

Aluminium Mobilization as an Aspect of the Chemical Degradation of the Soil

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Soil acidification, one of the chemical soil degradation processes is often responsible for the low productivity of soils and for unfavourable environmental phenomena. One consequence of this may be the mobilization of several Al compounds in the soil, i.e. the accumulation of toxic Al species in the soil solution (BACHE, 1986). Environmental hazards may arise because a high concentration of dissolved aluminium is toxic to plants (WRIGHT et al., 1989) and, due to the movement of the soil solution, aluminium may get into ground and drinking waters and into the food chain.

The aim of the experiments was to study the conditions under which toxic Al species accumulate. The quantity of dissolved Al^{3+} was measured and that of different Al species in the liquid phase of acidic soils was calculated at different moisture contents.

Materials and Methods

Samples of soils having different pH and base saturation values (Table 1) were used in the experiments and calculations. These were:

- a) the 0-20 cm layer of an acidic brown forest soil from Ragály (forest soil 1);
- b) a strongly acidic soil prepared from forest soil 1 by treating it with HCl (forest soil 2);
- c) as a comparison, the 0-25 cm layer of a chernozem soil from Debrecen (chernozem).

After the usual pretreatment of the soils (air-drying, grinding, passing through a 2 mm sieve), the samples were moistened with CO_2 -free distilled water to field capacity (FC, corresponding to 20 kPa moisture potential) and maximum water capacity (MC, corresponding to 0.1 kPa moisture potential). Saturation pastes (RICHARDS, 1954) were also prepared. The wet soils were

Table 1
Selected physical and chemical characteristics of the studied soils

Soil properties	Forest soil 1 (Ragály)	Chernozem soil (Debrecen)
pH (H ₂ O)	4.6	6.0
* CaCO ₃ content, %	0	0.1
* Total soluble salts, %	0.02	0.09
* Clay content (< 0.002 mm, %)	31.8	27.4
* Organic matter, %	3.1	3.1
* CEC, me/100 g soil	19.0	28.3
* BS %	28.3	76.4
* y ₁	50.1	6.8
** SP, g moisture /100 g soil	58.0	43.7
** MC, g moisture/100 g soil	38.1	41.5
** FC, g moisture/100 g soil	27.1	24.8
** ρ , g/cm ³	1.39	1.22

*: in terms of air-dried soil; **: of soil dried at 105 °C; SP: saturation percentage, i.e. the moisture content of the saturation paste, expressed as a weight percentage; MC and FC: maximum water capacity and field capacity of the undisturbed soil, expressed as a weight percentage (moisture contents corresponding to 0.1 kPa and 20 kPa moisture potentials of the soil, respectively); CEC: cation exchange capacity; BS %: base saturation, i.e. the proportion of the amount of exchangeable Ca²⁺ + Mg²⁺ + K⁺ + Na⁺ as a percentage of CEC; y₁: hydrolytic (surface) acidity determined by applying 0.05 mol/L Ca-acetate solution at pH 8.2); ρ : dry bulk density of the soil.

kept in air-proof plastic vessels for 7 days and were mixed 3-4 times. The liquid phases were separated by centrifugation. The rotor speed corresponded to 1500 kPa suction, to a value representing the wilting point of plants, i.e. the conventional upper limit of the suction exerted by plant roots. It can be presumed that using this centrifugation method the soil solution available to plants can be separated. Saturation extracts were also obtained by centrifugation, applying a rotor speed corresponding to 500 kPa (a pressure applied in the routine pressure filtering methods).

In the solutions the concentrations of Ca, Mg and Na (and of Al and Mn in the acidic soils) were measured with an ICP spectrometer, the HCO₃⁻ and Cl⁻ concentrations were determined by titration, while the SO₄²⁻ and NO₃⁻ contents were determined by gravimetric and colorimetric methods, respectively (PAGE et al., 1982; BUZÁS, 1988).

