

# Studies on migration and speciation of magnesium in soils under the influence of acid rain

B. Walna<sup>1</sup>, J. Siepak<sup>2</sup>, S. Drzymała<sup>3</sup>

## Zusammenfassung

Zur Simulation der Wirkung von Niederschlägen (pH 2.0, 3.0, 5.6) auf Bodenmonolithe wurden Laborexperimente durchgeführt. Vor und nach dem Experiment wurden Bodenanalysen durchgeführt. Dabei wurden austauschbare und lösliche Formen von Magnesium im Boden und in den Filtraten während der Berechnung bestimmt.

In den untersuchten Sand- und Lehmböden stieg die Konzentration des löslichen Magnesiums durch die Berechnung signifikant an, besonders in der oberen Schicht. In den Lehmkernen nahm die Menge des austauschbaren Magnesiums ab. Die Menge des ausgeschwemmten Magnesiums zeigt die während der Simulation des sauren Regens erfolgte chemische Bodendegradation.

## Summary

In the laboratory experiment natural soil monoliths were treated by systematic artificial precipitation (pH 2.0, 3.0, 5.6). The chemical characteristics of soils before and after the experiment, exchangeable and soluble forms of magnesium in soils and magnesium in the percolates were investigated.

In the sandy and loamy monoliths the concentrations of soluble forms of magnesium increase upon sprinkling quite significantly, particularly in the surface layer. Exchangeable forms decrease over the whole profile in loamy cores. The total amount of magnesium leached out during the experiment proved the chemical degradation of soils.

## Introduction

Magnesium belongs to those elements necessary for plant nutrition as well as animal and human organisms. Its shortage results in serious developmental consequences and disruption of physiological processes. The fundamental source of magnesium is the soil, and in it the following minerals: olivine, serpentine, talcum, biotite, hornblende, augite, dolomite, magnesite.

Long term precipitation monitoring tests at the Ecological Station of A. Mickiewicz University [1] (western Poland) provided material indicating their considerable acidification, sometimes dropping even below a pH of 3.0. This fact must influence the degradation of geocosystems, including the releasing and leaching out of magnesium from soils [2, 3].

Soil is a three-phase system. The solid phase is made of minerals, organic and mineralorganic components. The liquid phase is water with chemical compounds dissolved, making the so-called soil solution. The colloidal phase is made by the colloidal fragment of the solid phase. Sorptive abilities of soil are essential for plant nutrition, buffering effect of undesirable pollutants. The most important for exchange sorption are clay minerals and humus. The exchange sorption takes place between the sorptive complex and soil solution. The sorptive complex plays a role of readily accessible store of components: it sorbs the components if their concentration in the soil solution increases

and gives them back when this concentration decreases.

The functional definition [4] of the magnesium speciation distinguishes:

- magnesium in solid phase, hardly available and strongly bound in minerals organic compounds. The process of releasing this form of magnesium is usually a long-term one, however under the influence of anthropogenic factors, it can be considerably quickened [5, 6];
- magnesium in the sorption complex, characterized by mobility; in process of ion-exchange can enter the soil solution [7];
- magnesium in soil solution which has the greatest bio-availability and mobility in soil profile [8, 9].

Migration of magnesium from one phase to another depends on the interaction of physical and chemical factors, of which the most important is the pH of precipitation [10]. With the help of appropriate analytical procedures, it is possible to determine its particular forms and to describe its leaching out, depending on the acidification of precipitation in the types of soils tested.

The aim of this study is to investigate the release of magnesium and the process of migration of its forms in chosen natural soil monoliths from the Wielkopolski National Park under the influence of acid rain. Analytical data show the distribution of concentrations of particular magnesium forms before and after experiment of simulated acid rain.

<sup>1</sup> Adam Mickiewicz University, Jezioro Ecological Station, 62-050 Mosina, P.O. Box 40, Poland, tel.+48-61-8132711, e-mail walna@amu.edu.pl (for correspondence)

<sup>2</sup> Adam Mickiewicz University, Department of Water and Soil Analysis, Drzymała 24, 60-613 Poznań, Poland

<sup>3</sup> Agricultural University of Poznań, Soil Science Department, Mazowiecka 42, 60-623 Poznań, Poland

**Methodology of the study**

The experiment was conducted on naturally occurring soil monoliths under laboratory conditions. Soil core samples with a diameter 15-cm were gathered from the upper layer of soils at a depth of 50 cm. The acid rain simulation was conducted for 30 days, by every day sprinkling the soil with an aqueous solution of sulfuric acid with a pH of 2.0 and 3.0 and a control sample of distilled water with a pH of 5.6. The total amount of simulated precipitation was approximately 400 mm, i.e. an amount equal to the average annual precipitation for 1994. The volume of the collected filtrate was measured each day and its composition, pH and electrical conductivity determined.

