

# Evaluation of chemical properties of througfall, forest floor and seepage water in Spruce and Beech stands in the Highlands area of the Czech Republic

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The objective of the transformation of spruce monocultures to close-to-nature forests is to create natural relationships between the species composition and the soil environment in a forest ecosystem. The aim of the paper is to evaluate the input of chemical substances via precipitation into forest floor, chemical properties of the forest floor with a view to the aluminum (Al), and the output of chemical substances via seepage water from the forest floor to the soil profile in an unmixed, 30 to 40-year old beech and spruce stand during the time period of 2004 through 2008. The study was carried out in the Rájec-Němčice field research station of the Department of Forest Ecology, Mendel University in Brno. The station is located in the Drahanská vrchovina Upland (on the eastern edge of the Bohemian Massif) in the Czech Republic. The aim of the study was to evaluate (i) the concentration and deposition of BC substances (= Ca, Mg, K), N (=  $NO_3^{-}$ ,  $NH_4^{+}$ ), pH, conductivity of throughfall, (ii) concentration and reserves of substances (Al, ,, BC, N), pH, C/N, Ca/Al ratio, BC/Al ratio, cation exchange capacity (CEC) and base saturation (BS) in the forest floor, (iii) concentration, pH, conductivity, output of substances (Al, BC, N) in seepage water from the forest floor to the soil profile. The results obtained demonstrate significant differences between spruce and beech stands. The values of determined characteristics show better conditions in the beech stand, eg: pH = 5,6; Al = 0,02 [mmol. l-1]; BC/Al = 8,3in seepage waters. In the spruce stand: pH = 5,0; Al = 0,01 [mmol.  $l^{-1}$ ]; BC/Al = 11,4. Based on the results obtained, it is possible to notice effects of the stand species on the condition of the forest floor and its development. These effects were less favorable for the 34-year old spruce monoculture aged as compared to the 40-year old the beech monoculture (for the latter we found some positive, soil-improving effects) grown over a time period of two generations of unmixed spruce stands.

- Keywords: aluminum; forest floor; tree species composition; Drahanská vrchovina Upland; Czech Republic
- Abbreviations: Al aluminum, BC basic cation (Ca+Mg+K), BS base saturation, C carbon, Ca calcium, CEC – cation exchange capacity, F – fermentation layer of forest floor, H – humus layer of forest floor, K - potassium, L leaf layer of forest floor, N – nitrogen, Na – natrium, NH<sub>4</sub><sup>+</sup> – ammonium ion, NO<sub>3</sub><sup>-</sup> – nitrate ion, Mg – magnesium, pH – throughfall, seepage and soil acidity.

# Introduction

Natural conditions were rather variable in the expansive and geographically different regions of Europe, before the arrival of man, and mixed broadleaved forests predominated there (Axelsson et al. 2002). More or less intensive use of the forest took place, from the Middle Ages to the beginning of the 19th century, sometimes resulting in total deforestation (Spiecker 2004). In this period, autochthonous coniferous stands grew at higher altitudes, in regions with lower temperatures (boreal forests) and on sandy, nutrient-poor soils, whereas natural forests covering central and Western Europe were deciduous, broadleaved and mixed coniferous/broadleaved forests (Adams, Woodward 1992). The Consequences of changes in the species composition of stands on the health of forests and landscape ecology have always been discussed (Miles 1985; Rehfuess 1990; Ellenberg 1996). It is certain that tree species have important effects on biochemical processes in forest ecosystems (Stone 1975; Kreutzer 1994; Binkley, Giardina 1998).

