

Chemistry of Aluminium and Base Cations in Coarse Woody Debris

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Abstract

Dead trees decaying in the forest ecosystem (called also CWD – coarse woody debris) fulfil a variety of beneficial functions like promoting the diversity of mycorrhizal fungi or enrichment of soil by supplying nitrogen and other nutrients. In specific conditions, decaying trees may become micro-sites for seed germination.

We investigated some chemical properties of the samples collected from twelve CWD profiles (derived from decaying Norway spruce and silver fir trees) with particular attention paid to aluminium and other exchange cations. While investigating the mechanism controlling pH in the examined CWD samples, we tested the Henderson-Hasselbalch equation. Our results confirmed that to arrive at a full explanation of the mechanism, the H-H model has to be modified. A successful modification was done by employing the theory claiming that Al behaves like a base cation in acid soils. The role of aluminium in the ion exchange properties of CWD samples is limited, mostly due to the lack of its mineral sources, and thus its toxic impact is not expected.

Keywords: CWD, aluminium, Carpathians, soil chemistry, ion exchange

Introduction

Coarse woody debris (CWD) is dead and decaying woody material. The maintenance of large pieces of decaying wood in the forest ecosystem used to be considered mostly in its negative aspects, such as timber loss. Kayahara et al. [1] additionally reported that decaying wood increased soil acidification and intensity of podzolization processes. Recently, it has been accepted that decaying stems, logs or stumps also have a positive influence on the forest environment and its biodiversity. The great variety of ecological functions of CWD in forest ecosystems has resulted in a number of studies carried out in recent decades. Several papers have dealt with the contribution of CWD to long-term carbon storage [2-4]. Such an investigation was also made in several natural reserves

in Poland [5]. CWD was even included in models describing carbon circulation in forest ecosystems [6]. Due to its high level of water retention ability, decaying wood was investigated in its function of refugia for tree root ectomycorrhizal fungi, particularly in dry seasons or during fire. Its role in promoting the diversity of mycorrhizal fungi also was observed [7]. One of the most important and frequently investigated aspects of CWD in forest ecosystems is the enrichment of soil by supplying nitrogen and other nutrients released during decomposition. The nutrients originate not only from the decaying wood but also from the pools secondarily fixed by organisms living in CWD [4].

Decaying wood in the more advanced stages of decomposition may affect the forest regeneration process. In specific conditions, rotten trees and stumps may become a substrate creating micro-sites available for seed germination. Even though fallen trees are not the most favourable surface for seed retention, the regeneration conditions are good

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enough for successful germination and survival, especially for coniferous species [8]. Decaying CWD (if large enough) acts as a kind of platform elevating seedlings over the ground level, which gives some physical advantage for germinants: first of all, less intense competition with the herb cover, and secondly, some protection from animal pressure [8]. However, recent research questions the statement that fallen logs are able to protect young trees from being devastated by ungulates [9].

Regeneration of tree species from seeds germinating on the surface of CWD is a common phenomena in Babia Góra National Park in southern Poland. According to Szewczyk and Szwagrzyk [8], in one of the experimental sites located in the park, wood in different classes of decay covered about 6% of total area of the forest floor. The authors, investigating regeneration of trees on different micro-sites, reported that decaying wood is a superior substrate for germination and survival of coniferous species. Roots of seedlings growing on CWD tend to reach mineral soil, deriving nutrients from decomposed wood until they succeed. Following decomposition of CWD, the growing tree may successfully survive as a specific "stilt-rooted" form, which commonly appears in Babia Góra [10].

The observation of the communities of tree seedlings and plants growing on the surface of CWD in a more advanced stage of decomposition raised interest in the potential capacity of such micro-sites for plant nutrition. This resulted in studies on CWD regarded as a soil-like substrate. The above-mentioned studies were carried out by Maciaszek et al. [10] in several natural reserves in southern Poland. Large CWD objects with plants growing on their surface were studied on the basis of their cross-sections (profiles). As observed, the properties of decomposing wood material were changing with depth. In most cases, two layers were described. The upper layer (designated as Odh: O – organic, d – dendro, h – humified) was a mixture of decomposed litter, bark, phloem tissue, and wood; the abundance of plant roots suggested high nutrient content due to the advanced humification process and dark colour. The deeper horizon (designated as Od) derived from soft decaying wood matrix, had the colour of decomposing wood (yellow-orange) with a grey hue; white fungal tissue was more visible than were plant roots. The CWD objects studied by Maciaszek et al. [10] were of IV and V decomposition class (according to Maser et al. [11]). The depth of studied profiles reached 80 cm. The results obtained from the analysis of plants gathered on the investigation sites showed that the nutrient status of plants growing on CWD and on neighbouring soils was similar. These authors did not provide a comparison between the chemical properties of CWD samples and the underlying soils.

