The effect of understory on cation binding reactions and aluminium behaviour in acidic soils under spruce forest stands (Southern Poland)

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Abstract Acidic forest soils with two dominant understories, bilberry (*Vaccinium myrtillus* L.) or alpine lady fern (*Athyrium distentifolium* Tausch ex Opiz), have been investigated to evaluate the influence of the understory on sorption properties and aluminium behaviour. We investigated acidity, cation exchange properties, organic matter content (SOM) and quality as well as Al bonding to organic matter in humus horizons of soils taken from two different locations. SOM was the major contributor to total cation exchange capacity (CEC_t) and effective cation exchange capacity (CEC_e), and a strong relationship was found between SOM and both CEC_t and CEC_e , independently of the understory and location. SOM differed in quality, having more fulvic acids in soils under bilberry than in soils under alpine lady fern. For that reason, SOM in soils under bilberry complexed more Al in the exchangeable form in the soluble fulvic acid fraction such that they could be easily washed out, while in soils under alpine lady fern aluminium was mainly bound more stably. We also found that the chemical character of Al depended on the understory

type. In soils under bilberry the relation between base saturation and pH could be successfully modelled by a modified Henderson–Hasselbalch equation when Al was considered as a base cation, which is typical for forest podzols. However, in soils under alpine lady fern, this model was efficient only when Al was treated as an acid cation. We concluded that alpine lady fern as the main understory species reduces solubility and potential toxicity of aluminium, thus significantly affecting soil biogeochemistry.

Keywords Bilberry · Alpine lady fern · Aluminium · Fulvic acids · Sorption properties

Introduction—theoretical background and assumptions

It is assumed that in humus horizons, cation binding is regulated primarily by soil organic matter (SOM) and to a lesser extent it occurs on the surfaces of some clay minerals (Blaser et al. 2008; James et al. 2016). Under acidic conditions the principal functional groups of SOM involved in these reactions are the acidic carboxyl and hydroxyl groups of SOM, which dissociate protons at a pH of about 3. In this way, negatively charged sites are formed for which Al and protons compete, determining soil pH values and Al solubility (Skylberg 1999). Al cations interact with SOM by

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neutralizing the electrical charge on organic molecular surfaces through both weak and strong binding processes (Huang 1988; Li et al. 2016). In such conditions the most effective SOM compounds taking part in cation exchange reactions (weak binding) are fulvic acids (FAs), which exhibit higher total acidity values than humic acids (HAs) (Tan 2005).

Hence, in forest soils the amount and quality of SOM greatly modifies the nature of soil acidity, but soil acidity and complexation of metals to SOM may also affect the stability of organic matter (Arbestain et al. 2003; Berggren and Mulder 1995; Mulder et al. 2001). Mueller et al. (2012) confirmed this conception from their study on the influence of tree species on carbon stocks and acidity in mineral soils in a common garden experiment. According to them, the link between SOM and acidity operates in two directions. An amount of SOM contributes to variation in total acidity by providing exchange sites for protons, Al and Fe ions, and/or the amount of soil acidity contributes to variation in SOM through cation-bridging or other constraints on microbial decomposition of SOM.

In acidic forest soils, aluminium occurs in high amounts in compounds that when hydrolysing produce Al^{+3} , AlOH^+ or $\text{Al}(\text{OH})_2^{2+}$ cations (Skjellberg 1999). On theoretical grounds, Mulder et al. (2001) and Mueller et al. (2012) defined the $\text{pH}_{\text{threshold}}$, that is, the soil pH below which $\text{Al}(\text{OH})_3$ is unstable and pH is controlled by chemisorption of Al to soil organic matter. According to Gruba et al. (2013), $\text{pH}_{\text{threshold}}$ can be estimated for any acidic soil by the following equation:

$$\text{pH}_{\text{threshold}} = 6.06 - 0.47\text{pH}_{\text{KCl}} \quad (1)$$

Binkley and Giardina (1998) attributed the impact of forest stands on soil acidity to the acid litter input to the soil and to the apparent dissociation constant (K_{app}) of soil organic acids. The K_{app} value differs due to differences in the functional groups of SOM derived from different forest tree species. In acidic, organic matter-rich forest soils the value of pH solution can be described by the Henderson–Hasselbach equation, which after the modification of Bloom and Grigal (1985) takes the following form:

$$\text{pH} = \text{p}K_{\text{app}} + n\text{Log}[(\text{BS}_e/1 - \text{BS}_e)], \quad (2)$$

where $\text{p}K_{\text{app}}$ stands for the negative logarithm of the apparent dissociation constant, n is an empirical stoichiometric constant of the reaction, BS_e is the

effective base saturation, i.e. the fraction of the effective cation exchange capacity (CEC_e) neutralized by base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+). Thus, $1 - \text{BS}_e$ refers to the fraction of exchangeable acidity ($\text{H}_e + \text{Al}_e$).