However, problems have started to occur related to the large-scale forest dieback in many places of central Europe from the second half of the 20th century. These problems were largely caused by acid atmospheric precipitation, which destabilized the ecological site valence of mainly allochtonous spruce monocultures. As a response to this ecological load, long-term natural acidification accelerated in soils of these stressed stands. This acidification of soils in Europe is considered to be one of the most serious environmental problems. Acidification is particularly caused by depositions of anthropogenic nitrogen NO3, NH4, NO2, NO and HNO3. An elevated nitrogen deposition increases the production of biomass on nutrientpoor sites and subsequently nutrition imbalance occurs (Schulze et al. 1989). The oxidation of NH<sub>4</sub> on NO<sub>5</sub> also results in soil acidification. If NH<sub>4</sub> becomes the main source of N reserves, antagonistic effects may reduce the uptake of Mg, Ca and K and accelerate the rhizosphere acidification (Evers, Huttl 1990). Further sources of acidification in soil profile are SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and acid rain containing higher concentrations of H<sub>2</sub>O<sup>+</sup>(H<sup>+</sup>) at present. The acidification shows a number of negative consequences for forest ecosystems, e.g., decrease of water alkalinity, pH values of water and soil creating an imbalance among ions (Schulze et al. 1989), decrease of the base-exchange complex saturation (Eilers et al. 1992) causing and increase in the content of dissolved Al in water (Johnson et al. 1991), iron and manganese (Gobran et al. 1993), qualitative and quantitative changes in the topsoil (Kreutzer 1994), eluviation of potassium (Ulrich 1991), reduction of the uptake of phosphorus by plant communities (Andersson, Persson 1988), disturbance of mycorrhizae (Strohmeyer 1992), effecting the soil catalase inhibition (Franzluebbers et al. 1995), and causing retardation of cellulose decomposition (Uchmanski et al. 1995) with the result of replacing the nutrient cations Cu<sup>2+</sup>, Pb<sup>2+,</sup> Zn<sup>2+</sup> a Cd<sup>2+</sup> (Postel 1986).

Last but not least, increased acidification of forest soils due to atmospheric deposition inhibits ammonization and nitrification (Brown 1985) resulting in a generally lower stability of microbial communities. This type of acidification increase affects processes of forest regeneration in a forest ecosystem (Huttermann, Ulrich 1984).

The toxic level of metal cations (particularly of Al) in the soil solution depends on their ratio of basic cations, largely of Ca. The Ca/Al and BC/ Al ratios determine the growth and activity of roots in the forest floor and organomineral horizons (Rost-Siebert 1983; Sverdrup 1990). Various tree species show a different sensitivity to Al content in the forest floor and soil (Raynal et al. 1990). The presence of Ca mitigates toxic effects of Al, such as the pH reduction (indirectly), and directly serves as an antagonistic factor towards Al (Rengel 1992). Although plants tolerate high amounts of Al in their leaves and needles, Al in the soil solution can be highly toxic (Ilvesniemi 1992; Bengtsson et al. 1988). The main protection is to reduce the uptake of monovalent and bivalent cations, which are available for the absorption of nutrients or as a result of the competition among Al, Ca and Mg (Ilvesniemi 1992; Asp, Berggren 1990; Bengtsson et al. 1988; Pahlsson 1990; Cape et al. 1990). Soil acidification reduces the development of mycorrhiza, which protects from Al toxicity. To a certain extent this was demonstrated in conifers (Boudot et al. 1994) and resulted in changes in the species composition of mycorrhiza on roots (Dighton, Skeffington 1987).

The forest floor is a connecting link between stand and soil and its condition and form are one of the key factors relating to the element cycle (nutrients) and dynamics of decomposition as well as to the problem termed acidification (Waring, Running 1998; Emmer 1999; Sparks 2003). The organic horizon consists mainly of leaves, twigs and woody materials, a small proportion of mosses, partly decomposed plant residues and well-decomposed plant and animal residues where it is not possible to distinguish structures (Juma 1999). The organomineral horizon is created at the soil surface in the zone of leaching or eluviations of organic materials, in a solution or suspension. Further, it can be created at the maximum accumulation (decomposition) of dead rhizosphere (basically soil biota) and organic excrements of organic matter in situ (or by combination) (Green et al. 1993; Samec, Formánek 2007). The importance of soil organic matter (the complex of all nonliving organic components of the soil) consists of the soil's nutrient cycle, the dynamics of soil water, maintenance of a suitable soil structure for the structure and acceleration of the decomposition of harmful substances as well as for the temperature regime of soils and many other factors (Juma 1999; Stevenson 1994; Piccolo 1996).

Based on precipitation, seepage waters and soil samples of the forest floor were taken in an unmixed spruce and beech stand in the course of 2004 – 2008. This study evaluates (i) the concentration and deposition of BC substances, N (=  $NO_3^-$ ,  $NH_4^+$ ), pH, conductivity in throughfall, (ii) concentration and reserves of substances (Altor, BC, N), pH, C/N, Ca/Al ratio, BC/Al ratio, CEC and BS in the forest floor, (iii) concentration, pH, conductivity, output of substances (Altor, BC, N) in seepage waters from the forest floor to the soil profile. These characteristics were evaluated and statistically compared. On the basis of the results obtained we tried to find answers to the

- Which type of substance input occurs in the forest floor and what is the output to the soil profile?
- 2) Which is the condition of the chemical properties of the forest floor (principally Al?) and to what degree affect given stands the soil environment of the forest floor?