In the present study, cation exchange properties and factors controlling pH in the investigated CWD samples were tested using the Henderson-Hasselbach model. Since organic matter is the primary source of negative charge in acid forest soils, in accordance with the Henderson-Hasselbalch equation, the dissociation degree of weak acid explains solution pH [12]:

$$pH = pK_{app} + n \log \frac{(A^-)}{(HA)} \quad (1)$$

...where pK_{app} is an apparent dissociation constant, n is the stoichiometry coefficient, and A^-/HA is the ratio of the dissociated to undissociated forms of functional groups. Successive dissociation of acid groups builds up negative charge, which is ready to fix a cation other than H^+ . In other words, pH of soil is controlled by the relationship between base cations and hydrogen. Traditionally, base cations are Ca^{2+} , Mg^{2+} , and K^+ and acid cations are H^+ and $Al^{(3-n)+}$.

Thus, the equation (1) was further modified by Bloom and Grigal [13]:

$$pH = pK_{app} + n \log \left(\frac{BSe}{1 - BSe} \right) \quad (2)$$

...where BSe is effective base saturation. Equation (2) says that effective soil saturation with base cations is closely related to soil solution pH. Recent investigations have failed with the application of this model for acid forest soil [14, 15]. According to the equation, there are not enough base cations to keep pH at a certain level, and the only explanation is that aluminium in such soils (with $pH < 4.5$) behaves like base cation [14, 15]. Thus, exchangeable (KCl-extractable) Al plays a key role in cation exchange and pH control of acid forest soils.

Even though the content of exchangeable Al in soil solution is much larger than that of Al^{3+} (which is considered to be most toxic for plants), the quantity of exchangeable Al reflects the content of potentially toxic Al^{3+} , i.e. there is a correlation found between KCl-extractable Al and Al^{3+} in soil solution [16].

Samples taken from CWD are acid, but the content of aluminium is limited due to separation from its sources. Our hypothesis is that in such an exceptional (aluminium-free) system, pH is controlled mostly by calcium, not aluminium. Based on other models describing aluminium solubility [17], in these conditions the aluminium toxicity problem should not exist. The objective of this study was to investigate selected chemical properties of samples taken from Norway spruce and silver fir-CWD, with particular regard to its cation exchange properties, tested by means of the modified Henderson-Hasselbach theory.

Materials and Methods

Site Description

Investigation sites were located in Babia Góra National Park, southern Poland, western Carpathians (19°30' E, 49°40' N) at elevations ranging from 870 to 1,200 m above sea level. The average annual precipitation is about 1,400 mm, with average annual temperatures 3–4°C [18]. Soils are acidic, derived from the parent rocks typical for the Carpathian flysch: layers of fine-grained sandstone alternating with thin beds of shale [19]. At higher elevations

(over 1,000 m above the sea level) the vegetation cover consists almost solely of pure spruce (*Picea abies* (L.) Karst.) forest with *Vaccinium myrtillus* (L.) predominant in the forest floor layer. At lower elevations the forest was mixed, including spruce, beech (*Fagus sylvatica* L.), and fir (*Abies alba* L.). Logs chosen for sampling were characterized with advanced decomposition stage (IV and V class according to Maser [11]): wood was soft, easy to sample, shape, no branches, logs were partly sunk in forest floor, its shape was more oval than round.