As shown above, the effect of tree species composition on pH value regulation, cation binding properties, Al solubility and their relations with SOM in acidic forest soils has already been extensively investigated in acidic soils of different regions such as: Scandinavia (Skjellberg 1999; Skjellberg et al. 2001), northern USA (Johnson 2002; Mueller et al. 2012), Brazil (Abreu et al. 2003) and Poland (Gruba and Mulder 2008, 2015). However, to our knowledge the effect of understory type on such parameters and their relationships has not been considered yet.

Since it has already been ascertained that the type of forest understory (domination of Alpine lady fern or bilberry) affects the course of pedogenic processes as expressed by the quality of humus and the mobility of Fe and Al within the soil profiles of the Carpathian subalpine spruce forest stands (Ciarkowska and Miechówka 2017), one can suppose that the understory type also affects cation binding properties and the behaviour of aluminium in these soils. The aim of this work was to verify this hypothesis by: (i) determining relationships between parameters describing cation exchange properties at sites with the different understories and locations, (ii) evaluating the role of SOM in cation binding properties and pH regulation, as well as (iii) comparing the share of Al forms with different solubilities in top mineral horizons of acidic spruce forest soils with bilberry (*Vaccinium myrtillus* L.) or alpine lady fern (*Athyrium distentifolium* Tausch ex Opiz) as the dominant understory. An understanding of the solubility of aluminium in acidic soils may also be important in predicting the amount of toxic Al that is present in soils.

Study area and sampling

The investigations were carried out in Beskid Żywiecki Mts. (N 49° 34'–37', S 19° 29'–37') and in the Gorce Mts. (N 49° 32', S 20° 09'–8'), which are both situated in the West Carpathian Mountain Range (Southern Poland). They are located in the cool climatic zone, with a mean annual temperature from

+4 to + 2 °C. The mean annual rainfall measured at the Markowe Szczawiny weather station (Beskid Żywiecki, northern slopes of Babia Góra Mt. 1180 m a.s.l.) is 1490 mm (Obrebska-Starkel 2004) and at the Turbacz weather station (Gorce, northern slopes of Turbacz Mt. 1310 m a.s.l.) 1290 mm (Miczyński 2006).

In Beskid Żywiecki, all research areas were situated in the Babia Góra range at the altitude of 1090–1370 m a.s.l., on northern slopes of Cyl Mt. (1515 m a.s.l.), Diablak Mt. (1725 m a.s.l.), Sokolica Mt. (1367 m a.s.l.) and Polica Mt. (1369 m a.s.l.). The Gorce Mts. research areas were situated on the northern slope ridge extending to the east between Turbacz Mt. (1310 m a.s.l.) and Jaworzyna Mt. (1288 m a.s.l.) at the altitude of 1205–1250 m a.s.l. Slope exposures of the research areas ranged from 15 to 25°. These mountain ranges are representative for the Outer West Carpathians in terms of their ecology and landscapes, in which the natural ecosystems, especially acidic spruce forest of the upper montane belt, have survived relatively well. Both the Beskid Żywiecki and Gorce mountain ranges are built from the Magura nappe, which in the area of Poland is the biggest nappe and the most internal one of the Outer Carpathians (Cieszkowski 2006).

Studied soils were derived from the Upper Cretaceous and Paleogene flysch rocks of the Magura Nappe, in Gorce from Krynica subunit (sandstones of Magura or Szczawnica formations), while in Beskid Żywiecki from the Raczańska subunit. All sites are covered by spruce forests (*Plagiothecio-Piceetum* association) with bilberry (*V. myrtillus*) or alpine lady fern (*A. distentifolium*) as the main understory species (Loch 2002; Parusel et al. 2004). Soils with alpine lady fern as the dominant understory (referred to here as fern soils) were Dystric Skeletic Cambisols; soils with bilberry prevalent in the understory (referred to here as bilberry soils) were Skeletic Podzols (WRB, IUSS Working Group 2015). Detailed morphology of the studied soils is given in Ciarkowska and Miechówka (2017). Also, in our study we included soils that did not have bilberry or alpine lady fern as understory species (or only a very small amount present), which we used as reference soils. Such soils occurred on much smaller areas than bilberry or fern soils, on the edges of occurrences of fern or bilberry soils.