# Materials and methods

#### Sites studied

The study is based on the research carried out at the permanent field research station Rájec-Němčice (49°29´31´´ N and 16°43´30´´ E) of the Department of Forest Ecology, Faculty of Forestry and Wood Technology, Mendel University in Brno. The field research station is situated in the region of the Drahanská vrchovina Upland (representing about 2.7% of the Czech Republic). It refers to a considerably forested region (668 km<sup>2</sup> = over 40% of its total area) covering mainly the Culm Drahanská and Konická Highlands as well as the Moravian Karst of Devonian origin and part of mainly Brno granitic eruptive rock. In the region of the field research station, acid granodiorite of the Brno massif creates a parent rock. A more comprehensive description of the two experimental stands composed of (1) Norway spruce, (Picea abies (L.) Karst.) and (2) European beech (Fagus sylvatica (L).), is given in Tab. 1.

## Sampling

Samples of the forest floor (L – litter horizon, F – soil skeleton horizon, H – mull horizon) were always taken at 10 repetitions in each of the horizons and years, and in the organomineral horizon (A) in 5 repetitions in each year. The sampling was carried out in 2004, 2006, and 2008 always at the end of the growing season (in November), after the leaf fall . The mixed samples were prepared for the analyses from each particular layers of soil the forest floor and organomineral horizon and of each year.

Samples of the throughfall water were taken from permanently open sampling collectors (Block, Bartels 1985; Niehus, Bruggemann 1995) of a collecting area of 335 cm<sup>2</sup>, in five repetitions in each of the stands (variant) and in an open area. Samples of seepage waters were taken in three repetitions in each of the stands (variant)

#### Tab. 1: Basic characteristic of forest stand.

following questions:

	Age [years]	Stand structure [%]	Form of forest floor <sup>†</sup>	Reserve of forest floor [t.ha <sup>-1</sup> ]	<b>Soil type</b>	a.s.l. [m]	Rainfall [mm]	Temp [°C]	Forest typology
Spruce stand	34	Picea abies (L.) Karst 100	moder	35,9**	Modal oligotrophic	(10	(20*	< <b>F</b> *	5S1–Abieto- Fagetum
Beech stand	40	Fagus sylvatica L. 100	mull-moder	18,8**	Cambisol Cambisols (CM) <sup>††</sup>	010	038	0.5	with Oxalis acetosella <sup>+++</sup>

<sup>†</sup>(Němeček et al. 2001); <sup>++</sup>(WRB 2006); <sup>++</sup>taxonomy by FMI (Forest Management Institute, Brandýs nad Labem); <sup>\*</sup>(Hadaš 2002); <sup>++</sup> (Menšík et al. 2009), (Fabiánek et al. 2009) (gravitation lysimeters of an area of 1600 cm<sup>2</sup> placed on the boundary-line of the forest floor H layer and organomineral horizon (A)). Sampling periods were the years 2006, 2007 and 2008. Samples of the throughfall and seepage waters were taken once every two weeks (14 days) during the growing seasons. Water was sampled once a month only from the throughfall precipitation collectors in the winter. In total, 51–53 samples of throughfall and 28–30 samples of seepage waters were taken.

# Analyses of soil, throughfall and seepage water

The forest floor samples (L, F, H) and the samples of the organomineral horizon (A) were air-dried and then in an oven at a temperature of 60°C up to a constant weight. The values of active and exchangeable soil acidity in the forest floor and organomineral horizon were determined by potentiometry (CSN ISO 10390) by means of a digital pH meter OP-208/1 (Radelkis Budapest, Hungary). Available nutrients in the forest floor horizons (L, F, H) and the organomineral horizon (A) were determined after extraction via an acid solution of ammonium nitrate and ammonium fluoride (Zbíral 1995). (Mehlich 1984) using the method of flame atomic absorption spectrometry (Ca and Mg) and the method of atomic emission spectrometry (Na and K). Cation exchange capacity (CEC) was determined using the summation method (Zbíral et al. 1997). The determination of the soil adsorption complex by hydrogen was carried out using the method of double measurement (Zbíral et al. 1997). The total content of Al in the forest floor (L, F, H) and organomineral horizon (A) was determined by the method of flame atomic absorption spectrometry (FAAS) (Zbíral 2002).