The amounts of ion species were calculated from the mass balance equations:

$$c_t = c_f + c_p + c_k \quad (1)$$

where: c_t denotes the measured "total" concentrations, c_p and c_k are the concentrations of the ion-pairs and complexes, respectively, and c_f is the concentration of "free" ions. From equation (1) it follows that

$$c_f = c_t - \Sigma(c_p + c_k) \quad (2)$$

In the case of *acidic soils* the dominant cations are Al^{3+} , Mg^{2+} , Ca^{2+} , Mn^{2+} and Na^+ , so their species are significant in the soil solution. In the case of aluminium the presence of hydroxocomplexes and the $AlSO_4^+$ ion-pair was supposed, while for other cations the $MeSO_4$ pairs were assumed. So the mass balance equations can be written as:

$$[Al^{3+}]_t = [Al^{3+}]_f + [AlOH^{2+}] + [Al(OH)_2^+] + [AlSO_4^+] \quad (3a)$$

(where [] denotes concentrations), and for other cations (similarly to Ca^{2+}):

$$[Ca^{2+}]_t = [Ca^{2+}]_f + [CaSO_4^0] \quad (3b)$$

In the case of the *chernozem soil* the associations between Ca^{2+} , Mg^{2+} , Na^+ and HCO_3^- , SO_4^{2-} were taken into account. Therefore, the mass balance equations are:

$$[Ca^{2+}]_t = [Ca^{2+}]_f + [CaHCO_3^+] + [CaSO_4^0] \quad (4a)$$

and

$$[Na^+]_t = [Na^+]_f + [NaHCO_3^0] + [NaSO_4^-] \quad (4b)$$

The amounts of ion-pairs and complexes were expressed as the ratio of the product of the cation and anion (or ligand) activities, and the equilibrium constants of the species:

$$[MA]^{z-y} = \frac{(M^{z+})(A^{y-})}{K_{(MA)}^{z-y}} \quad (5)$$

where "z" and "y" are the charges of the cation and anion (or ligand). The values of the $K_{(MA)^{z-y}}$ constants are given in handbooks (e.g. LINDSAY, 1979).

(The activities of ion-pairs $/(\text{MA})/$ were assumed to be equal to their concentrations $/[\text{MA}]/$, while in the case of hydroxy-Al complexes, their activities were calculated using the Davies equation (LINDSAY, 1979; SPOSITO, 1981).)

The distribution of the species was calculated with successive approximation by applying computer programmes developed earlier by CSILLAG & DARAB (1985), and CSILLAG, FILEP & PINTÉR (1991).

In the first step it was supposed that $c_i = c_f$. Therefore, at first the ionic strength of the solution (I_1), the ion activity coefficients (γ_1^+ , γ_1^-) and the ion activities (a_{f1}) were calculated from the measured data. Ion-pair concentrations were then calculated from the ion activity values according to eq. (5). Using eq. (2) the modified ion concentrations (c_{f1}) could be obtained. In the second cycle the above parameters (I_2 , γ_2^+ , γ_2^- , c_{f2} , a_{f2}) were calculated from the modified ion concentrations (c_{f1}). The iteration procedure is stopped when the differences between free ion concentrations (c_{fn-1} , c_{fn}) obtained in the last successive steps become negligible for every ion.

Results

The chemical composition of the liquid phase of soil samples having different moisture contents are given in Table 2.

It can be seen from the data of Table 2 that with decreasing soil moisture content the salt concentration (ionic strength) of the soil solution increases, and that the amount of dissolved salts and the ionic composition of the solution correlate well with the chemical properties (pH, y_1 , BS%) of the soil.

Depending on the pH and moisture content of the soil, the amounts of ionic species present in the liquid phase are represented in Figs. 1-3. As the ion concentrations in the solutions differ by several orders of magnitude (Table 2), the measured concentrations could be represented only on deformed scales. (If the concentrations increase to 1, 10, 10^2 , 10^3 , 10^4 times, the areas of the columns in Figs. 1-3 increase 1, 2, 3, 4, 5 times.)

