Distribution of aluminium among its mobilizable forms in soils of the Jizera Mountains region

L. Mládková, L. Borůvka, O. Drábek

Czech University of Agriculture in Prague, Czech Republic

ABSTRACT

Labile Al forms can be dangerous in acid soils due to their potential toxicity to plants. This paper deals with the distribution of exchangeable, weakly organically bound, and total organically bound Al forms in soils on 98 sites of the Jizera Mountains region. For the extraction of these Al forms, 0.5M KCl (Al_{KCl}), 0.3M $CuCl_2$ (Al_{CuCl_2}), and 0.05M $Na_4P_2O_7$ ($Al_{Na_4P_2O_7}$) solutions were used, respectively. Aluminium concentrations in all extracts were determined by means of ICP-OES. Following mean concentrations of Al forms were found in the O and B horizons (mg/kg): Al_{KCl} – 1236 and 832, Al_{CuCl_2} – 4268 and 1945, and $Al_{Na_4P_2O_7}$ – 5043 and 8420. Basic soil characteristics were determined by commonly used methods. Their influence on Al forms distribution was assessed. Factor analysis showed that the most important soil factors controlling Al forms distribution were soil reaction and the total content of Ca (or Ca and Mg in the B horizon).

Keywords: aluminium; labile Al forms; forest soils; soil acidification; Al extraction

Aluminium is the most abundant metal in the Earth crust (7.5% of weight). It is contained in 250 minerals; thereout approximately 40% are alumosilicates. In soils, Al represents approximately 8% of the total mineral content (Polański and Smulikowski 1978, Gauthier 2002).

Aluminium concentration in soil solution depends mainly on soil pH, as it has been observed and proved by many researches. However, the influence of soil pH on Al behaviour is strongly modified by the presence of complexing fractions of soil organic matter (Berggen and Mulder 1995, Hees et al. 2000). Normal chemical weathering of alumosilicates by carbonic acid or various organic acids (i.e. abundantly occurring weak acids), as the principal source of Al in soils, generally causes only a short-lived mobilization of Al (Sposito 1996).

The anthropogenic effects on the lithospheric Al cycling increase the biospheric burden of aluminium. In addition, these activities are accelerating this cycle to allow a much more rapid flux of the metal into the biosphere and in particular into humans (Exley 2003). However, since the Al pool within the soil environment is so large, even a small perturbation of normal weathering (i.e. soil acidification) may cause a large increase in Al mobility and profoundly increase the concentration of this element in soil solution or in natural waters (Sposito 1996).

The form of Al plays a decisive role in its potential bioavailability and toxicity. Toxicity to plants qualitatively decreases in the order: Al_{13} (not in a form of phosphates or silicates), Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$. Aluminium bound in fluoride or organic complexes and $Al(OH)_3$ are supposed to be nontoxic (Boudot et al. 1994, Sposito 1996, Gauthier 2002). The complexation of Al by natural organic substances is of considerable significance in regulating concentrations of the highly toxic Al^{3+} ion in acid soils and natural waters (Sposito 1996).

The Jizera Mountains region was strongly affected by human activities in the last few decades. High concentrations of acidificants in atmosphere led to the damage of forest and soils. Breakdown of the forest structure was followed by grass expansion (Soukupová 1996). At present, the concentrations of acidificants in atmosphere are below emission limits. However, forests still stay threatened by long-term changes of soil conditions (lower base saturation, lower pH and higher labile Al forms concentrations). Distribution of basic soil characteristics in this region was shown in Mládková et al. (2003a, b). The effect of soil horizons and forest types on Al forms is described by Mládková et al. (2004).

The aim of this paper is to describe the effect of basic soil characteristic on the Al distribution among its mobile or potentially mobilizable forms in soil.