Reference soils were either Dystric Skeletic Cambisols or Skeletic Podzols (WRB, IUSS Working Group 2015).

In each location, Gorce and Beskid Żywiecki, we selected six research areas of about 100 m² each with uniform vegetation (three with Alpine lady fern and three with bilberry as the dominant understory) separated by several meters. With the use of an auger, systematic sampling was done every 10 m, and 10 soil samples were collected from top mineral horizons (A or AE) from each research area, which resulted in 60 samples each of fern soils and bilberry soils. As soils without bilberry or Alpine lady fern (or with a small amount of them) in understory occurred rather rarely we found three areas of about 10 m² from which we took 10 soil samples altogether.

Laboratory methods

Analyses were performed on air dried soil samples sieved with a 2 mm sieve. The pH values were established potentiometrically in distilled H₂O and in a 1 M KCl suspension with a soil:extractant ratio of 1:2.5. Clay content was determined according to the hydrometer method (Tan 2005).

Organic carbon content (C_d) was determined through the Walkley–Black wet combustion method with the use of a 0.1 M K₂Cr₂O₇ solution with a concentrated H₂SO₄ addition. Measured C_t contents were converted into organic matter (SOM) using a coefficient of 1.724 (Tan 2005).

Humic acids (HAs) and fulvic acids (FAs) were extracted by centrifugation of soil samples with 1 M NaOH, as recommended by the International Humic Substance Society (IHSS; Calderoni and Schnitzer 1984). In the collected supernatant, the sum of total HAs and FAs was obtained. HAs were separated from the precipitate by its acidification to pH 1. The C content in fractions was determined via the Walkley–Black wet combustion method.

Exchangeable Ca, Mg, K and Na was determined by extraction with 1 M NH₄OAc (pH 7) and evaluation with a Perkin-Elmer atomic emission spectrometer ICP-OES Optima 7300 DV, and multi-element ICP-IV Merck standard solution. Exchangeable acidity, taken as the sum of exchangeable H⁺ (H_e) and exchangeable Al³⁺ (Al_e), was determined by

extraction with by 1 M KCl and then titration with 1 M NaOH; Al_e was determined by back-titrating the filtrate after Al neutralization with 1 M KF and H_e calculated as a difference between exchangeable acidity and Al_e (Tan 2005).

Total acidity (T_A) was determined using 1 M $Ca(CH_3COO)_2$ in a 1:2.5 soil/solution ratio. Suspensions were shaken for 1 h, filtered and titrated with 0.1 M NaOH to pH 8.2. The total acidity was calculated from the amount of base used (Ostrowska et al. 1991). Al (Al_t) extracted with 0.1 M $Na_2P_2O_7$ at pH = 10, was treated as total Al.

On the basis of the determined parameters, the following calculations and designations were made:

$$\begin{aligned} \text{Sum of exchangeable cations (cmol}_c\text{kg}^{-1}) : BC \\ = Ca^{2+} + Mg^{2+} + K^+ + Na^+ \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Cation exchange capacity (cmol}_c\text{kg}^{-1}) : CEC_t \\ = BC + T_A \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Effective cation exchange capacity (cmol}_c\text{kg}^{-1}) : \\ CEC_e = BC + H_e + Al_e \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Saturation with basic cations (cmol}_c\text{kg}^{-1}) : BS \\ = BC/CEC_t \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Organic (residual) aluminium (cmol}_c\text{kg}^{-1}) : Al_{org} \\ = Al_t - Al_e \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Organic (residual) hydrogen (cmol}_c\text{kg}^{-1}) : H_{org} \\ = H_t - H_e \end{aligned} \quad (8)$$

$$\text{Total hydrogen (cmol}_c\text{kg}^{-1}) : H_t = T_A - Al_t \quad (9)$$

Statistical analysis

The parameters of the studied soils were presented as the arithmetic means with standard deviations (SD). A one-way ANOVA was used to determine the differences in the examined parameters among the studied soils grouped according to the understory cover and location. Prior to the variance analysis, it was verified whether the tested variables were normally distributed (Shapiro–Wilk testing) and if there was a homogeneity of variance (Levene test). Owing to the presence of a

normal distribution, parametric variance analysis could be applied. In order to estimate the least significant differences between the mean values of homogenous groups, a Bonferroni post hoc correction was employed (at $p < 0.05$).