Soil Sampling and Analysis

The intention of presenting only a limited number of data from soil investigation was to make a sample interpretation of the Henderson-Hasselbalch theory with the soil data applied. Twelve soil samples were taken from the organic (6) and upper mineral (6) horizons. The thickness of the organic horizons varied from 5 cm to 9 cm (average 6.4), mineral horizons were sampled up to a depth of 12 cm. Samples were air-dried and sieved (1 mm) in accordance with the procedures outlined in Polish Soil Taxonomy [20]. The pH of the soil was measured electrochemically with a combination electrode in a suspension of distilled water and 1M KCl, respectively (1:2.5 mass to volume ratio) after 24 h equilibration. The content of soil organic C was measured by wet combustion with $K_2Cr_2O_7$. Exchangeable Ca, K, and Mg were extracted with 1M NH_4 -acetate and determined by atomic absorption spectroscopy (AAS). Exchangeable Al was determined after extracting 40 g of soil with 100 ml 1M KCl for 1 hour, followed by filtration. Some 25 mL sub-

samples of the extract were titrated potentiometrically to pH 8.2, with and without the addition of 0.8 M NaF. The results are supposed to demonstrate exchangeable acidity and exchangeable H, respectively [21]. Al_{KCl} was calculated as the difference between exchangeable acidity and exchangeable H^+ .

CWD Sampling and Analysis

In the present study we used 28 CWD samples taken from cross-cuts made through logs (Fig. 1). The samples represent Norway spruce (13 samples, 6 profiles) and silver fir (15 samples, 6 profiles). As mentioned above, each CWD represents an advanced stage of decomposition with plant succession present on its surface. It was difficult to recognize how long before the trees fell. In one case, we could see an about 60-year-old spruce tree growing on well decomposed CWD. We took 12 samples from Odh horizons and 16 samples from Od horizons.

Live roots were sampled together with whole plants (seedlings or herbs). Samples were air-dried, crushed and sieved through a 2 mm sieve. The major part of analysis was done in accordance with soil analysis procedures described below with some modifications: the pH of CWD samples was measured in suspensions of 5 g of CWD sample mixed with 50 mL of water, the content of exchangeable base cations and exchangeable acidity, including exchangeable Al, was determined as described for soil samples. Loss on ignition (LOI) was reached in an oven at 400°C. The content of organic carbon (C_o) was calculated from LOI by dividing it by 1.72 [21].

Calculation for the Henderson-Hasselbalch Equation (2)

$$BSe = \frac{BCe}{CECe} \quad \text{or} \quad BSe^* = \frac{BCe^*}{CECe}$$

...where: $BCe = Ca^{2+} + Mg^{2+} + K^+$;
 $BCe^* = Ca^{2+} + Mg^{2+} + K^+ + Al^{3+}$;
 $CECe = Ca^{2+} + Mg^{2+} + K^+ + Al^{3+} + H^+$.

Results and Discussion

Selected Chemical Properties of CWD

Studying the properties of soil samples taken from well-decomposed CWD (i.e. properties tested by means of methods usually applied for soils), we found that several features were similar to the soil's organic horizon, while others were considerably different. The latter included, first of all, a very high content of organic matter and a little admixture of mineral fraction in Odh. Such a small content of mineral fraction is due to the elevated position of the CWD surface over the ground level, preventing it from mixing with mineral soil. Another observed difference between CWD and

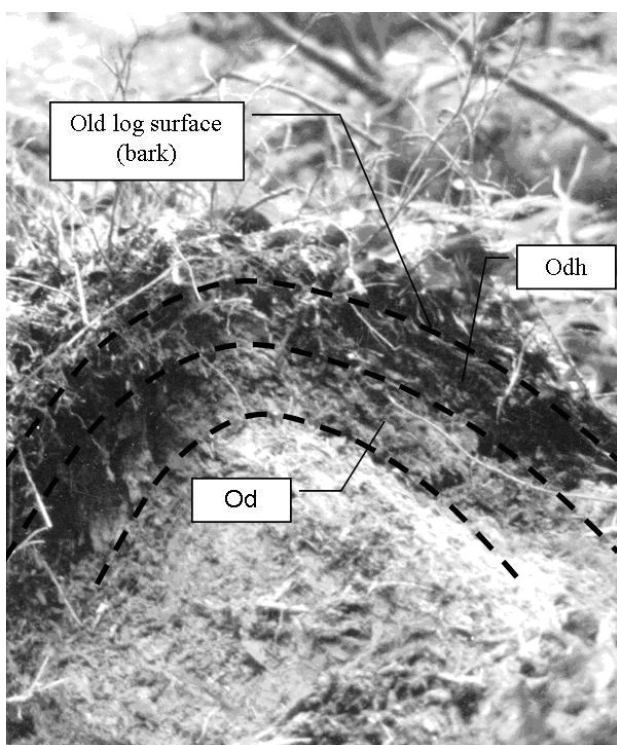


Fig. 1. Example of CWD profile with the layer descriptions.