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Table 1. Mean values of studied variables in the O and B horizons

Horizon	Al_{exch}	Al_{KCl}	Al_{CuCl_2}	$Al_{Na_4P_2O_7}$	Ca_{tot}	Mg_{tot}
	(mg/kg)					
O	–	1 236	4 268	5 043	578.9	846.6
B	1 956	832	1 945	8 420	221.2	2 468.2

Horizon	C/N	A_{400}/A_{600}	pH_{H_2O}	pH_{KCl}	CEC (mmol/100 g)	C_{org}	C_{tot}	N_{tot}	S_{tot}
						(%)			
O	19.6	7.4	3.9	3.2	–		28.9	1.5	0.3
B	21.7	9.1	4.0	3.6	7.8	4.3	4.5	0.2	0.0

MATERIAL AND METHODS

This contribution is focused on the Jizera Mountains region, which is located in the North of Bohemia. A set of 98 sampling sites was studied in this region. Altitudes of these sites ranged from 400 to 1000 m. Beech, spruce and mixed forests are the prevailing vegetation cover. The highest parts of the mountains are to a large extent covered by grass (*Calamagrostis villosa*). Soil samples from sufficiently deep horizons were collected on these places. In all cases, one sample was collected from organic O (L + F) horizon and at least one sample from mineral horizon (cambic or spodic B horizons). Samples were air dried and passed through 2 mm sieves. Basic soil characteristics were determined by commonly used methods: pH_{H_2O} and pH_{KCl} potentiometrically; humus quality was assessed by the ratio of absorbances of pyrophosphate soil extract at the wavelengths of 400 and 600 nm (A_{400}/A_{600}, Pospíšil 1981). Organic carbon quantity (C_{org}) was determined oxidimitrically by a modified Tjurin method (Pospíšil 1964); this analysis was done only on samples from mineral horizons. Total contents of C, N and S (C_{tot}, N_{tot}, S_{tot}) were measured by automated analyser LECO CNS-2000 (MI USA). Effective cation exchange capacity (CEC) of mineral horizons was determined according to Mehlich with unbuffered 0.1M $BaCl_2$ extraction solution (Podlešáková et al. 1992). At the same time, the concentration of exchangeable base cations (Ca, Mg, K) and exchangeable Al form (Al_{exch})

Table 2. Correlations among three forms of Al and basic soil characteristics in the O horizon (correlation coefficients)

Variable	Al_{KCl}	Al_{CuCl_2}	log $Al_{Na_4P_2O_7}$
Al_{KCl}		0.438***	0.270**
Al_{CuCl_2}	0.438***		0.584***
log $Al_{Na_4P_2O_7}$	0.270**	0.584***	
C/N	0.062	–0.207*	–0.301**
A_{400}/A_{600}	0.184	0.067	0.012
pH_{H_2O}	–0.426***	–0.010	0.281**
pH_{KCl}	–0.347***	0.230*	0.404***
log Ca_{tot}	–0.509***	–0.150	–0.187
log Mg_{tot}	–0.269**	–0.214*	–0.250*
C_{tot}	0.397***	0.448***	0.268**
N_{tot}	0.371***	0.526***	0.401***

*, **, *** significant at the probability level 0.05, 0.01, and 0.001, respectively

Table 3. Correlations among four forms of Al and basic soil characteristics in the B horizon (correlation coefficients)

Variable	Al_{exch}	log Al_{KCl}	log Al_{CuCl_2}	$Al_{Na_4P_2O_7}$
Al_{exch}		0.710***	0.303**	0.159
log Al_{KCl}	0.710***		0.362***	–0.003
log Al_{CuCl_2}	0.303**	0.362***		0.381***
$Al_{Na_4P_2O_7}$	0.159	–0.003	0.381***	
C/N	0.059	0.100	0.114	0.246*
A_{400}/A_{600}	–0.032	–0.099	–0.047	0.222*
pH_{H_2O}	–0.664***	–0.544***	–0.072	0.066
pH_{KCl}	–0.724***	–0.660***	0.007	0.187
Ca_{tot}	–0.080	–0.011	0.153	0.133
Mg_{tot}	–0.243*	–0.176	0.083	0.292**
CEC	0.847***	0.718***	0.283**	0.050
C_{org}	0.423***	0.324**	0.268*	–0.033
C_{tot}	0.505***	0.385***	0.359***	0.034