Relationships between variables were investigated by performing correlation and regression analyses. We used the Pearson product–moment correlation coefficient (r) to measure the degree of linear association between variables. With the use of principal component analysis (PCA), the relationship between the examined variables (selected soil parameters) and soils of different sites was presented. Plotting of soil parameters in PC1–PC2 space allowed us to specify which parameters affected cation binding properties of the surface horizons under different understories and the direction of the effect (ter Braak and Smilauer 2012). Statistical analyses were conducted using Statistica PL v 12 packet (StatSoft Inc., 2014, Poland) and Canoco 5 (ter Braak and Smilauer 2012).

Results

Parameters related to cation exchange properties

Humus horizons of all studied soils were of sandy loam or loamy sand textures with similar mean clay contents (9–11%), except for soils in Gorce under bilberry (BG) where the amount of clay was lower than in other soil samples (Table 1). Mean pH_{H_2O} was almost the same in all soil groups, around 3.8–3.9, while pH_{KCl} was higher in reference soils (Ref) and in soils under fern (both at 3.0) than under bilberry (2.8) independently of the location. The threshold value of pH (see Eq. 1) ranged between 4.61 in fern soils in Gorce (FG), 4.66 in Ref soils, 4.70 in fern soils in Beskid Żywiecki (FB) and 4.74 in bilberry soils both in Gorce (BG) and Beskid Żywiecki (BB); thus, the pH of all soils was below $pH_{threshold}$.

Mean SOM content was higher in A horizons under fern (76.57 and 80.28 g kg^{-1} in FG and FB, respectively) than in AE or A horizons of the Ref soils (69.86 g kg^{-1}) or the AE horizons of soils under bilberry (61.75 g kg^{-1} in BG and 67.37 g kg^{-1} in BB). The share of fulvic acids in SOM (% FA) was statistically lower under fern (about 36%) than in soils under bilberry (more than 40%) in both locations,

Table 1 Characteristics of analysed and calculated soil parameters (arithmetic mean $\pm$ SD)

Parametres	Referential soils (Ref)	Gorce		Beskid Żywiecki	
		Fern soils (FG)	Bilberry soils (BG)	Fern soils (FB)	Bilberry soils (BB)
Clay	9.4 ^b $\pm$ 2.9	11.0 ^b $\pm$ 2.1	5.00 ^a $\pm$ 1.0	10.0 ^b $\pm$ 2.0	9.0 ^b $\pm$ 1.5
pH _{H2O}	3.88 ^a $\pm$ 0.33	3.90 ^a $\pm$ 0.42	3.89 ^a $\pm$ 0.18	3.89 ^a $\pm$ 0.17	3.83 ^a $\pm$ 0.19
pH _{KCl}	2.99 ^b $\pm$ 0.35	3.09 ^b $\pm$ 0.51	2.81 ^a $\pm$ 0.14	2.92 ^b $\pm$ 0.23	2.82 ^a $\pm$ 0.12
pH _{threshold}	4.60 ^a $\pm$ 0.20	4.61 ^a $\pm$ 0.21	4.74 ^b $\pm$ 0.07	4.65 ^a $\pm$ 0.11	4.74 ^b $\pm$ 0.06
SOM	69.86 ^{ab} $\pm$ 22.34	76.57 ^{ab} $\pm$ 18.78	61.75 ^a $\pm$ 15.24	80.28 ^b $\pm$ 11.87	67.37 ^{ab} $\pm$ 16.83
FA	38.68 ^{ab} $\pm$ 8.52	35.80 ^a $\pm$ 7.58	40.83 ^b $\pm$ 4.69	36.59 ^a $\pm$ 6.16	42.24 ^b $\pm$ 5.47
CEC _e	10.54 ^a $\pm$ 5.45	13.96 ^b $\pm$ 2.94	10.05 ^a $\pm$ 3.06	15.66 ^c $\pm$ 1.79	12.85 ^b $\pm$ 3.58
CEC _t	20.10 ^{ab} $\pm$ 5.12	29.85 ^c $\pm$ 4.57	16.10 ^a $\pm$ 3.77	31.36 ^c $\pm$ 2.50	17.61 ^a $\pm$ 4.41
H _t	10.26 ^{ab} $\pm$ 2.51	16.34 ^c $\pm$ 0.94	6.44 ^a $\pm$ 1.16	15.88 ^c $\pm$ 1.04	6.88 ^a $\pm$ 1.09
Al _t	8.51 ^a $\pm$ 1.52	13.09 ^b $\pm$ 3.28	9.92 ^a $\pm$ 1.03	16.33 ^c $\pm$ 3.38	9.82 ^a $\pm$ 0.89
BC	1.13 ^b $\pm$ 0.22	1.04 ^b $\pm$ 0.13	0.54 ^a $\pm$ 0.11	1.19 ^b $\pm$ 0.17	0.49 ^a $\pm$ 0.12