The pH value of the water samples was determined by potentiometry according to the (CSN ISO 10523), and the conductivity of precipitation and seepage waters was determined by conductometry according to the (CSN EN 27888). The sub-samples of water for the determination of metals (Na, K, Mg, and Ca) were acidified by adding 0.5 ml of reagent-grade nitric acid per 100 cm<sup>3</sup> and analyzed using the flame atomic absorption spectrophotometry for Ca and Mg determination, and flame atomic emission spectrophotometry in case of Na and K (spectrometer AA 30 F4 VARIAN, air-acetylene flame). The sub-samples for the determination of anions were deep frozen and kept in the freezer until the analyses could be carried out. Anions were analyzed using ion exchange chromatography with KOH gradient elution (DX-600 ion chromatographic system equipped with a GP50

gradient pump, an ED50 electrochemical detector, an EG40 eluent generator and an IonPac® AS11-HC AS11 HR (250 × 2 mm) analytical column with an AG11 HR ( $50 \times 2$  mm) guard column, operated under PeakNet 6.0 software, all parts Dionex Corp.). Ammonium nitrogen in rainfall and seepage water samples was determined by flow injection analysis with a FIA-lab 2500 analyzer (FIAlab Instruments, Inc., USA) according to the standard (CSN EN ISO 11732). Al in the precipitation and seepage waters was determined by the method of atomic absorption spectrometry with atomization of the samples in a graphite cuvette according to (CSN EN ISO 12020). From the concentration of substances expressed in mg.l-1 and from the amount of precipitation and the area of rain gauges depositions of particular substances were calculated and converted to ha.

#### Statistical analysis

Spruce and beech stands were compared on the basis of soil analyses and data from the analysis of precipitation and soil water underneath the stands. We prefer median to mean due to the positive skewness of the characteristics distribution measured. Data were transformed by a decimal logarithm for further statistical processing. Significance was assessed at the level  $\alpha = 0.05$ . All analyses except MANOVA one, which were done in the SPSS 17.0 program were carried out in the STATISTICA (8.0) program. Potential differences in precipitation and soil water of the spruce and beech stands were tested by a twosample t-test. Significantly different characteristics were also tested by a one-tailed two-sample t-test for the unevenness differentiation. Reciprocal relations between measured characteristics were performed by Pearson's coefficient of correlation analysis. Measured characteristics were used as pH predictors. Selection of the most important predictors was carried out by means of Principal Component Analysis (PCA). On the basis of the plot of eigen values, five factors were selected, which were applied as new independent predictors to a multiple regression analysis with a dependent variable pH. Significant predictors raised from the multiple regression were examined by individual contributions and correlations of the particular characteristics to predictors themselves. The best correlated and the biggest contributed measured characteristics were found as the best fitting for pH predicition in spruce and beech stands. Soil properties of spruce and beech stands at the level of forest floor layers were compared by MANOVA analysis with the factors stand type and forest floor layer.

# Results

#### Throughfall water

Mean pH values of the throughfall waters in the spruce stand were 5.42, and in the beech stand 5.91 during the period monitored (Tab.3). pH values of the throughfall were lower in the spruce stand (t = -3.8; P < 0.001). The mean concentration of the individual cations in throughfall of the spruce stand and the in beech stand are given in Tab. 3. The NO<sub>3</sub><sup>-</sup> concentration in the spruce stand was 0.07 and NH<sub>4</sub><sup>+</sup> was 0.09 mmol.l<sup>-1</sup>, in the beech stand 0.06 and 0.07 mmol.l<sup>-1</sup>. Statistically significant differences were determined only in the magnesium concentration (t = 2.6; P = 0.006) and nitrate anion (t = 2.4; P = 0.009) with higher concentrations always in the spruce stand.

The total deposition underneath the spruce stand was: 14.8, 5.9, 1.7, 252 and 17.7 kg.ha<sup>1</sup>. year<sup>1</sup> of nitrogen, calcium, magnesium, natrium and potassium, respectively. In the beech stand total deposition was: 14.6, 3.7, 1.0, 2.05 and 20.0 kg.ha<sup>1</sup> year<sup>1</sup> of nitrogen, calcium, magnesium, natrium and potassium respectively.