*, **, *** significant at the probability level 0.05, 0.01, and 0.001, respectively

was determined. In almost all cases, however, the concentrations of exchangeable Ca, Mg and K were under the detection limit hence these variables were not used in statistical treatment. Total contents of Ca and Mg (Ca_{tot}, Mg_{tot}) were measured after soil digestion with aqua regia (Zbíral 1996). Contents of three different Al forms were determined according to Drábek et al. (2003); exchangeable Al forms were extracted with 0.5M KCl solution (Al_{KCl}), an assessment of weakly organically bound and total organically bound Al forms was based on Al amounts extracted with 0.3M $CuCl_2$ (Al_{CuCl_2}) and 0.05M $Na_4P_2O_7$ ($Al_{Na_4P_2O_7}$) solutions, respectively. Aluminium concentrations in all extracts were determined by means of ICP-OES (VARIAN Vista Pro, VARIAN, Australia).

Statgraphics Plus 4.0 for Windows (Manugistics 1997) was used to perform correlation and factor analysis.

RESULTS AND DISCUSSION

Table 1 shows average values of all studied variables. The major part of the variables had normal distribution in both horizons. Logarithmic transformation was used for the normalisation of Ca_{tot}, Mg_{tot} and $Al_{Na_4P_2O_7}$ in the O horizon and Al_{KCl} and Al_{CuCl_2} in the B horizon. The total content of S did not have a normal distribution in any horizons in this study and the total content of N did not have a normal distribution in the B horizon even after the transformation. Therefore, they were not used in further statistical analysis. Correlation analysis showed significant relationships among all three Al forms in the O horizon (Table 2). In the B horizon, $Al_{Na_4P_2O_7}$ did not show any correlation with Al_{exch} and Al_{KCl}, significant correlation exist among the other Al forms (Table 3).

On the basis of correlation analysis results in the O and B horizons, which showed relationships among studied variables (Tables 2 and 3), values of basic soil characteristics and mobile Al forms contents were treated with factor analysis. Tables 4 and 5 show models of factor analysis in the O and B horizons. In both cases, four factors were extracted. These four factors accounted for 78.6% of the variability in the original data for the O horizon and 74.3% for the B horizon. Variance percentage explained by individual factors is shown in Tables 4 and 5. Communality values of studied Al forms show that the model for the O horizon better explains their variability than the model for the B horizon.

The most important factor in the O horizon is that of organic matter content. It accounted for 30.6% of the variability in the original data and the highest factor loadings showed variables C_{tot} and N_{tot}. The second factor was interpreted as the factor of soil reaction, the third one can be interpreted as the factor of Ca_{tot} and Al forms contents, and the fourth one was interpreted as the factor of humus

Table 4. Factor loading matrix after varimax rotation for the O horizon and estimated communality (E.C.)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	E.C.
C/N	–0.124	–0.627	–0.056	0.208	0.455
A_{400}/A_{600}	0.203	–0.049	0.081	0.858	0.786
pH_{H_2O}	–0.147	0.789	–0.262	0.216	0.759
pH_{KCl}	–0.104	0.880	–0.075	0.172	0.821
log Ca_{tot}	0.103	0.285	–0.655	0.548	0.822
log Mg_{tot}	–0.634	0.141	–0.142	0.593	0.794
Al_{KCl}	0.242	–0.317	0.825	0.097	0.848
Al_{CuCl_2}	0.399	0.351	0.646	0.071	0.705
log $Al_{Na_4P_2O_7}$	0.264	0.605	0.560	–0.101	0.760
C_{tot}	0.937	–0.104	0.157	0.175	0.944
N_{tot}	0.940	0.141	0.200	0.088	0.952
Variance %	30.6	24.0	14.6	9.4	