Clay amount %, SOM soil organic matter (gkg⁻¹), FA fulvic acids share in SOM (%), H_t, Al_t: total hydrogen and aluminium, CEC_e, CEC_t effective and total cation exchange capacity, BC basic cations (Ca²⁺+Mg²⁺+K⁺+Na⁺), H_t, Al_t, CEC_e, CEC_t and BC are given in cmol⁺kg⁻¹

while in Ref soils the share of FA was in between the fulvic acid share of the fern and bilberry soils (Table 1).

Effective cation exchange capacity values (CEC_e) were diversified according to understory and location, being the highest in FB (15.66 cmol_c kg⁻¹) and the lowest in BG and Ref (10.05 and 10.54 cmol_c kg⁻¹, respectively). In bilberry soils, total CEC values (CEC_t) amounted to 16.1 and 17.61 cmol_c kg⁻¹, respectively for GB and BB. In soils under fern, CEC_t values were significantly larger than in bilberry soils, about 30 cmol_c kg⁻¹ both in FG and FB, while in Ref soils the CEC_t value was in between the values of the fern and bilberry soils. Thus, soils rich in SOM had also high CEC_e and CEC_t. The CEC_t/C_t ratio was significantly larger for fern soils (0.67 cmol_c g⁻¹ C for both FG and FB) than for Ref soils (0.51 cmol_c g⁻¹ C) and bilberry ones (0.45 cmol_c g⁻¹ C for both BG and BB). CEC_e constituted about 50% of CEC_t in fern and Ref soils and significantly more in bilberry soils, 73% in BB and 63% in BG. The sum of basic cations was higher in Ref soils and in soils under fern than under bilberry, independently of the location. BC in the A horizons of fern soils and in the A or AE horizons of Ref soils exceeded 1 cmol_c kg⁻¹ and it was about 0.5 cmol_c kg⁻¹ in AE horizons of bilberry soils (Table 1).

Share of cations in total CEC

Total hydrogen content (H_t), composed of organic (H_{org}) and effective (exchangeable) H (H_e), was much lower in bilberry soils (i.e. did not exceed 7 cmol_c kg⁻¹) than in fern soils (about 16 cmol_c kg⁻¹) in both locations (Beskid Żywiecki and Gorce), while in Ref soils its value amounted to about 10 cmol_c kg⁻¹. Independently of the understory, H_{org} prevailed over H_e, but the prevalence of H_{org} was much lower in bilberry soils (twofold) than in fern (threefold) and especially in Ref soils where H_{org} prevailed over H_e about ninefold (Fig. 1a, b).

In both locations, total aluminium content (Al_t) was also lower in bilberry soils than in fern soils, with higher values in FB (exceeding 16 cmol_c kg⁻¹) than in FG (13 cmol_c kg⁻¹). Al_t content in Ref soils was similar to its content in bilberry soils. In bilberry soils, regardless of the location, the share of exchangeable Al (Al_e) was about four times higher than organic Al (Al_{org}), while in fern soils the shares of Al_{org} and Al_e depended on the location. In FB there were almost equal amounts of Al_e and Al_{org} (about 8 cmol_c kg⁻¹), while in FG, Al_e share was about twice as high as Al_{org}, 8.4 and 4.7 cmol_c kg⁻¹, respectively. In Ref soils there were similar amounts of Al_e (8.26 cmol_c kg⁻¹) and Al_{org} (6.31 cmol_c kg⁻¹) (Fig. 1c, d).

Fig. 1 Share of exchangeable hydrogen (H_e) and organic hydrogen (H_{org}) in total hydrogen (H_t): **a** Beskid Żywiecki, **b** Gorce, share of exchangeable aluminium (Al_e) and organic

aluminium (Al_{org}) in total aluminium (Al_t), **c** Beskid Żywiecki, **d** Gorce in soils under Alpine lady fern and bilberry compared to reference soils (Ref)

The ratios of H_e/CEC_t , Al_e/CEC_t and BC/CEC_t were arranged in the same order: BC/CEC_t (0.03–0.06) < H_e/CEC_t (0.08–0.16) < Al_e/CEC_t (0.28–0.51) in all studied soils. H_e/CEC_t ratios were similar in fern and bilberry soils but lower in Ref soils, while Al_e/CEC_t and BC/CEC_t differed according to the dominant understory. In fern soils there was about a 30% higher share of BC and about a twofold lower share of Al_e in CEC_t than in bilberry soils. In Ref soils, the Al_e/CEC_t ratio ranged in between bilberry and fern soils, while the BC/CEC_t ratio was the highest, i.e. twofold higher than in bilberry and 1.5-fold higher than in fern soils (Fig. 2a, b).