Table 1. Means and their standard deviations (in brackets) obtained for selected chemical properties of the investigated CWD and soil samples.

Properties analyzed		CWD		soil	
		OdH	Od	organic	mineral
		number of samples			
		12	16	6	6
pH _{H₂O}		3.83 (0.41)	3.62 (0.16)	3.67 (0.14)	4.08 (0.31)
C _t	g kg ⁻¹	558.8 (17.7)	575.9 (3.8)	168.7 (58.9)	45.5 (17.6)
H ⁺	cmol _c kg ⁻¹	4.78 (0.95)	4.62 (1.24)	1.21 (0.95)	0.54 (0.24)
Al ³⁺		3.18 (2.27)	2.27 (0.86)	12.25 (2.23)	13.23 (2.85)
Ca ²⁺		14.05 (13.44)	9.07 (3.98)	2.84 (1.11)	0.78 (0.45)
Mg ²⁺		2.15 (0.89)	1.45 (0.65)	0.67 (0.16)	0.41 (0.53)
K ⁺		1.01 (0.31)	0.57 (0.42)	0.53 (0.09)	0.16 (0.05)
Na ⁺		0.19 (0.06)	0.21 (0.10)	0.07 (0.01)	0.05 (0.02)
CECe		27.76 (8.69)	19.89 (8.34)	17.56 (2.07)	15.17 (3.02)
BS	%	17.41 (14.18)	11.30 (4.85)	4.10 (1.28)	1.40 (0.71)

soil is an increase in C content with increasing depth, while the reverse is true (in most cases) in soils. Both the samples derived from spruce CWD and the soil samples are very acidic (Table 1). Similar values of pH for CWD were reported by Maciaszek et al. [10]. But, they also found pH ~ 6 in samples derived from beech CWD.

The content of base cations (Ca²⁺, Mg²⁺, K⁺) in samples derived from the investigated CWD (Table 1) is characterized by highly variable coefficients of base cation content. This observation is in agreement with the results reported by Maciaszek et al. [10], who noticed major differences between the results obtained from samples of CWD of the same tree species, and suggested that this variability may depend on the nutrient content in tree tissues at the moment of tree death.

Exchangeable (KCl-Extractable) Al

Justification for the small number of soil samples taken for analysis is good agreement of obtained relationships

with data reported for similar soils from this region [22] or other acid soil [15]. Data in Fig. 2 show that the content of extractable Al significantly increases with decreasing pH; however, there is no significant relationship for CWD samples. Due to the lack of Al sources in CWD, the increase of Al is limited at low pH. This and further analysis do not show significant differences between Odh and Od horizons, as well as between spruce and fir CWD, thus these data are not differentiated on the graphs.

The Henderson-Hasellbach Theory Application

In very acidic soils, with pH < 4.5, soil organic matter is the primary source of effective cation exchange capacity (CECe) [15]. When CECe is shown as a function of the content of organic carbon (CECe = α Corg + β) (Fig. 3), the gradient (α) of this relationship measures effective

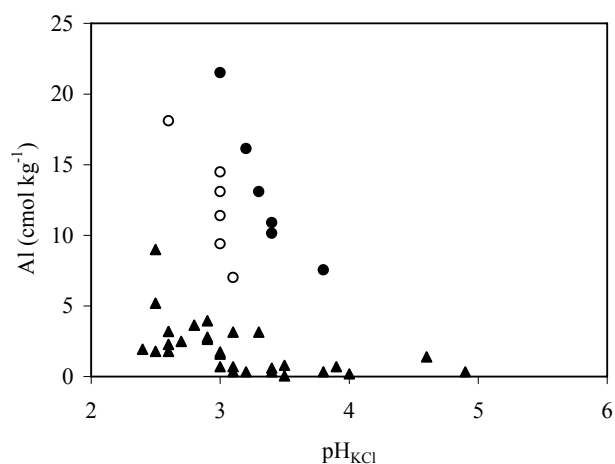


Fig. 2. Relationship between the amount of determined exchangeable Al and pH_{KCl} of the investigated samples; data designations: (o) soil organic, (●) soil mineral, (▲) CWD (OdH and Od horizons; fir and spruce CWD are not differentiated).