The kind of soils studied were: sandy soil, previously used for agricultural

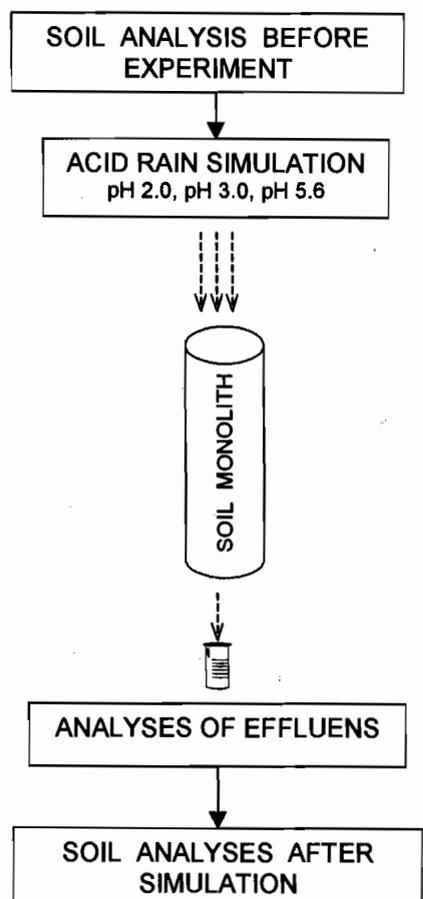


Fig. 1: A general scheme of the experimental procedure applied.

Tab. 1: Basic properties of the investigated soils – 1, 2, 3 (before treatment). (TEB – total exchangeable bases, CEC – cation exchange capacity, BS – base saturation)

Soil	Depth cm	Genetic horizon	Bulk density Mg/m <sup>3</sup>	Ignition loss %	Soil Particles Ø mm			TEB cmol(+)/kg	CEC	BS %
					0–0.1	0.1–0.02	< 0.02			
1	0–12				73.6	22.4	4.0	0.14	2.64	5.3
	12–25	A	1.51	1.84						
	25–50	C	1.60	0.51	73.2	22.7	4.1	0.11	2.51	4.4
2	0–5				62.7	31.0	6.3	0.23	1.23	18.7
	5–18	A	0.99	8.32	80.1	11.4	2.5	0.81	9.81	8.3
	18–50	AE	n.d.	n.d.	81.7	9.8	3.4	0.25	4.45	5.6
3		BC	1.53	1.53	75.7	9.7	5.9	0.19	2.24	8.5
	0–10	A	1.46	1.46	53.1	13.7	31.2	2.06	5.96	34.6
	10–40	B	1.73	1.73	48.5	18.3	31.6	4.00	5.95	67.2
	40–50	C	n.d.	n.d.	41.9	22.1	33.5	6.34	7.29	87.0

n.d. not determined

Abbreviation of genetic horizons: A organic matter accumulation, B illuvial (leaching), C parent material, E eluvial (enrichment), AE mixed (A and E), BC mixed (B and C)

purposes – site 1, sandy forest soil – site 2, loamy forest soil (glacial till) – site 3. Before sampling of the monolithic (core) samples, an excavation was made and genetic levels were assigned to determine basic physical and chemical properties. Classical methods were used in the soil testing procedure. They were determined using commonly known methods: bulk density – in soil cores of 100 cm<sup>3</sup>, ignition loss – in oven at 550°, soil particles distribution using sieves and hydrometric method. Soluble magnesium was determined in a water solution (1:5, m/m), exchange magnesium by Kappen's method (0.1 M. HCl), total magnesium obtained following mineralization (HNO<sub>3</sub>, + HF). Determinations were performed by means of atomic absorption. Following completion of this experiment, soil cores were subjected to analogous analysis. The values presented in the Tables were obtained by repeating a given analysis for two monoliths.

The procedure of studies is schematically presented in Fig. 1.

**Results**

A shortage of magnesium in plants is most often observed in very light soils (to 10 % of the fraction < 0.02 mm) as

well as in light soils (10–20 % fraction < 0.02 mm) [7]. These soils usually show strong acidification. They are, due to their low buffering potential, particularly susceptible to the unfavorable action of acidic deposits [5, 6, 10].