Discussion

Relationships between parameters describing cation exchange properties and understory species

The first component from PCA analysis, PC1, explained 90.9% of variance and could be interpreted as the understory effect on cation binding properties in the studied soils (Fig. 3a). High values of highly

correlated parameters, such as pH, CEC_e , CEC_t , Al_{org} , H_{org} , H_t/CEC_t , H_e/CEC_t , BC, SOM and clay, shaped the properties of fern soils (FB and FG). Whereas soil properties under bilberry cover (BB and BG) were influenced by higher FA values and Al_e/CEC_t , Al_t/CEC_t and CEC_e/C_t ratios. PC2, which explained only 8.0% of variance, seemed to divide the soils according to their differences in clay contents. It suggested a closer similarity of fern soils (FG and FB) than bilberry soils (BG and BB).

Moreover, the discrimination between sites at Beskid Żywiecki (FB vs. BB) could be explained by the pH H_2O vector, while the discrimination between two sites at Gorce (FG vs. BG) could be explained by the pH KCl vector. BG and FG differed more in pH_{KCl} values than BB and FB. The difference in pH_{KCl} values between BG and FG were caused by the difference in the sorption complex, which resulted from the much higher SOM and clay content and thus CEC_e values in FG than in BG soils (Table 1). Whereas, between FB and BB soils the differences in these values were smaller, thus the relationship between understory and soils in Beskid Żywiecki was

Fig. 2 Share of basic cations (BC), exchangeable aluminium (Al_e) and exchangeable hydrogen (H_e) in total cation exchange capacity (CEC_t) according to location: **a** Beskid Żywiecki, **b** Gorce in soils under Alpine lady fern and bilberry compared to reference soils (Ref)

Fig. 3 Principal component analysis (PCA) showing the relationship between the examined variables (selected soil parameters) and humus horizons of soils of different understory (**a**) and with Ref soils included (**b**). In PCA following soil parameters were included: clay, pH_{H2O}, pH_{KCl}, organic aluminium (Al_{org}) and hydrogen (H_{org}), soil organic matter (SOM), % of fulvic acids in SOM (FA), basic cations (BC),

total cation exchange capacity (CEC_t), effective cation exchange capacity (CEC_e), share of exchangeable hydrogen and aluminium in total cation exchange capacity (H_e/CEC_t and Al_e/CEC_t), share of total hydrogen and total aluminium in total cation exchange capacity (H_t/CEC_t, Al_t/CEC_t), ratio of effective cation exchange to total carbon (CEC_e/C_t)

better expressed by the ions that were not connected with sorption complex (pH_{H2O}).

In BB soils, which had a comparable clay content to fern soils, cation exchanging properties were probably a little more affected by the mineral content than BG soils. For this reason, the effect of the parameters (FA, Al_e/CEC_t, Al_t/CEC_t and CEC_e/C_t) appeared to be weaker in BB than in BG soils. Our results supported the study of Gruba et al. (2013), who emphasized that

even small changes in clay content, which in our study resulted from the local mud intercalations in magurian sandstones, may modify the cation exchange properties that influence of Al solubility.

Sorption properties are formed by organic and/or mineral soil colloids and the difference in the role of these two components is well seen in the PCA analysis when the Ref soils were included. A major factor PC1, explaining 65.2% of variance divided the studied soils

according to understory effect, setting Ref soil properties in between bilberry and fern soils (a little bit closer to bilberry than fern). A second factor PC2 (31.2% of variance) indicated differences in the sorption complex structure resulting from the stronger effect of spruce needles and/or the share of mineral colloids (inherited from the parent material) in forming sorption properties of studied soils. This factor clearly differentiated Ref soils from bilberry and fern soils, indicating that in the case of a lack of an understory dominating effect (Ref soils), mineral colloids played a more important role in the formation of ion exchangeable properties in A or AE horizons of studied forest soils (Fig. 3b). For this reason as shown in Fig. 3b (with Ref soils included), BC was not as strongly correlated with SOM, as was the case without Ref soils included, shown in Fig. 3a.