From the figures the following conclusions could be drawn:

Changes in the ionic composition, concentration and pH of the soil solution may lead to the dissolution of certain minerals or, inversely, may result in the formation of poorly soluble compounds (FILEP, 1988; SPOSITO, 1989). A shift in the cation exchange equilibria between the solid and liquid phases of the soil may also take place. A change in the ratios of the different species present in the liquid phase may influence the above processes (LINDSAY, 1979; SPOSITO, 1981). The amounts of the ionic species are determined by the ionic strength,

Table 2

Measured "total" ion concentrations (expressed in mmol/L) in the liquid phases of soils having different moisture contents

Soils	Ions	SP	MC	FC
<i>Forest soil 1</i>	Al^{3+}	0.11	0.13	0.10
	Mn^{2+}	0.19	0.42	0.30
	Ca^{2+}	0.90	0.95	1.05
	Mg^{2+}	0.92	0.99	1.14
	Na^{+}	0.34	0.45	1.16
	SO_4^{2-}	1.45	1.80	1.97
	Cl^{-}	0.76	1.70	1.95
<i>Forest soil 2</i>	Al^{3+}	1.83	1.98	4.18
	Mn^{2+}	6.36	8.17	10.94
	Ca^{2+}	8.19	9.51	14.22
	Mg^{2+}	7.91	9.67	14.33
	Na^{+}	0.86	1.04	1.44
	SO_4^{2-}	0.21	0.34	0.56
	Cl^{-}	52.80	70.90	97.75
<i>Chernozem soil</i>	Ca^{2+}	5.49	4.69	8.64
	Mg^{2+}	1.42	0.84	2.95
	Na^{+}	0.83	0.74	1.90
	HCO_3^{-}	0.83	2.77	1.14
	SO_4^{2-}	0.51	1.84	2.57
	Cl^{-}	2.20	3.22	1.88
	NO_3^{-}	11.02	7.00	20.58

SP, MC, FC: See Table 1

pH and ionic composition of the solution. In Figs. 1-3 the difference between the behaviour of mono-, di- and trivalent cations is well demonstrated and the effect of a change in soil moisture content is also shown.

In the case of the *acidic soil*, the amounts of Al^{3+} , Mn^{2+} , Ca^{2+} and Mg^{2+} suddenly increased in the solution after acid treatment (Figs. 1 and 2; Table 2). This can be attributed mainly to the decomposition of certain soil minerals and Al compounds. The desorption of exchangeable Ca^{2+} and Mg^{2+} may also play a role. Besides Al^{3+} , the concentration of AlOH^{2+} also increases (with an order of magnitude of 1.5-2 or approx. 0.5, respectively, depending on soil moisture content) as the pH of the solution decreases, i.e. as a consequence of acidification. The concentration of $\text{Al}(\text{OH})_2^{+}$ was somewhat higher (approx. an order of magnitude of 0.3) in the liquid phase of the original soil, while the amounts of $\text{Al}(\text{OH})_3^0$ and $\text{Al}(\text{OH})_4^{-}$ were negligible in both acidic soils.