The environment characteristics analyzed by multiple regression (Fig. 2) explained roughly a half of the pH variability: precipitation in the stand of spruce trees showed lower fit ( $R^2$ =0.43); precipitation in the beech stand showed better fit ( $R^2$ =0.55). In precipitation waters of the spruce stand, pH was mostly affected by characteristics of the content of NH<sub>4</sub><sup>+</sup> potassium and NO<sub>3</sub><sup>-</sup> In the beech stand it was the conductivity, as well as the content of calcium and natrium. In the beech stand, NH<sub>4</sub><sup>+</sup> correlates markedly negatively with Ca (Fig. 2b); in the spruce stand the negative correlation is weaker (Fig. 2a).

## Forest floor

It is evident that a higher soil environment acidity determined from the leachate of the forest floor was found in the spruce stand, where it was: pH = 3.4; in contrast to the beech stand where reaching pH = 4.6 (Tab. 2). This difference is also statistically significant for all three layers L, F and H (F = 48.4; P = < 0.001) according to the MANOVA test (Fig. 1).

Statistically significant differences occur also in the C/N ratio (F = 38.3; P = < 0,001) and BC/ Al (F = 5.9; P = 0.02).Differences of other characteristics determined between both stands were not significant, neither at the level of stands or at the level of particular layers. The reserves of Al in the forest floor and the amount of Al in the H layer were higher in the spruce stand (reserve = 13.3 kg.ha<sup>-1</sup> and amount = 358.1 mmol) by 0.1 kg<sup>-1</sup>.ha<sup>-1</sup>than in the beech stand (reserve = 6.7 kg.ha<sup>-1</sup>; amount = 328.4 mmol. 0.1 kg<sup>-1</sup>).

# Seepage water underneath the forest floor

The mean pH values of seepage waters underneath the forest floor during the period monitored in the spruce stand were 5.1 and in the beech stand 5.6 this difference is highly significant (Tab 3).

The NO<sub>3</sub> concentration in seepage water in the spruce stand was 0.06 mmol.l<sup>-1</sup>and in the beech stand 0.1 mmol.l<sup>-1</sup> The NH<sub>4</sub> concentration was 0.07 mmol.l<sup>-1</sup> in spruce stand and 0.09 mmol.l<sup>-1</sup> in beech stand (Tab.3). The mean conductivity of seepage waters underneath the forest floor for the period monitored in the spruce stand and in the beech stand was 46.8 (54.0)  $\mu$ S.cm<sup>-1</sup>. Concentrations of magnesium (t = 2.6; P = 0.006) and nitrate anions (t = 2.4; P = 0.009) were higher in the spruce stand. The Al concentration in the spruce stand was 0.02 mmol.l<sup>-1</sup>, in the beech stand 0.03 mmol.l<sup>-1</sup>. The concentration of natrium was statistically lower in the spruce



Fig. 1:Mean differences of (a) pH, (b) C/N ratio and (c) BC/Al ratio between layers of the forest floor, significant by MANOVA analysis, in spruce (dashed line) and beech (full line) stands.

Tab. 2: Results of Ca/Al – c	fsoilanaly calcium to	ısis (mean - a aluminum r.	ırithmetic atio; BC/.	mean; medic <u>Al – basic ca</u> <b>Layers</b>	un – media tion (Ca, <b>s of Fore</b>	n; L-layerc Mg, K) to alı st Floor – I	ofleaf; F- uminum ra L, <b>F</b> , <b>H</b>	layer of fern ttio; CEC –	ıentation; cation exc	H – layer o hange capa	f humus; pH city; BS – b	[-soil acidity; ase saturation] Layer o	C/N-toti of Forest	al carbon to : <b>Floor –</b> ]	o total nitr H	ogen ratio;
	Ηd	(KCl)	C	N/N	pool of A	d [kg.ha <sup>-1</sup> ]	Ca	/AI	BC	/A1	CEC [mm	ol . 0,1 kg <sup>-1</sup> ]	BS	[%]	Al [mg	.kg <sup>-1</sup> ]
	mean	median	mean	median	mean	median	mean	median	mean	median	mean	median	mean	median	mean	nedian
<b>Spruce stand</b>	3.4	3.2	28.7	25.8	11.7	12.3	6.3	6.5	8.5	8.8	360.7	358.1	20.3	20.3	685.0	684.0
<b>Beech stand</b>	4.6	4.8	28.5	24.9	5.3	6.7	14.6	8.9	20.6	13.9	285.7	328.4	38.7	42.8	196.7	165.5