Role of organic matter (SOM) in cation binding

Despite the variability of the stands, both CEC_t and CEC_e were strongly correlated with SOM, indicating that the organic matter was an important source of cation exchange capacity, and much less correlated with the clay fraction (Fig. 4a–d). A strong association of CEC_t with SOM was suggested by a high correlation coefficient and a small intercept ($0.204 \text{ cmol}_c \text{ kg}^{-1} \text{ soil}$) of the linear relationship between SOM and CEC_t ($r = 0.7341$, $n = 130$, all sites; Fig. 4a). Regression analysis of CEC_e as a function of SOM also showed a significant correlation ($r = 0.6073$, $n = 130$, all sites; Fig. 4b). However, the gradient of the relations between CEC_e and SOM varied among both the sites and understory cover. CEC_e /SOM correlations were significant for both bilberry soils ($r = 0.524$ for BG and $r = 0.592$ for BB), for fern soils ($r = 0.417$ and $r = 0.670$, for FG and FB, respectively) and for Ref soils, ($r = 0.6153$ at $p < 0.05$).

The relationship between CEC_t and SOM was stronger than for CEC_e and SOM. The smaller intercept in the CEC_t versus SOM regression indicates that factors other than SOM probably contribute little to CEC_t . According to Johnson (2002), the vegetation determines CEC_e /SOM relations in soils when the organic matter is the principal source of exchange sites. The quality of SOM is influenced by both living plants and plant residues. Living plants release organic acids to the soil in root exudates and leaf washings (Huang 1988) while dead plants leaves residues of

various susceptibility to decomposition (Ciarkowska 2017; Kraus et al. 2003). SOM accumulated in soils under bilberry contained more fulvic acids and thus less humic acids, than SOM in soils under alpine lady fern soils. Litter of *Vaccinium* species decomposes slowly because of their woody texture and high content of lignin and condensed tannins; which, according to Ciarkowska and Miechówka (2017), results in a lower decomposition and the formation of humus with a high fulvic acid content.

As FAs often contain 2 to 3 times more carboxyl groups than the HAs isolated from the same soil (Tan 2005), they complex Al mainly through electrostatic attraction, which allows Al to be more easily be leached down the profile. In contrast, the binding of metals by HAs is predominantly through coordination bonds which are more stable. In this way HAs, by chelating metal ions and decreasing their solubility, play an important role in reducing a toxic effect of aluminium to plants and further to humans and animals (Abreu et al. 2003; Huang 1988). For that reason accumulation of SOM in upper soil horizons in alpine lady fern soils as well as in Ref soils resulted in a decrease in the levels of exchangeable Al and H together with the increase of organic forms (Al_{org} and H_{org}) bound to SOM in non-exchangeable way compared to bilberry soils. As a consequence, in A horizons of soils under alpine lady fern and Ref soils the solubility of organic matter was lower while the amount of SOM and pH values were higher than in soils under bilberry.

Our findings are consistent with results of Tůma et al. (2012), who noted an effect of fern cover on lowering soil acidity and cation leaching in acid soils. At the end of a five-year experiment examining the effect of alpine lady fern on soils of deforested areas, they found that in soils with fern cover Mg^{2+} and K^+ contents increased when compared to bare soil. This effect was due to the fern's ability to accumulate nutrients in living material, in dead plant biomass and especially in below-ground biomass which resulted in soil enrichment with nutrients. In our study, Ref soils were forest soils rather than bare ground. Thus, the effect of alpine lady fern was a bit masked by the influence of trees, though we could still observe that pH and BC values in fern soils were similar or even higher than in Ref soils.

Fig. 4 a, b Relationships between total (CEC_t) and effective cation exchange capacity (CEC_e) and soil organic matter (SOM); c, d relationships between total (CEC_t) and effective

cation exchange capacity (CEC_e) and clay. Lines are functional relations and are displayed in cases of strong statistical correlations

Aluminium behaviour in forest soils under bilberry and Alpine lady fern in the understory

The $pH_{threshold}$ is assumed to be a good predictor for the pH at which maximum Al bonding (both Al_e and Al_{org}) occurs (Mueller et al. 2012). At pH below $pH_{threshold}$, a further dissolution of $Al(OH)_3$, if still present, is kinetically constrained and further inputs of strong acids are neutralized by decomplexation of organically bound Al (Gruba and Mulder 2015). The significantly higher $pH_{threshold}$ observed in bilberry soils than in other soils means that the dominant buffering process in soil changes from $Al(OH)_3$ to organically bound Al at a higher pH_{H_2O} than in fern and Ref soils.