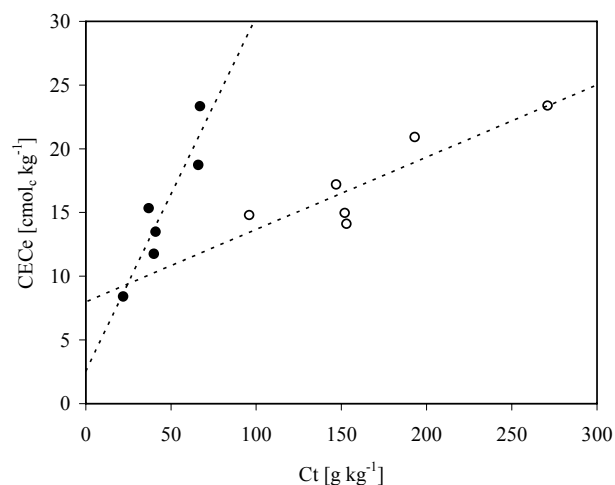


Fig. 3. Relationship between CECe and total carbon in the investigated soils; (o) soil organic, (●) soil mineral. For functional parameters of the presented linear relationships see Table 2. Both relationships are statistically significant at $p < 0.05$.

Table 2. Functional parameters of the relationships between CECe and C (soil) or LOI (CWD), where α and β are the relations gradient and intercept, respectively.

Figure ref.	data from:	α	β	r^2
Fig. 3	soil - organic	0.057	7.99	0.78
	soil - mineral	0.278	2.54	0.87
Fig. 4	CWD	insignificant		

exchange capacity of soil organic matter. That gradient is strongly related to the degree of soil organic matter humification [15, 22]. Our investigation confirmed these statements for soils from Babia Góra. From the parameters of linear relationships (Table 2) we gather that – on average – 1 kg of organic carbon produces 278 cmol_c of CECe in mineral soils, whereas for organic horizons it was only 56 cmol_c of CECe per kg of organic C. The relationships visible in Fig. 3 are similar to those obtained by Johnson [15]. Gruba and Mulder [22] suggest that the relationship

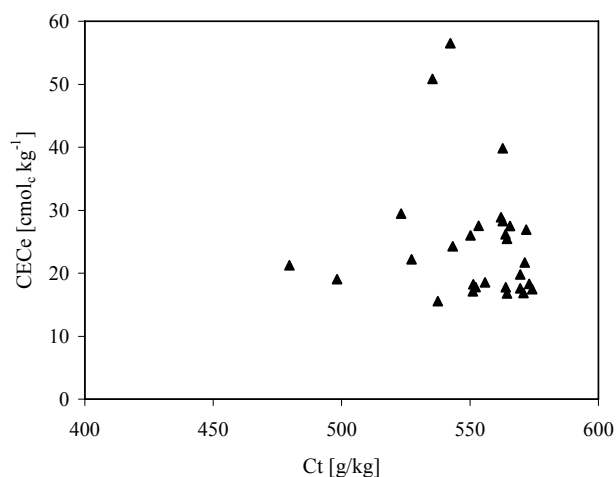


Fig. 4. Relationship between CECe and Ct of the investigated CWD samples. Data from the Odh and Od horizons, fir and spruce are shown as one population.

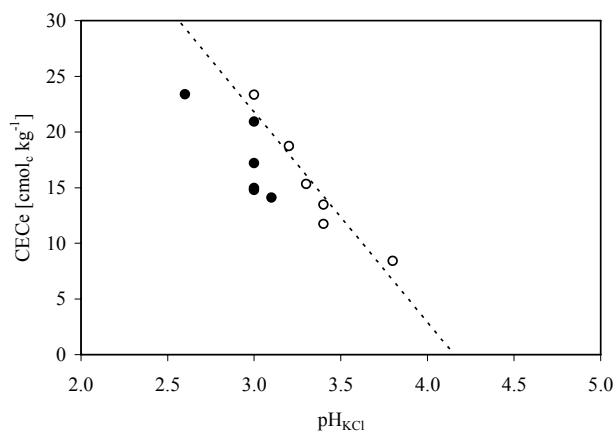


Fig. 5. Relationship between CECe and pH_{KCl}. Data from the investigated soils as described in Fig. 3.

between CECe and the content of total organic carbon may be strongly influenced by the clay content in sample, due to the contribution of clay minerals to CECe.