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		Spruce st	and		Beech st	and	É	. test		Sprucest	tand	4	Beech sta	and	1- L	est
	Z	mean	median	z	mean	median	F	Р	z	mean	median	z	mean	median	÷	Ъ
Ca [mmol. l <sup>-1</sup> ]	51	0.028	0.023	52	0.018	0.017	1.89	0.06	28	0.018	0.015	24	0.021	0.019	-0.22	0.83
Mg [mmol. l <sup>-1</sup> ]	51	0.012	0.009	52	0.008	0.007	2.55	0.01*	28	0.013	0.013	24	0.012	0.011	0.97	0.33
Na [mmol. l <sup>-1</sup> ]	51	0.018	0.015	52	0.017	0.014	0.86	0.39	28	0.043	0.033	24	0.077	0.060	-3.52	<0.001**
K [mmol. ] <sup>-1</sup> ]	51	0.079	0.054	52	0.101	0.043	0.55	0.54	28	0.132	0.109	24	0.167	0.122	-1.19	0.24
NO <sub>3</sub> <sup>-</sup> [mmol. l <sup>-1</sup> ]	51	0.087	0.073	52	0.066	0.062	2.42	0.01*	28	0.057	0.052	23	0.095	0.049	-1	0.32
$\mathrm{NH}_4^+$ [mmol. ] <sup>-1</sup> ]	52	0.099	0.088	52	0.132	0.068	1.24	0.22	30	0.072	0.056	24	0.091	0.059	-0.94	0.35
ЬH	53	5.423	5.455	53	5.913	5.994	-3.81	<0.001**	30	5.070	4.989	24	5.627	5.588	-3.66	<0.001**
Conductivity [µS.cm <sup>-1</sup> ]	53	42.42	39.04	53	40.40	31.43	1.18	0.23	30	46.80	39.29	24	54.03	44.52	-1.01	0.32
Al [mmol. l <sup>-1</sup> ]	ı	ı	ı	ı	ı	ı	ı	ı	29	0.019	0.012	24	0.029	0.020	-1.55	0.13
Ca/Al	i.	ı	ı	ī	ı	ı	ı	ı	28	1.977	1.020	24	1.965	0.821	0.80	0.43
BC/A1	T			,	'	ı	'	ı	28	16.86	11.378	24	15.98	8.250	0.57	0.57

stand (t = -3.5; P < 0.001). Potential differences in Al concentrations were not found. Ca/Al ratio was very similar in both stands, particularly in the rage of 0.8 to 1.0 and BC/Al ratio was higher in spruce stand (11.4) then in beech stand (8.3).

About 4.0 kg.ha<sup>-1</sup>.year<sup>-1</sup> of nitrogen were leached from the forest floor to the mineral horizon in the spruce stand and 2.7 kg.ha<sup>-1</sup>.year<sup>-1</sup> in the beech stand. As for Al, 1.37 kg.ha<sup>-1</sup>.year<sup>-1</sup> were leached in the spruce stand and 1.06 kg.ha<sup>-1</sup>. year<sup>-1</sup> in the beech stand. Concerning of leaching in spruce stand, we found: 1.8, 0.7, 2.3 and 12.1 kg.ha<sup>-1</sup>.year<sup>-1</sup> of calcium, magnesium, sodium and potassium. In beech stand were measured this value: 0.7, 0.3, 2.0 and 6.7 kg.ha<sup>-1</sup>.year<sup>-1</sup> of calcium, magnesium, sodium and potassium.

In the spruce stand there was a significant correlation between NO<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (r = 0.6; P = <0.001), and NO<sub>3</sub> and BC/Al (r = 0.6; P = <0.001). In the beech stand, it was between

 $NO_{3}^{-}$  and  $NH_{4}^{+}$  (r = 0.6; P = <0.001),  $NO_{3}^{-}$  and BC/ Al (r = 0.7; P = <0.001). Exchangeable soil acidity was not significantly correlated with any of the characteristics. Al showed a negative correlation to all characteristics, except natrium, namely in both stands (Fig. 3a, b). In the spruce stand the pH variability in seepage waters underneath the forest floor was best described by conductivity, Mg and NO<sub>3</sub>. As for the beech stand, important predictors could not be determined due to the inconclusiveness of a multiple regression model. In the spruce stand, Al negatively correlates with NH<sup>+</sup> and NO<sup>-</sup> (fig. 3a); in the beech stand, Al correlates negatively with magnesium in particular (Fig. 3b). The beech stand characteristics measured in the seepage water showed only minimum on measured characteristics (R<sup>2</sup>=0.06). To explain and reliably predict the pH values in both stands it would be necessary to find other predictors.



