

# Speciation of Aluminium Released Under the Effect of Acid Rain

J. Siepak, B. Walna<sup>1\*</sup>, S. Drzymala<sup>2</sup>

Adam Mickiewicz University, Department of Water and Soil Analysis, Drzymaly 24,  
60-613 Poznań, Poland

<sup>1</sup>Adam Mickiewicz University, Jeziory Ecological Station, 62-050, Mosina, p.box 40, Poland

<sup>2</sup>Agricultural University of Poznan, Soil Science Department, Mazowiecka 42, 60-623 Poznan, Poland

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## Abstract

The influence of simulated acid rain precipitation on selected soil profiles typical of Wielkopolski National Park was studied. The results prove the release and migration of aluminium among soil phases, depending on soil pH and type. The model studies illustrate the influence of natural and anthropogenic factors on chemical degradation of soil, in particular on metastability of aluminium.

**Keywords:** aluminium migration, speciation, acid rain, Wielkopolski National Park

## Introduction

For the purpose of this work we assume that soil can occur in three physical states: solid phase, sorption complex and soil solution. The functional definition of the aluminium speciation distinguishes:

- aluminium in solid phase, hardly available, and strongly bound in the form of aluminosilicates, Al-oxides, Al-hydroxide. Migration of this form of aluminium is very slow, however, it can be substantially sped up under the effect of anthropogenic factors [1, 2, 3, 4],

- aluminium in the sorption complex, characterized by significant mobility which in the process of ion-exchange can enter the soil solution [5],

- aluminium in soil solution occurring in different hydrated forms (hydrocomplexes) and in the form of free aluminium cation bioavailable and sometimes highly toxic [6, 7].

Migration of aluminium from one phase to another depends on the interaction of physical and chemical factors, of which the most important is the pH of precipitations [8, 9]. With the help of appropriate analytical procedures, the amount of aluminium in particular soil phases can be determined and the phenomenon of aluminium metastability in the types of soil studied can be described [6].

The aim of this paper was to provide evidence for aluminium release and migration within soil phases in selected natural soil monoliths from the Wielkopolski National Park under the effect of acid rain on the basis of distributions of aluminium concentrations in particular soil phases before and after the simulated acid rain.

## Methods

The experiment was performed on natural soil monoliths under laboratory conditions. Soil cores of 15 cm in diameter were collected from the 50 cm deep top layers of soil. Simulation of acid rain precipitation was conducted for 30 days, by every day sprinkling the soil with water solutions of sulphuric acid of pH 2.0 or 3.0. Control samples were sprinkled with distilled water of pH 5.6. The total amount of simulated precipitate was of about 400 mm, i.e. equal to the annual precipitate in 1992. On each day the volume of the filtrate, its composition, pH and electrical conductivity were measured.

The soil samples studied were acidic or strongly acidic - pH in KCl 3.4 to 4.6, of small sorption capacity and very low saturation of their sorption complex with bases [10, 11]. The samples were collected from three sites representing typical soils in the area: sandy soil of formerly agricul-

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\* Corresponding author, tel. +48-61-8132711, e-mail: walna@amu.edu.pl

tural use collected from Kqtnik (K), sandy soil from the Jeziory forest area (J), and loamy soil from Grabina forest area (G). Simultaneously, the profiles of soil cores (monoliths) from the above sites were exposed to determine genetic horizons and characterize their morphology. The analytical methods used in this study were the classical methods developed in pedology [12]. Hydrolytic acidity ( $H_h$ ) was determined by the Kappen method from (1M  $CH_3COONa$ ), whereas the exchange acidity ( $Al_{exch} + H_{exch}$ ) with 1M KCl. The fraction of solvable aluminium was determined in water extract (1:5 m/m) using eriochromocyanine [13], the exchange aluminium according to the method proposed by Sokolow [12], and the total amount of aluminium was established after mineralization ( $HNO_3 + HF$ ) with eriochromocyanine. The soil cores were subjected to the same analytical procedures after the experiment. The procedure of studies is schematically presented in Fig. 1.