Contrary to the results obtained for soil, after plotting the carbon content against CECe for data from the CWD samples, a non-correlated scatter was obtained (Fig. 4). This suggests that only a small fraction of CWD is a source of CECe. In Fig. 4, the data from the CWD-Odh and CWD-Od are not separated because neither Odh nor Od data presented consistent, significantly correlated relationships.

In Fig. 5 we plotted CECe against pH_{KCl} of the investigated soil samples. For the visibly consistent pattern of mineral samples we obtained a good correlation ($r = 0.95$). In contrast, there was no significant correlation between pH_{KCl} and CECe in the soil organic horizons of the investigated soils. Similarly, we did not find correlation between pH_{KCl} and CECe determined for CWD samples (Fig. 6). According to Johnson's explanation [15], correlation between CECe and pH is due to Al complexation by soil organic matter. Some authors have reported that the content of Al binding to soil organic matter increases along the growing pH; thus a negative correlation between CECe and

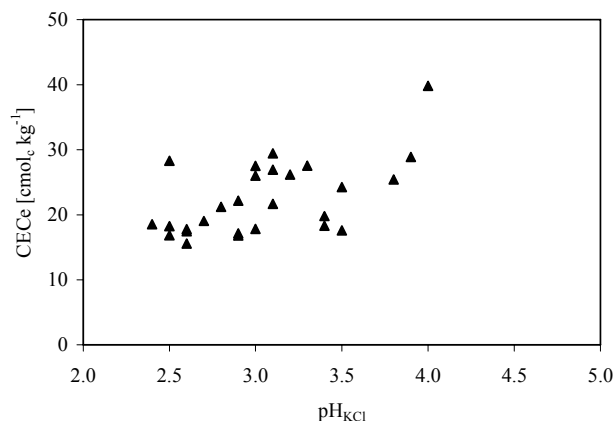


Fig. 6. Relationship between CECe and pH_{KCl}. Data from the investigated CWD samples (not differentiated into horizons and species).

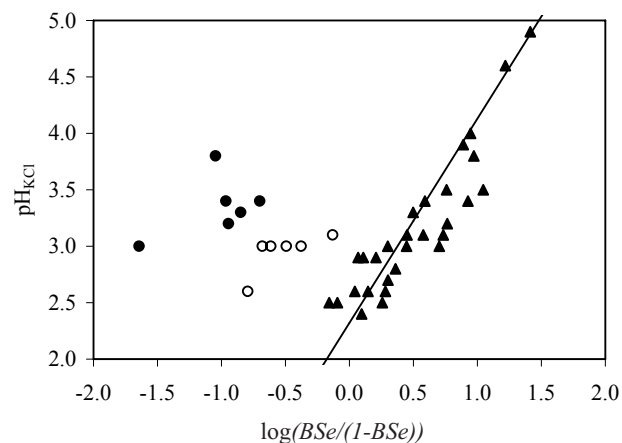


Fig. 7. Henderson-Hasselbalch relationships between pH_{KCl} and effective base saturation (BSe). Sample designations as in Fig. 2.

Table 3. Functional parameters of Henderson-Hasellbach relationships, where α and β are n and pK_{app} of Eq. 3, respectively.

Figure ref.	data from:	α	β	r^2
Fig. 7	CWD	1.82	2.32	0.82
	soil	insignificant		
Fig. 8	CWD	2.39	1.55	0.86
	soil	2.12	0.33	0.70

pH_{KCl} is limited to samples with considerably high content of Al (i.e. mineral samples). In this case, correlation between CECe and pH is not expected in CWD samples (Fig. 6).

The results of testing the application of equation (2) as a model are presented in Fig. 7, plotting pH_{KCl} against $\log(BSe/(1-BSe))$. A high degree of data correspondence for CWD samples is visible and confirmed by the correlation coefficient in Table 3. This means that the pH values obtained in the suspensions of sample material in 1M KCl solution are controlled by saturation of effective exchange capacity (derived from organic matter) by basic cations: Ca^{2+} , Mg^{2+} , K^+ , and Na^+ .