quality. Factors 2 and 3 are the most important from the point of view of Al forms distribution in the O horizon. Two variables influence this distribution the most: Ca_{tot} content and soil pH (Figure 1). Concentration of Ca_{tot} more strongly influences position of Al_{KCl} in the plot (along the y-axis). The higher the Ca_{tot} concentration, the lower is the Al_{KCl} concentration in soils. Al_{KCl} stays furthest from both pH types along the x-axis. It confirms that low pH increases the concentration of Al_{KCl}. A similar situation is in the case of Ca_{tot} content versus Al_{CuCl_2} and $Al_{Na_4P_2O_7}$. However, the influence of pH is weaker and the low pH even decreases the concentrations of Al_{CuCl_2} and $Al_{Na_4P_2O_7}$.

A different situation is in the B horizons. The most important is the factor of exchangeable Al forms and soil reaction. It accounts for 36.8% of the total variability in the original data. The second factor

Table 5. Factor loading matrix after varimax rotation for the B horizon and estimated communality (E.C.)

Variable	Factor 1	Factor 2	Factor 3	Factor 4	E.C.
C/N	–0.104	0.251	0.117	0.715	0.598
A_{400}/A_{600}	–0.041	–0.221	–0.111	0.814	0.725
pH_{H_2O}	–0.857	0.147	0.144	0.205	0.819
pH_{KCl}	–0.847	–0.241	0.228	0.247	0.889
Ca_{tot}	–0.098	–0.114	0.750	0.154	0.609
Mg_{tot}	–0.265	–0.391	0.569	0.336	0.661
Al_{exch}	0.883	0.275	0.071	0.122	0.875
log Al_{KCl}	0.806	0.213	0.168	0.028	0.725
log Al_{CuCl_2}	0.208	0.371	0.639	0.091	0.597
$Al_{Na_4P_2O_7}$	0.066	–0.002	0.515	0.486	0.505
CEC	0.793	0.459	0.030	0.034	0.841
C_{org}	0.204	0.921	–0.070	–0.009	0.894
C_{tot}	0.276	0.916	0.022	0.017	0.916
Variance %	36.8	16.6	11.7	9.2	