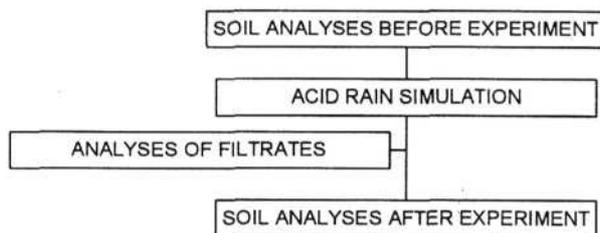


Fig.1. A general scheme of the experimental procedure applied.

## Results and Discussion

Chemical properties of the soil samples taken from the three sites selected (K, J and G), were determined at three depths before and after acid rain simulation carried out in three variants: A - after sprinkling with  $H_2O$  of pH 5.6, B - with a solution of pH 3.0 and C - with a solution of pH 2.0. The results are collected in Table 1 which specifies hydrolytic acidity ( $H_h$ ), exchange aluminium ( $Al_{exch}$ ), exchange hydrogen ( $H_{exch}$ ) and exchange acidity (a sum of  $H_{exch} + Al_{exch}$ ).

The values given in Table 1 are averages for two soil monoliths. The results obtained for them were very similar

(even identical) for sandy samples (K, J), but for loamy (G) showed some differences. According to the data collected before the experiment, the three soil profiles differ in the concentrations of exchange hydrogen ( $H_{exch}$ ). The main contribution (90%) to the exchange acidity ( $Al_{exch} + H_{exch}$ ) is brought by aluminium. A high value of hydrolytic acidity ( $H_h$ ) in the top layer of the profile from Jeziory is undoubtedly related to a significant contribution of organic matter in this particular layer [10]. The exchange acidity of this layer is also higher than in the other profiles. The samples from two upper layers of the Grabina profile are characterized by a low contribution of exchange hydrogen similar to those from Katnik. These profiles also have similar values of hydrolytic acidity. The bottom layer from the Grabina profile shows an exceptionally low level of exchange acidity (0.05  $cmol(+)/kg$ ). The contribution of aluminium in the exchange acidity before sprinkling varies from about 92% in the top layer to 60% in the bottom one.

A comparison of the values obtained before and after sprinkling (variants A, B and C) indicates a significant increase in the concentration of exchange hydrogen after sprinkling with a solution of pH 2.0 with one exception for J (18-40). This increase is particularly pronounced in the top layer in which its mean concentration is over 3 times higher than before the experiment. Also in the middle layer (samples K and J) the exchange acidity is almost twice higher than the initial value. When solutions of high pH were used for sprinkling (variants A and B), the exchange acidity did not change much.

The concentrations of exchange aluminium obtained for the three variants of sprinkling in sandy profiles (K, J) and upper layer of loamy sample (G) indicate an increase in its amount upon sprinkling with solutions of pH 3.0 or pH 2.0. After the experiment the concentration of exchange aluminium reaches about 2  $cmol(+)/kg$  and sometimes is twice as high as before the simulation. The contribution of aluminium in the exchange acidity depends on the variant of sprinkling. For example, applying variant C, a much increased contribution of hydrogen in the exchange acidity of the samples is observed in upper layers, which is a consequence of a rapid increase in the amount of the exchange hydrogen cations.

In the soil cores from Grabina, there are significant

Table 1. Hydrolytic acidity ( $H_h$ ) and exchange acidity ( $Al_{exch} + H_{exch}$ ) in soil samples before and after the experiment (0 - before experiment, A - after sprinkling with  $H_2O$  of pH 5.6, B - with a solution of pH 3.0, and C - with a solution of pH 2.0).