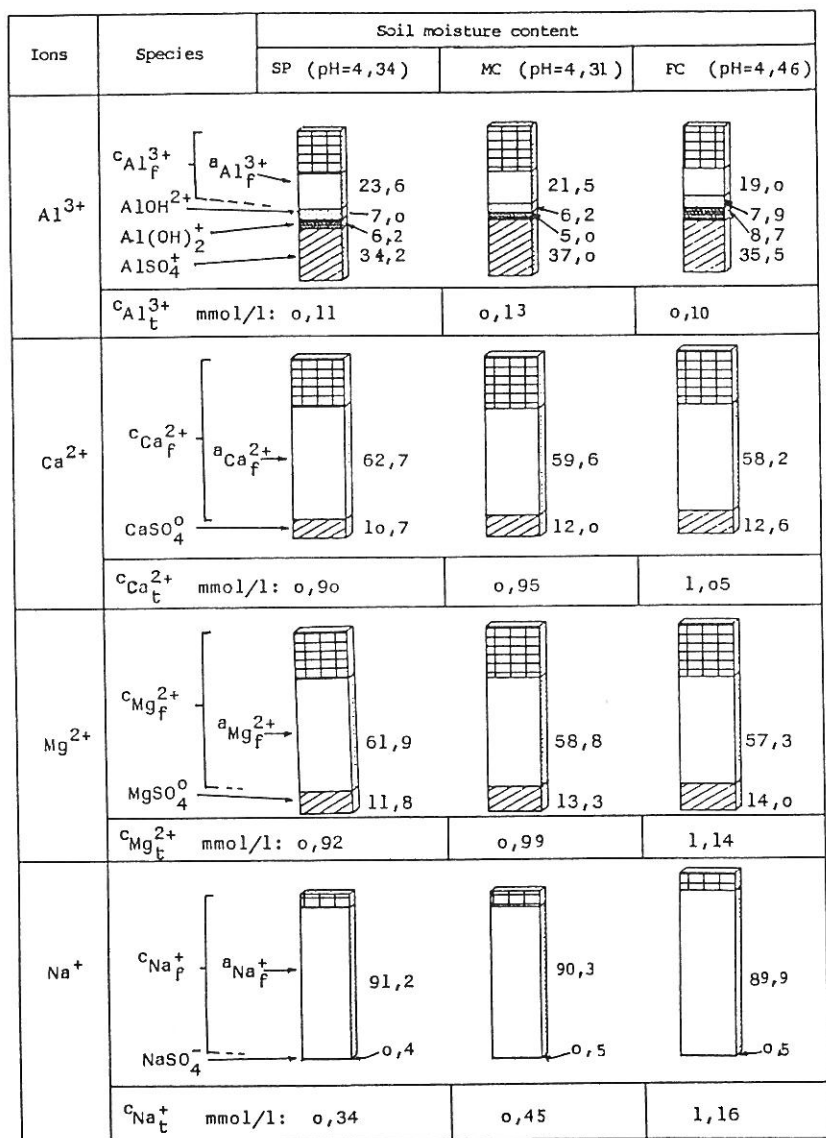


Fig. 1

Distribution of species in the liquid phase of the original forest soil (Ragály, forest soil 1) depending on soil moisture content (pH values denote pH of the solutions; c_t : measured, "total" ion concentration; c_f and a_f : "free" ion concentration and activity, resp.; SP: saturation percentage; MC and FC: maximum water capacity and field capacity; the numerical values to the right of the columns denote the amounts in percentages)