To explain the lack of correlation for data obtained from the investigated soil samples, we need to take into consideration the theory that Al behaves like a base cation in acid soils [14, 15, 22]. The relations shown in Fig. 8 are modified by including exchangeable Al with other base cations. The scatter of points representing data from soil samples (Fig. 7) has changed into a relatively consistent pattern in the relation shown in Fig. 8. Data of BSe from CWD samples computed while taking into account Al (Fig. 8) present a pattern similar to that shown in the previous graph. This means that in the investigated soil samples aluminium is a main cation that keeps pH at a certain level, while in acidic CWD samples pH depends mostly on the content of Ca^{2+} , Mg^{2+} , and K^+ , as is true in soil with higher pH (>4.5) [14].

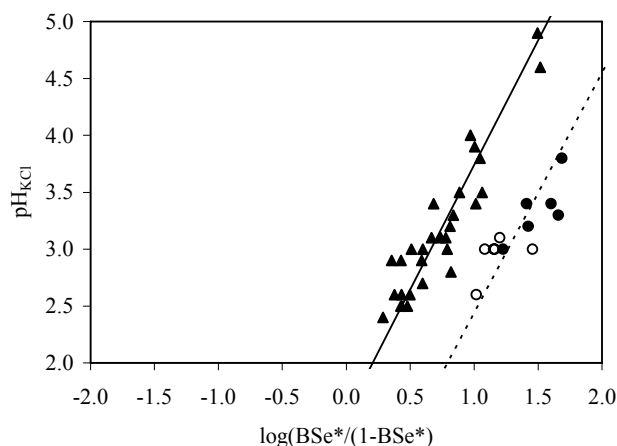


Fig. 8. Henderson-Hasselbalch relationships between pH_{KCl} and effective base saturation, calculated by including Al as a base cation (BSe^*). Samples designation as in Fig. 2.

The presented models show that despite different organic matter content in samples of CWD and soil, similar mechanisms regulate the exchange reactions and pH. The main difference is the role of aluminium, which is marginal in CWD but important in soil samples, particularly in mineral ones. The factor that probably decreases the correlation coefficient for mineral soil is the content of clay minerals contributing to soil CECe. A similar observation for soils from the Polish Carpathians was reported by Gruba and Mulder [22].

From the models describing the solubility of aluminium in soil solution [17, 22] we know that the concentration of potentially toxic forms of Al^{3+} are strongly dependent on pH and aluminium bound to soil organic matter. Thus in CWD samples the concentration of soluble should be very low.

Possible Implications for Growth Conditions

In acidic soils containing large amounts of aluminium, dissolved Al^{3+} is one of the cations that may have a toxic impact on plant roots [23], resulting in growth reduction or increased mortality [24]. The investigation of reactions between soil solution and soil solid phase suggests that the gradient of Al^{3+} release from soil organic matter is about twice smaller than from gibbsite-like minerals but, due to large capacity, the organic matter is able to release large amounts of Al^{3+} when pH decreases [16, 22]. One of the main indicators of Al toxicity is the Ca^{2+}/Al^{3+} ratio. In the CWD samples this ratio was 33.4 (average, for exchangeable forms), while values from 0 to 1 are referred to be toxic [23, 24]. Calculated for soil organic and mineral samples Ca^{2+}/Al^{3+} ratios were 2.7 and 1.5, respectively. Separation from mineral sources of Al excludes this potentially toxic element from cation exchange reactions in CWD samples. Thus the soil-like CWD substrates seems to be safe from Al toxicity threat; however, they are highly acidic. On the other hand, some of the seedlings growing on CWD may find enough nutrients to survive, at least until their roots reach soil surface. The most commonly observed result of the aluminium stress to stress is reduction of magnesium uptake [25], thus the reduction of Mg content in needles is expected when roots reach a mineral soil. When not, Al^{3+} toxicity is the factor limiting plant growth on CWD, other deficiencies are expected to be critical, e.g. water or nitrogen supply [10, 26].

Conclusions

In conclusion, decaying CWD, which fulfils the role of soil-like substrate for plants providing nutrients, has several unique features. However, there are many similarities to "genuine" soil as well. The comparison showed that decaying CWD is able to supply the plants growing on its surface with nutrients such as N, Ca, Mg, and K. The huge predominance of organic fraction in CWD mass does not significantly affect the cation exchange properties of samples taken from this material. The main difference is the role of aluminium, whose content is strongly limited in CWD samples.

Consequently, the risk of aluminium toxicity at low pH is much smaller than in soil adjacent to the investigated CWD profiles. This contributes to the theory that it can be considered a kind of safe micro-site.

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