Sample depth (cm)	Hydrolytic acidity $H_h$				Exchange aluminium $Al_{exch}$				Exchange hydrogen $H_{exch}$				Exchange acidity $Al_{exch} + H_{exch}$			
	cmol(+)/kg															
	0	A	B	C	0	A	B	C	0	A	B	C	0	A	B	C
K (0-12)	2.50	3.05	2.78	3.68	0.70	0.81	1.11	1.03	0.08	0.09	0.07	0.30	0.78	0.90	1.18	1.33
K (12-25)	2.40	2.40	2.95	3.05	0.70	0.76	0.84	1.18	0.09	0.08	0.06	0.15	0.79	0.84	0.90	1.33
K (25-50)	1.00	1.07	1.18	1.58	0.44	0.40	0.47	0.90	0.03	0.03	0.03	0.04	0.47	0.43	0.50	0.94
J (0-5)	9.00	5.50	6.43	9.85	1.80	1.48	2.02	2.21	0.30	0.23	0.18	0.82	2.10	1.71	2.20	3.03
J (5-18)	4.20	3.70	3.72	4.60	1.49	1.58	1.55	1.87	0.13	0.18	0.11	0.20	1.62	1.76	1.66	2.07
J (18-40)	2.05	2.68	2.23	3.13	0.95	1.22	1.14	1.91	0.10	0.08	0.04	0.08	1.05	1.30	1.18	1.98
G (0-10)	3.90	3.10	3.13	5.23	0.93	0.30	0.22	2.34	0.08	0.07	0.06	0.23	1.01	0.37	0.28	2.57
G (10-40)	1.95	2.28	2.10	2.48	0.47	0.27	0.60	0.89	0.06	0.04	0.03	0.07	0.53	0.31	0.63	0.96
G (40-50)	0.95	1.73	2.15	1.63	0.03	0.22	0.44	0.14	0.02	0.02	0.03	0.03	0.05	0.24	0.47	0.17

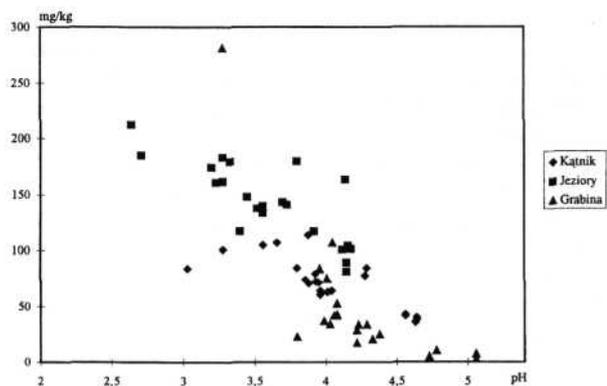


Fig. 2. The amount of the exchange aluminium in soil versus its pH (soil samples from Kałtnik, Jeziory, Grabina).

differences in the concentration of exchange aluminium depending on the depth (variants 0 and C); the highest values which were 17 times higher than those for the bottom layers, were found in the top layer after sprinkling with a solution of pH 2.0 (C). When the soil samples were sprinkled with water and weak acid, variants A and B, respectively, the concentrations of aluminium in the top layer were lower than before the sprinkling (0). This effect is related to washing out and migration of movable or released aluminium to deeper layers.

The relationships between the amount of the exchange aluminium and the aluminium in the water extracts and the pH of the samples are illustrated in Figs. 2 and 3.

The dependence of exchange aluminium content in the samples on their pH confirms a release of significant amounts of aluminium when pH drops below 4.5. The type of soil (K, J, G) also affects the way and the amount of aluminium released. A similar relationship was observed between the amount of aluminium and pH of water extracts from the soil samples.

During the acid rain simulation experiment, the amount of aluminium in the filtrate was measured every day. Knowing the volume of the eluate, the total amount of aluminium washed out from the soil samples as a result of the three variants of sprinkling was determined. These values were compared with the total amount of aluminium determined in the samples before the experiment (Table 2). The amount of the aluminium washed out when applying the C variant of sprinkling (pH 2.0) was expressed in the

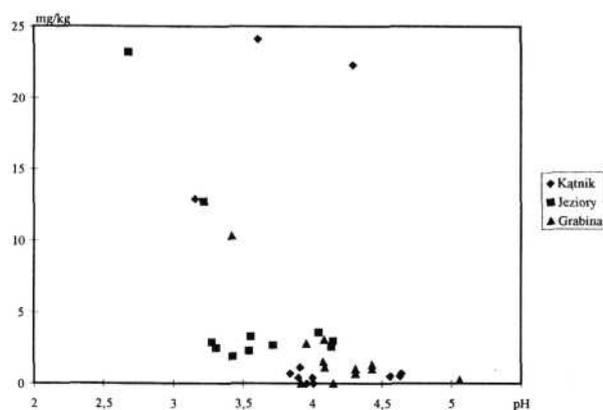


Fig. 3. The amount of aluminium dissolved in water extract versus soil pH (soil samples from Kałtnik, Jeziory, Grabina).

