organics from forest litter and their role in metal dissolution. Soil Sci Soc Am J 52:265–271

Prechtel A, Alewell C, Michalzik B, Matzner E (2000) Different effect of drying on the fluxes of dissolved organic carbon and nitrogen from a Norway spruce forest floor. J Plant Nutr Soil Sci 163:517–521

Puhe J, Ulrich B (2001) Global climate change and human impacts on forest ecosystems. Springer, Berlin

Rastin N, Rosenplänter K, Hüttermann A (1988) Seasonal variation of enzyme activity and their dependence on certain soil factors in a beech forest soil. Soil Biol Biochem 20:637–642

Rastin N, Schlechte G, Hüttermann A, Rosenplänter K (1990) Seasonal fluctuation of some biological and biochemical soil factors and their dependence on certain soil factors on the upper and lower slope of a spruce forest. Soil Biol Biochem 22(8):1049–1061

Rustad LE, Cronan CS (1995) Biogeochemical controls on aluminum chemistry in the O horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA. Biogeochemistry 29:107–129

Scheel T, Dörfler C, Kalbitz K (2007) Precipitation of dissolved organic matter by aluminum stabilizes carbon in acidic forest soils. Soil Sci Soc Am J 71:64–74

Strobel BW (2001) Influence of vegetation on low-molecular-weight carboxylic acids in soil solution—a review. Geoderma 99:169–198

Tipping E, Woof C (1990) Humic substances in acid organic soils: modelling their release to the soil solution in terms of humic charge. J Soil Sci 41(4):573–586

Turpault MP, Gobran GR, Bonnaud P (2007) Temporal variations of rhizosphere and bulk soil chemistry in a Douglas fir stand. Geoderma 137:490–496

Turpault MP, Righi D, Uterano C (2008) Clay minerals: precise markers of the spatial and temporal variability of the biogeochemical soil environment. Geoderma 147(3–4): 108–115

Umemura T, Usami Y, Aizawa S, Tsunoda K, Satake K (2003) Seasonal change in the level and the chemical forms of aluminum in soil solution under a Japanese cedar forest. Sci Total Environ 317:149–157

van Hees PAW, Andersson A-MT, Lundström US (1996) Separation of organic low molecular weight aluminium complexes in soil solution by liquid chromatography. Chemosphere 33:1951–1966

van Hees PAW, Lundström US, Giesler R (2000) Low molecular weight organic acids and their Al complexes in soil solution—composition, distribution and seasonal variations in three podzolized soils. Geoderma 94: 173–200

van Hees PAW, Tipping E, Lundström US (2001) Aluminium speciation in forest soil solution—modelling the contribution of low molecular weight organic acids. Sci Total Environ 278:215–229

Vestin JLK, Norström SH, Bylund D, Mellander P-E, Lundström US (2008) Soil solution and stream water chemistry in a forested catchment I: dynamics. Geoderma 144:256–270

Walker WJ, Cronan CS, Bloom PR (1990) Aluminum solubility in organic soil horizons from northern and southern forested watersheds. Soil Sci Soc Am J 54:369–374

WRB (2006) IUSS world reference base for soil resources. Working Group, 2nd edn. World Soil Resources Reports No. 103. FAO, Rome

Yakovchenko VP, Sikora LJ (1998) Modified dichromate method for determining low concentrations of extractable organic carbon in soil. Commun Soil Sci Plant Anal 29(3–4):421–433

Zbíral J (2004) Analýza půd III—jednotné pracovní postupy. SKZÚZ, Brno (in Czech)