Soils from chosen sites were characterized by strong acidification, low cation exchange capacity (CEC) and base saturation (BS) (sites 1, 2) (Tab. 1). TEB total exchangeable base index is defined as a sum of base cations (Ca, Mg, K, Na) adsorbed by 1 kg of soil, CEC cation exchange capacity – sum of TEB and acid ions (H, Al.) adsorbed by 1 kg of soil, BS base saturation – ratio of TEB and CEC in %.

The soil pH has a fundamental effect on all other processes. Due to the low pH level of the soils, changes in its values under natural conditions are not always significant [11].

Performance of acid rain simulations in the laboratory, employing more extreme conditions allows determination of changes in the pH as well as the surface layer, and at deeper levels [12, 13].

The soil monoliths tested, subjected to acid rain simulation, showed a considerable lowering of pH – even by as many as 1.5 units in the case of the upper layer of the sandy monolith (site 1), sprinkled with solution of pH

Tab. 2: The pH of soils before and after acid rain simulation conducted on soil cores from three sites (1, 2, 3): 0 – before sprinkling, A – after sprinkling with water (pH 5.6), B – after sprinkling with a solution of pH 3.0, C – after sprinkling with a solution of pH 2.0

Soil	Depth cm	pH (H <sub>2</sub> O)			
		0	Type of treatment		
			A	B	C
1	0–12	4.75	4.41	4.17	3.15
	12–25	4.77	4.57	4.43	3.53
	25–50	5.22	5.27	5.12	4.03
2	0–5	4.19	4.07	3.94	3.01
	5–18	4.24	4.25	4.12	3.22
	8–40	4.65	4.50	4.46	3.80
3	0–10	4.80	5.02	4.99	3.58
	10–40	5.21	4.96	5.04	4.55
	40–50	6.25	5.70	5.16	5.10

2.0 (Tab. 2). These results are close to those obtained by the above-mentioned authors, where a change in pH under similar conditions was from 1.8 to 2.0.

The influence of lowered pH on the release and migration of magnesium can be observed by comparing the magnesium concentration in water extracts before and after simulation, as well as by observing the dynamics of leaching of this element from the monolith in the course of sprinkling (in effluents) [3].

The distribution of various magnesium forms – in soil solution, in the sorption complex and total magnesium is presented in Tab. 3. The results have been presented in mg/kg for three soil profiles and for various depths.

The data obtained indicate various locations of magnesium forms at three depths in the tested soils. In the sandy monolith having a small amount of humus (site 1) simulation of rain having a pH of 3.0 caused an increase of dissolved magnesium, both in the surface layer (1.7 fold), as well as in the middle layer (2.3 fold). On the other hand, more acidic precipitation (pH 2.0) caused an almost 6-fold increase of soluble magnesium. The small sorptive capacity of these soils provided little opportunity to observe greater changes in the amount of exchangeable magnesium, these are, however, significant in the upper layers.

Sandy core samples with large amounts of humus (site 2) showed a

higher initial level of soluble magnesium compared to the site 1. Treatment with a pH 3.0 solution caused an increase in soluble magnesium in the lower layer, which shows that the magnesium migration and leaching was stronger than its release from the stable state. In the case of more acid treatment (C), the content of soluble forms increases in the upper layers (when compare to 0) and decrease with the profile depth. The change in exchangeable magnesium is small and significant only in the very acidic option, particularly as regards the surface layer.

Loamy soil (site 3), under the influence of pH 3.0 acid rain simulation, releases soluble magnesium mainly in the upper layer – twice as much as in the initial state. Whereas pH 2.0 sprinkling increases the soluble magnesium quite significantly, particularly in the surface layer (5-fold increase). A considerable amount of exchangeable magnesium is determined in the initial state and increases along with the depth, decreasing over the whole profile following very acidic stimulation. On the other hand, less acidic treatment causes somewhat higher concentrations of magnesium in the upper layer, which confirms the preponderance of processes of release over those of leaching.

### Discussion

Throughout the acid rain simulation experiment, a concentration of magnesium was determined in the daily collection of filtrate. Knowing the volume of effluent, the total amount of magnesium leached out from monoliths (Tab. 4) could be found. These values were presented along with total amounts of magnesium that had been determined in samples before the experiment. The amount of magnesium leached out in variant C (pH 2.0) was expressed in percents of the total amount and presented in parentheses. As follows from the data presented in Tab. 4 it occurs, that in all cases, by far the greatest amount of magnesium was

Tab. 3: The content of soluble and exchangeable magnesium before (0) and after acid rain simulation for three sites (1, 2, 3): 0 – before treatment, A – after treatment with distilled water, B – after treatment with a pH 3.0 solution, C – after treatment with a pH 2.0 solution