Table 2. The total amount of aluminium in soil monoliths (determined before the experiment) and the total amount of aluminium washed out as a result of acid rain simulations (variants A, B, C) for the three types of soil studied.

Site	Total amount of Al (g)	Washed out Al (mg)		
		A H <sub>2</sub> O	B pH 3.0	C pH 2.0
Kałtnik	74.5	0.9	6.0	711 (1%)
Jeziory	111.1	12.7	16.3	500 (0.5%)
Grabina	180.9	0.8	0.1	52 (0.03%)

percent of its total amount and the number is given in parenthesis.

According to Table 2, the greatest amount of aluminium was washed out from all types of samples as a result of acid rain simulation with a solution of pH 2.0. In this variant of sprinkling, the total amount of the aluminium released varied from about 50 mg for the soil core from Grabina to over 700 mg for the core from Kałtnik. The amounts of aluminium washed out when applying variants B (pH 3.0) and A (pH 5.6) were similar.

The amount of the washed out aluminium was also found to depend on the properties of particular soil samples. For example, when applying the C variant of sprinkling, the greatest amount of aluminium was washed out from sandy soils: 1% - Katnik, 0.5% - Jeziory, while the least was from loamy soils 0.03% - Grabina. These differences can be explained by a higher pH of the soil from Grabina, especially in the deep layers, which together with much higher content of clay fraction ensure effective buffer properties of the soil [10]. In the sandy soils (K, J) a low pH, a significant content of organic substances and low contribution of colloidal particles create favourable conditions for aluminium release and migration. However, the significant amounts of the aluminium washed-out as a result of sprinkling with the most acidic solution make

Table 3. The contributions of different form of aluminium in the soils studied before (0) and after acid rain simulations (A, B, C). K - soil samples from Kałtnik, J - from Jeziory, G - from Grabina, 0 - before sprinkling, A - sprinkling with distilled water of pH 5.6, B - sprinkling with a solution of pH 3.0, C - sprinkling with a solution of pH 2.0.

Site depth (cm)	Water - soluble Al				Exchange Al				Total Al
	mg/kg								
	0	A	B	C	0	A	B	C	0
K (0-12)	0	0.4	0.7	12.9	62.3	72.9	99.1	92.3	4 350
K (12-25)	0	0.4	1.1	24.1	63.0	67.8	75.0	106.0	5 735
K (25-50)	0.7	0.5	0.5	22.3	39.0	35.6	42.1	80.8	6 225
J (0-5)	2.9	1.9	2.5	23.2	161.8	132.6	181.2	198.7	9 450
J (5-18)	3.3	2.7	2.3	12.7	133.8	142.0	138.9	167.7	7 825
J (18-50)	3.0	3.6	2.6	29.5	85.0	109.2	102.6	171.1	8 701
G (0-10)	2.8	0.7	1.0	10.3	83.5	26.2	19.4	210.4	13 275
G (10-40)	1.5	1.1	3.1	0.05	42.1	23.7	54.0	79.9	13 200
G (40-50)	0.2	1.0	1.3	0.05	2.7	19.4	39.2	12.2	16 700

a small percent of the total amount of aluminium in this kind of soil.

The distribution of aluminium in soil phases: soil solution (bioavailable aluminium), sorption complex (exchange aluminium) and solid phase (total aluminium) is characterized by the data collected in Table 3. The results are expressed in mg/kg for the three soil profiles and different depths.

The data indicate differences in the distribution of aluminium in the three profiles and in particular soil phases. The contribution of the aluminium bound in complexes (exchangeable) varies from 0.02% of the total aluminium amount in the soil from the bottom layer from the Grabina profile (before sprinkling) to 1.7% in the surface layer in the profile from Jeziory, in the same samples the bioavailable aluminium varies from 0.001% to 0.03%. The distribution of aluminium concentrations changes depending on the type of soil and pH of the simulated acid rain.

The results presented in Tables 1-3 provide evidence for aluminium migration from the matrix rock to the sorption complex and soil solution, migration of movable aluminium to deeper layers is also observed.

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