Fig. 2: Projection of the througfall water characteristics as pH predictors in spruce (a) and beech (b) stands on the factor-plane (PCA).



Fig. 3: Projection of the seepage water characteristics as pH predictors in spruce (a) and beech (b) stands on the factor-plane (PCA).

# Discussion

The study evaluates chemical properties of throughfall, forest floors, as well as seepage waters underneath the forest floor in an unmixed spruce and beech forest stand in the region of the Drahanská vrchovina Upland of the Czech Republic. Basic characteristics were determined, such as: pH, conductivity, BC, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> CEC, BS, Al and total C and N.

The mean pH value of throughfall and seepage waters underneath the forest floor in the spruce stand increased as compared with previous measurement results over the time period of 1976 through 1990 (pH of throughfall: 4.0; pH of seepage waters: 4.31) (Klimo et al. 1996). The decrease of acidity occurred particularly as a result of decreased acid deposition (Hadaš 2002) caused by air pollution from heavy industry in the 1980s and 1990s of the last century (Mrkva 1992).

At present, low values of conductivity (statistically insignificant differences) in throughfall and seepage waters underneath the forest floor of the spruce and beech stands show that significant washing out of ions from the soil profile does not occur. Currently, depositions of nitrogen substances (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) rank among the most important depositions into forest ecosystems. Nitrogen depositions in both stands amounted about 15 kg.ha<sup>-1</sup>.year<sup>-1</sup>. Nitrogen depositions of 16.6 kg.ha-1.year-1 in a 53-year old spruce stand, and of 9.1 kg.ha<sup>1</sup>.year<sup>1</sup> in a 65-year beech stand were found in Austrian spruce and beech stands near Vienna, (Berger et al. 2008). Rothe et al. (2002), mentioned nitrogen depositions of 27.7 kg.ha<sup>-1</sup>.year<sup>-1</sup> in a spruce stand, and of 13.3 kg.ha-1.year-1 in a beech stand situated in southern Germany (Hoglwald research). Drápelová, Kulhavý (2008), mentioned nitrogen depositions of 10-11 kg.ha<sup>-1</sup>.year<sup>-1</sup> in the Moravian-Silesian Beskids (Bílý Kříž) in a spruce and in a mixed spruce/beech stand of the same age. Results of the spruce and beech stands in the Drahanská vrchovina Upland are similar to the results of other authors in the given regions of Central Europe. High nitrogen deposition in seepage water may be a serious problem for the hydrosphere. The high nitrogen losses can lead to a significant eutrophisation of streamwaters or the pollution of groundwater (Rothe et al. 2002). The concentration of nitrates in seepage waters did not exceed 50 mg per liter, which is the limit for drinking water according to the standard. Thus, we can suppose that an increased danger of washing out nitrates from the whole soil profile mentioned, e.g. by (Zoettl, Huettl 1986), does not occur. Lower concentrations of

nitrates NO<sub>3</sub><sup>-</sup> were detected in throughfall (3.7 mg.l<sup>-1</sup>) during previous measurements (Klimo et al. 1996), which currently slightly increased. This is the result of the increased deposition of nitrogen from the atmosphere (Hadaš 2002; Zapletal 2006). This increase becomes evident also in higher nitrate concentrations in seepage waters underneath the forest floor (by 0.6 mg.l<sup>-1</sup>) compared to the situation of previous years (1976–1990, Klimo et al. 1996).

The final values for seepage waters underneath the forest floor are slightly above the critical values as compared with the critical values of pH and Al mentioned in the literature (Sverdrup 1990). It is a similar scenario with the Ca/Al and BC/Al ratio. In principle, none of the values of this ratio exceeded the critical limit of toxicity for living organisms in our spruce and beach stands in the course of the study period. In general, the content of Al was higher in the spruce stand with a higher accumulation of forest floors. Cronan, Grigal (1995) mentioned their statistical analysis of damage when the Ca/Al ratio was used as a main criterion of toxicity. When the ratio equals to 1, significant damage was noted at 50% of cases, when the ratio reached 0.5, the damage was evident already at 90% cases (Sverdrup 1990). In both analyzed stands, the mean value of the ratio was above 1 within the soil profile.