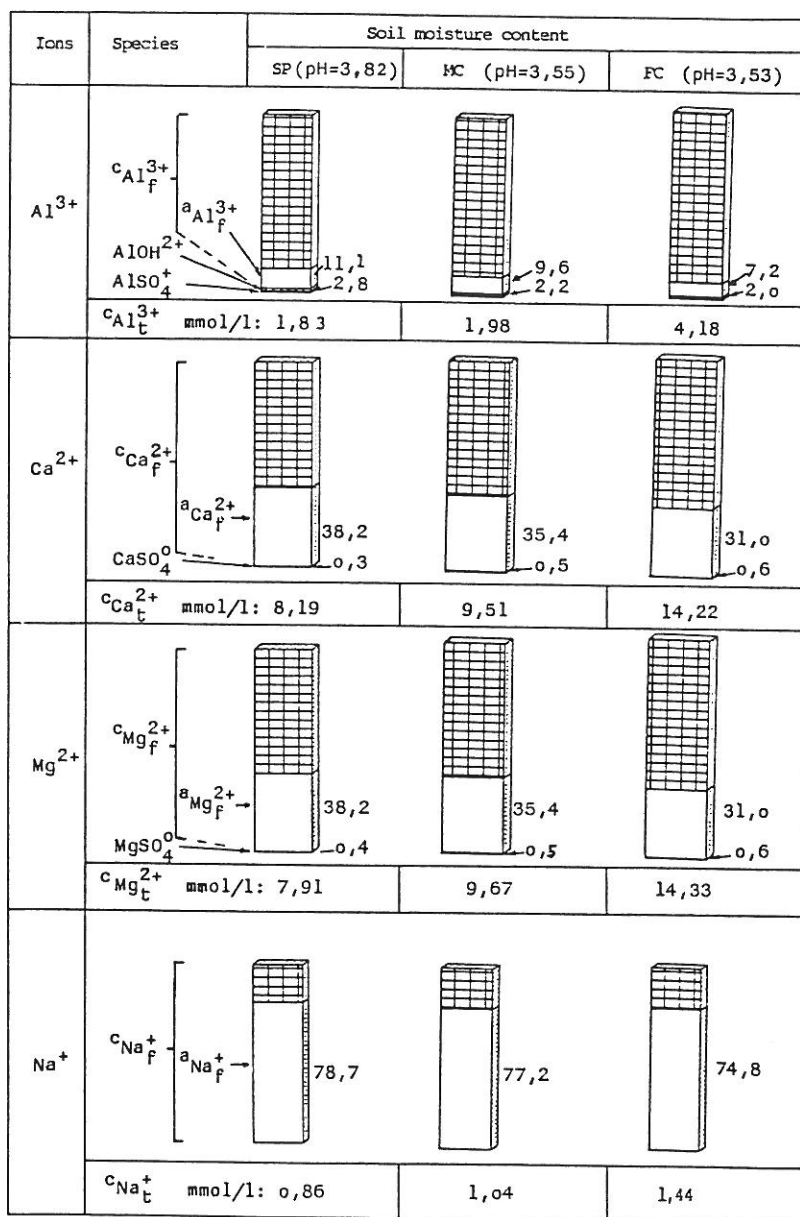


Fig. 2

Distribution of species in the liquid phase of the acidified forest soil (Ragály, forest soil 2) depending on soil moisture content

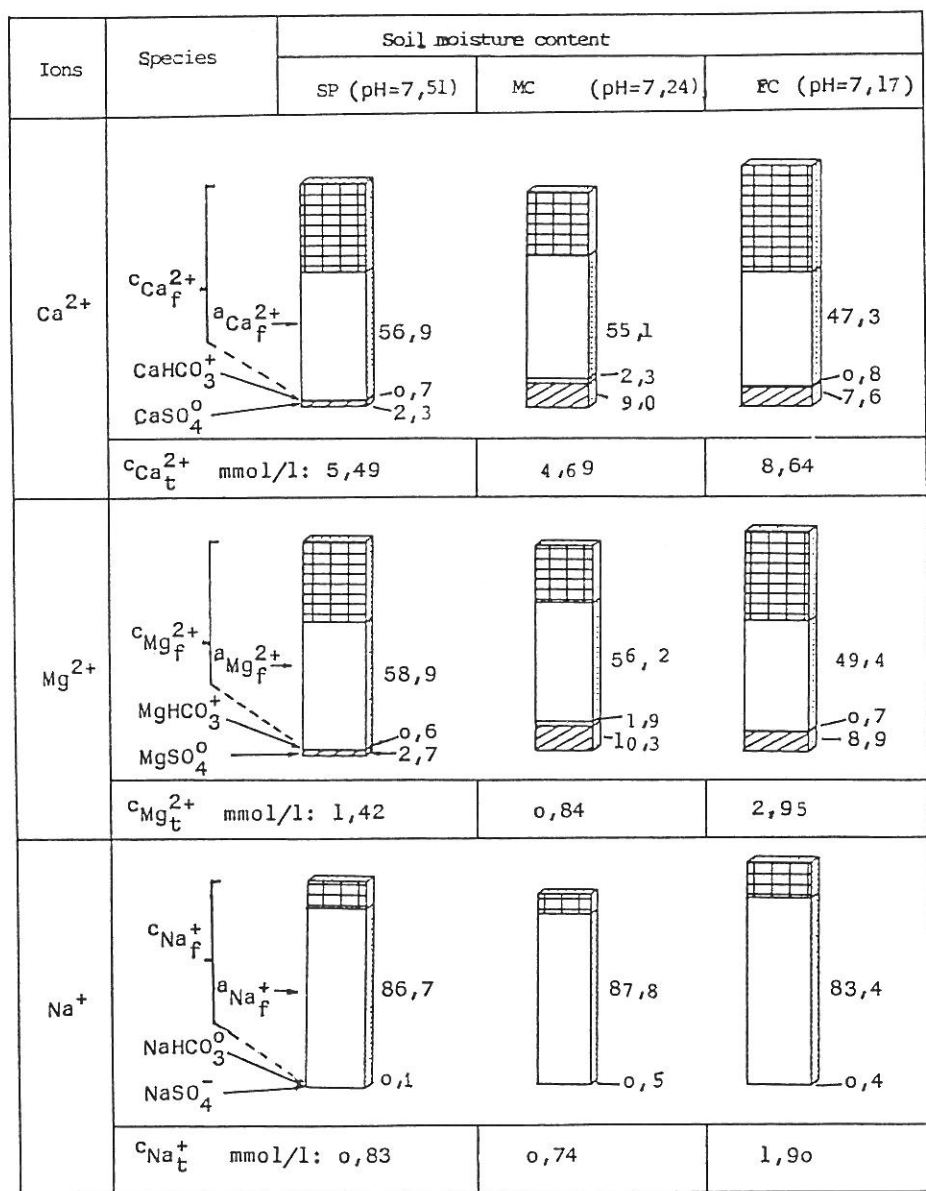


Fig. 3

Distribution of species in the liquid phase of the chernozem soil (Debrecen) depending on soil moisture content