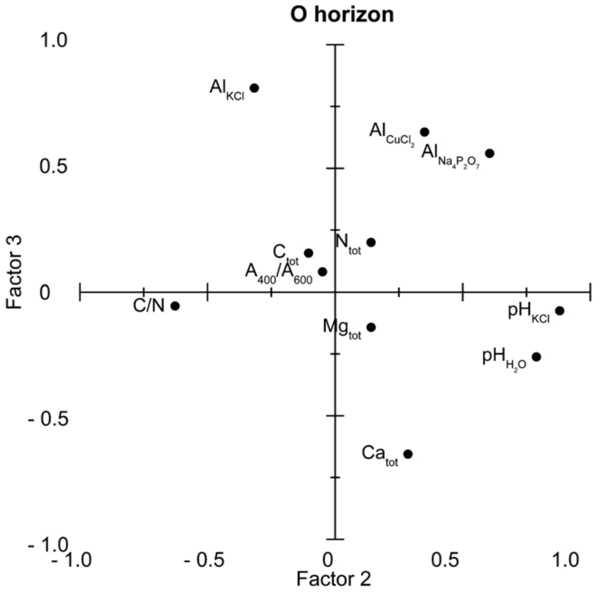

Figure 1. Plot of loadings of the 2nd and 3rd factors for the O horizon

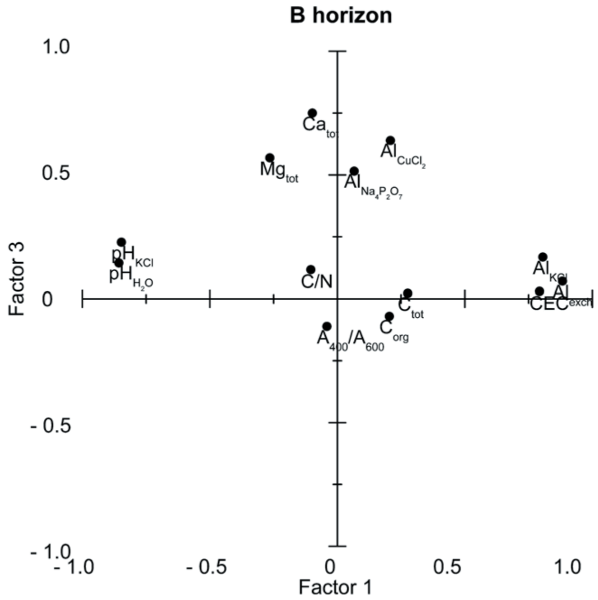

Figure 2. Plot of loadings of the 1st and 3rd factors for the B horizon

was interpreted as the factor of soil organic carbon content. The third factor can be interpreted as the factor of Ca_{tot}, Mg_{tot} and organically bound Al forms contents, and the fourth one as the factor of humus quality like in the O horizon. Factors 1 and 3 are the most important from the point of view of Al forms distribution in the B horizons. Two sorts of variables influence this distribution: soil pH and Ca_{tot}, Mg_{tot} contents (Figure 2). Exchangeable Al forms are mainly influenced by soil pH. This relationship is the same as in the O horizon. A strong relationship was found between organically bound Al forms and Ca_{tot} and Mg_{tot} contents. An increase of Ca_{tot} and Mg_{tot} concentrations lead to an increase of organically bound Al concentrations in the B horizon.

All results show that the distribution of Al among the determined forms vary between the O and B horizons. Nevertheless, the principal factors controlling this distribution are the same: soil reaction and Ca (and Mg) content as a potential pool of base cations. Phytotoxic Al forms are the most abundant in the most acidic soils with the lowest base cations contents.

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ABSTRAKT

Rozdělení hliníku mezi jeho mobilní formy v půdách Jizerských hor

Labilní formy hliníku jsou v kyselých půdách považovány za hrozbu díky jejich toxickému působení na rostliny. Tato práce se zabývá rozložením tří forem hliníku v půdách 98 sledovaných lokalit v Jizerských horách. Jde o formu výměnnou (vyluhovatelnou 0,5M KCl – Al_{KCl}), formu slabě organicky poutanou (vyluhovatelnou 0.3M $CuCl_2$ – Al_{CuCl_2}) a formu silně organicky poutanou (vyluhovatelnou 0.05M $Na_4P_2O_7$ – $Al_{Na_4P_2O_7}$). Koncentrace jednotlivých forem hliníku ve všech třech výluzích byly měřeny pomocí ICP-OES. Byly zjištěny následující průměrné koncentrace jednotlivých forem Al v horizontech O a B (mg/kg): Al_{KCl} – 1236 a 832, Al_{CuCl_2} – 4268 a 1945, $Al_{Na_4P_2O_7}$ – 5043 a 8420. Základní půdní vlastnosti byly stanoveny běžně užívanými metodami. Byl posouzen jejich vliv na rozložení forem Al v půdách. Po provedení faktorové analýzy se jako nejdůležitější faktory ovlivňující toto rozložení ukázaly půdní reakce a celkový obsah Ca, resp. Ca a Mg v horizontu B.

Klíčová slova: hliník; labilní formy Al; lesní půdy; acidifikace půd; extrakce Al

Corresponding author:

Lenka Mládková, Česká zemědělská univerzita v Praze, 165 21 Praha 6-Suchdol, Česká republika
phone: + 420 224 382 759, fax: + 420 234 381 836, e-mail: mladkova@af.czu.cz