The ratio of BC and Al is used more often, showing a higher informative value about the potential toxicity in the forest floor (Hruška, Cienciala 2001). Thus, the limit of the potential toxicity is considered to be less than 1. The forest floor underneath our both stands showed mean values that are several times higher then 1. Another situation occurred at the evaluation of BC/Al ratio, but only in the H layer of both stands. The values were below the limit of 1 in both stands. Therefore, there is a higher risk of damage to the root system due to Al toxicity. Al accumulation compared to the content of base cations underneath the spruce stand was, however, markedly higher (Tab. 3) than underneath the beech stand. In both stands, we can say that thanks to pH > 5.0 (Hruška, Cienciala 2001) the higher washing out amount of Al does not occur in the soil profile. Identical results appeared when comparing BC/Al and Ca/Al ratios and with analyses carried out from soil leachates (Tab. 2). The results of soil extract analyses (Tab. 2) showed statistically significant differences between the stands (Fig. 1). According to the determined values for soil characteristics, worse conditions of forest floors occur in the spruce stand, i.e. an environment higher in

acidity with increasing Al content, slower decomposition, lower values of cation exchange capacity, etc.

The range of pH values given by Czech authors for spruce forest floor is 4.0-5.0 and for beech forest floor 5.0–6.5 (Mařan, Káš 1948; Šály 1978). In both cases, the values are lower. In both stands, the BS does not reach the saturation in the H layer (<50%). This fact was described by (Šály 1978) for the majority of soils in the ČR. Rather small differences between active and exchangeable pH values show evidence of the relative sufficiency of base cations in the uppermost soil layers (Ulrich, Pankrath 1983).

The forest floor has an important role in the carbon and nitrogen dynamics in forest ecosystems. It is considered to be the source of carbon and nitrogen for plants and soil microorganisms as well as the reservoir of carbon and nitrogen entering the forest floor (Yano et al. 2000). The resulting values of the total C/N ratio are among the main indicators of the biomass decomposition rate given by the close relationship between the value of the ratio and soil transformations of nitrogen (Cote et al. 2000) that occur within the limits given for forest soils in Europe (30 to 40). However, the C/N ratio evaluation is not so clear and differs among some authors (Cote et al. 2000; Puhe, Ulrich 2001; Prescott et al. 2000; Vitousek et al. 1982; Binkley, Giardina 1998). In addition to the species composition of litter, we also have to take the pH value into account, the content of exchangeable cations (Caravaca et al. 1999). The anthropogenic deposition of NO<sub>x</sub> from the atmosphere (Puhe, Ulrich 2001) also contributes to the amount of nitrogen. The value of the C/N ratio reaching about 24 (Emmett et al. 1998) in coniferous stands is considered to be critical. At higher ratios, less than a 10% nitrogen washing out from an ecosystem occurs, at a ratio lower than 24, it is much higher. In broadleaved stands, a limit defined in such a way is not mentioned.

## Conclusion

Water entering the forest floor intercepted by means of rain gauges situated underneath tree crowns is slightly more acid underneath a spruce stand in comparison to a beech stand. Other determined characteristics show similar situations. Significant differences occur only in the content of nitrate anions (chemical results of assimilatory organs), the total N deposition is almost identical in both spruce and beech stands.

Significant differences were determined in the analysis results of soil solutions leached out from L, F and H layers. Basic differences occur in the determined value of exchangeable pH and the amount of Al and their subsequently calculated BC/Al ratios. There are well visible differences in forest floor conditions underneath the spruce stand, the concentration of Al and hydrogen ions (lower pH) already occurs in the upper layer of soil.

In comparison with the beech stand there is also a lower washing out of Alto mineral horizons. Marked accumulation of these elements causes an increase in the total volume of forest floor and its impoverishment (lower saturation by bases), which can even change to toxicity for living organisms. This condition did not occur within the whole forest floor profile (and theoretically, it can not even occur without changes of the present conditions), but the amount of Al determined in the H layer (at the level of the spruce roots in forest floor) already showed toxicity for organisms. The seepage water flowing through the whole profile of the forest floor and intercepted in gravitation lysimeters of the beech stand is slightly more Al-enriched as a result of the generally lower accumulation of elements in the upper soil layers and their higher enrichment of the deeper organomineral (A) and mineral horizon (B).

The correlation analysis by the Pearson correlation coefficient relationship clearly demonstrated particular characteristics, both in precipitation and seepage waters (except beech) affected by their seasonal variability pH.

Based on the results obtained, it is possible to notice the effects of the stand species on the condition of the forest floor and its development. These effects were worse in the case of the 34-year old spruce monoculture than in the case of the 40-year old beech monoculture (there positive soil-improving effects could be noticed as well) grown over a time period of two generations in unmixed spruce stands.

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