Although far more cations enter the liquid phase from the acidified soil (forest soil 2) than from the original soil (forest soil 1), the relative activities of "free" cations (as a percentage of the measured "total" concentrations) significantly decrease and the formation of ion-pairs and hydroxocomplexes is relatively repressed (Figs. 1 and 2). (This can be explained by the presence of a high amount of Cl^- due to the HCl treatment of the soil. As a consequence, the ionic strength of the solution increases, so ion activity coefficients decrease, while the ion-pair formation of the cations decreases).

"Total" and "free" ion concentrations increased with decreasing soil moisture content (Table 1, Figs. 1 and 2). (The Mn^{2+} content of the liquid phase and the amount of its ionic species were similar to those of Ca^{2+} and Mg^{2+} .) The influence of soil moisture content on ion-pair and complex concentrations was small for all the ions. The effect of the decrease in soil moisture content on the formation of hydroxy-Al complexes is negligible in the acidic soils, while the concentration of ion-pairs slightly increases.

In the liquid phase of the *chernozem* soil the amount of ion-pairs is low as compared to the "total" concentrations of cations (Fig. 3). Even the concentrations of CaSO_4^0 and MgSO_4^0 are only significant at moisture contents FC and MC. This can be attributed to the fact that in this soil NO_3^- is dominant among the anions, and the amounts of SO_4^{2-} and HCO_3^- , which readily form ion associations, are relatively low (Table 2).

Conclusion

The experiments proved that soil acidification (caused by acidic depositions or by the application of high doses of fertilizers) may result in the accumulation of toxic Al species (Al^{3+} , AlOH^{2+}) in the soil solution in the case of soils with low amounts of basic cations. These data, together with earlier results (CSILLAG, FILEP & PINTÉR, 1991), can serve as a chemical basis for measures and systems of the prevention of soil degradation.

References

- BACHE, B. W., 1986. Aluminium mobilization in soils and waters. J. Geol. Soc. London. 143. 699-706.
- BUZÁS, I. (ed.), 1988. [Methods for Soil and Agrochemical Analyses. 2.] (In Hung.) Mezőgazd. Kiadó. Budapest.
- CSILLAG, J. & DARAB, K., 1985. [New results in the study of the electrostatic interactions of ions in soil saturation extracts.] (In Hung.) Agrokémia és Talajtan. 34. 27-52.
- CSILLAG, J., FILEP, G. & PINTÉR, I., 1991. [Calculation of the activities of free Al^{3+} and Al hydroxocomplexes in the soil solution.] (In Hung.) Agrokémia és Talajtan. 40. 203-217.

- FILEP, G., 1988. [Soil Chemistry] (In Hung.) Akadémiai Kiadó. Budapest.
- LINDSAY, W. L., 1979. Chemical Equilibria in Soils. J. Wiley & Sons, New York.
- PAGE, A. L., MILLER, R. H. & KEENEY, D. R. (eds.), 1982. Methods of Soil Analysis. 2. Chemical and Microbiological Properties. 2nd ed. Am. Soc. of Agron., Soil Sci. Soc. of America, Madison, Wisc.
- RICHARDS, L. A. (ed.), 1954. Diagnosis and Improvement of Saline and Alkali Soils. USDA Handbook No. 60. USDA, Washington, D. C.
- SPOSITO, G., 1981. The Thermodynamics of Soil Solutions. Clarendon Press. Oxford.
- SPOSITO, G., 1989. The Chemistry of Soils. Oxford Univ. Press. New York - Oxford.
- WRIGHT, R. J., BALIGAR, V. C. & AHLRICHS, J. L., 1989. The influence of extractable and soil solution aluminium on root growth of wheat seedlings. Soil Sci. 148. 293-302.