All of the studied soils had similar pH_{H_2O} , but differed in $pH_{threshold}$; in fern and Ref soils the difference between $pH_{threshold}$ and pH_{H_2O} (ΔpH) was smaller than in bilberry soils. Thus, in bilberry soils decomplexation of organically bound Al was more advanced than in other soils. In fern soils the Al_{org}/H_{org} ratio was 0.6, in Ref soils it was 0.5 while in bilberry soils this ratio was 0.4 (Fig. 2). (Skylberg et al. 2001) observed that an increase in the Al_{org}/H_{org} ratio results in an increased pH value, which he explained by a weaker acidity of the organic Al-complex, as compared to the protonated forms of the same organic acid sites. Similarly Wesselink et al. (1996) observed that a pH decrease of 0.1 to 0.3 pH units in the pH range 3.2 to 3.6 in acidic Dutch soils

Table 2 Parameter estimates for Bloom and Grigal equation. Estimates were derived from gradients and intercepts of relations between pH_{KCl} and base saturation (BS_e) or pH_{KCl} and base saturation with exchangeable Al included (BS_e^*)

Data set	Equation BS_e			Equation BS_e^*		
	pK_{app}	n	r	pK_{app}	n	r
Ref	2.287	– 0.714	– 0.296	2.241	0.973	0.800*
FG	6.035	2.710	0.675*	2.753	0.885	0.438
BG	2.159	– 0.524	– 0.373	2.677	0.122	0.604*
FB	4.876	1.825	0.657*	2.810	0.354	0.232
BB	3.716	0.642	0.463	2.680	0.212	0.930*

N = 30 for FG, BG, FB and BB. N = 10 for Ref

was connected with a decreasing Al saturation of SOM.

To test the understory communities–related cation binding properties of soil organic matter we applied the Henderson–Hasselbalch equation with the modification of Bloom and Grigal (1985) (Eq. 2). In fern soils, positive correlations were observed between pH and $\log(\text{BS}_e/(1 - \text{BS}_e))$ for both FG and FB soils, while in bilberry soils these values were not correlated regardless of the location. Skjellberg (1999, 2001), Johnson (2002) and Gruba and Mulder (2008) have also observed negative or insignificant correlations between base saturation and pH, attributing their findings to the non-acidic behaviour of Al.

To explain Al behaviour, Johnson (2002) and Ross et al. (2008) proposed a revised form of Eq. (2), i.e. $\text{pH} = \text{pK}_{\text{app}} + n \log[\text{BS}_e^*/(1 - \text{BS}_e^*)]$, where BS_e^* is the base saturation calculated with Al included. When this equation is applied, significant positive correlations were observed between pH and $\log[\text{BS}_e^*/(1 - \text{BS}_e^*)]$ in bilberry soils (independently of the location) (Table 2). Furthermore, the estimated values of the parameters pK_{app} and n in the equations were quite consistent among the alpine lady fern data sets when Eq. 2 was applied, while for bilberry they were consistent when the modified Eq. 2 was used.

Effectively modelled relationships between pH and basic cation saturation with Al included for bilberry soils supported the hypothesis that in acidic forest soils under certain conditions, such as advanced podsolization processes, Al behaves like a base cation. Similarly to bilberry soils, the alkaline character of Al occurred also in reference soils, expressed by a positive correlation between pH_{KCl} and BS_e when Al_e was included in BS_e . This means that in acidic soils under

spruce forest stands, bilberry presence did not influence Al behaviour, while alpine lady fern as main understory species changed Al properties.

Conclusions

For nearly all of the parameters investigated in this study both bilberry and fern soils were different than the reference soils which in many cases were intermediate. Reference soils showed that both understories (alpine lady fern or bilberry) of the spruce forest affected soil chemistry, in different ways. High correlations between soil organic matter and both total and effective cation exchange capacity, showed that SOM was the main source of CEC in humus horizons of acidic forest soils. In soils with bilberry, a decrease of organic forms of H and Al bound to SOM in a non-exchangeable way was observed when compared to reference soils and soils under alpine lady fern. Moreover, in fern soils, Al behaved like an acid cation, in contrast to reference and bilberry soils, where the advanced podsolization processes occurred and Al behaved as a basic cation. A dominance of Alpine lady fern in the understory in spruce forests has environmental significance through reducing solubility of Al, preventing its leaching and decreasing its potential toxicity. In our work we showed that the influence of the understory on soils is significant due to its abundance and can greatly impact soil biogeochemical cycles.

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