Site	Depth cm	Soluble Mg				Exchangeable Mg				Total Mg
		0	A	B	C	0	A	B	C	
mg/kg										
1	0–12	0.80	1.10	1.35	4.65	6.0	9.6	7.2	8.4	169
	12–25	0.60	1.00	1.35	3.65	4.8	9.6	6.0	6.0	134
	25–50	1.00	1.35	0.95	1.15	4.8	4.8	3.6	4.8	152
2	0–5	3.10	2.30	2.50	5.00	25.2	16.8	22.8	37.2	375
	5–18	3.20	3.35	2.85	4.90	18.0	18.0	20.4	19.2	218
	18–50	2.20	4.15	4.30	3.85	12.0	12.0	15.6	16.8	525
3	0–10	4.80	9.30	9.70	16.25	72.0	80.4	84.0	54.0	1068
	10–40	11.90	7.40	8.75	12.00	170.4	84.0	103.2	124.8	1123
	40–50	9.60	8.15	10.00	14.10	259.2	183.6	170.4	183.6	1435

Tab. 4: Total content of magnesium in the soil monolith as well as the total amount of magnesium leached out in acid rain simulations (variant A pH = 5.6, B pH = 3.0, C pH = 2.0) for three investigated soils (1, 2, 3).

Site	Total magnesium content (mg)	Leached out magnesium (mg)		
		A H <sub>2</sub> O	B pH 3.0	C pH 2.0
1	2090	1.3	3.2	23.0 (1.1 %)
2	5618	10.4	8.9	61.8 (1.1 %)
3	15369	17.5	19.7	199.8 (1.3 %)

leached out in simulated rains with a pH of 2.0. The total amount of magnesium released amounted to approximately 23 mg, in the core taken from the site 1, to almost 200-mg in the core coming from the site 3. Similar amounts of magnesium, as in the case of pH 3.0, were leached-out during the sprinkling of soils with distilled water having a pH of 5.6.

Differentiated results were also obtained depending on the properties of given soils. During soil sprinkling with a pH of 2.0 the largest amount of magnesium was leached-out from loamy soils (site 3), and almost on tenth as much magnesium was leached out from sandy soil (site 1). In all three cases, however, leached out magnesium is almost as little as almost 1 % of the total magnesium. This results from the chemical (mineralogical) composition of these soils.

The quantity of leached out magnesium is also compared to the amount of exchangeable magnesium found in the soil before simulation. The values of obtain from the comparison were expressed in percents and gave – for sandy soils (site 1) 34 %, for sandy soils with large amounts of humus (site 2) 33 %, and loamy soils (site 3) – 8.5 %.

Similar results are found in the literature [8, 9] covering three years of field studies in which sandy and loamy soils were sprinkled with a mixture of sulfuric and nitric acid. The increased concentration of magnesium in soil solution is explained, as well, by replacement from the sorption complex, together with the disintegration of silicates (olivine, biotite).

The presented results, show a change in the speciation of magnesium occurring in the soils investigated under the influence of acid rain as well as the migration of magnesium to deeper layers, which is necessarily connected with the depletion and eventual deficit of bioavailable magnesium. Although the figures of magnesium leached out from 50-cm soil monoliths account for but a small percentage of the total magnesium, the proportion of this form is significant when compared to the exchangeable form of this element.

Acid rain causing a deep deficit of magnesium in light soils, are responsible for serious disturbances in vegetation development (see the studies of plant physiology). Due to the role magnesium plays in plant nutrition and in the long-term nature of the processes through which acid rain acts, the amounts of magnesium removed from the soil due to acid rain deserves particular attention [6, 14]. Complement of magnesium deficit in soils is in general very difficult and can be achieved by addition of dolomite.

## References

- [1] Walna, B.; Siepak, J.: Research on the variability of physico-chemical parameters characterising acid precipitation at the Jezioro Ecological Station in the Wielkopolski National Park (Poland). *The Science of the Total Environment* 239 (1999) 175–189.
- [2] Walna, B.: Soil degradation in the Wielkopolski National Park under the effect of acid rain simulation, (in Polish). Ph. D. Dissertation (1999) 228.

- [3] Walna, B.; Drzymala, S.; Siepak, J.: The impact of acid rain on calcium and magnesium status in the typical soils of the Wielkopolski National Park. *The Science of the Total Environment* 220 (1998) 115–120.
- [4] Broekaert, J.A.C.; Gucer, S.; Adams, F.: *Metal speciation in the environment*. Springer, Berlin 1990.
- [5] Likens, C.T.; Driscoll, C.T.; Buso, D.C.: Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272 (1996) 244–245.
- [6] Matzner, E.; Murach, D.: Soil changes induced by air pollutant deposition and their implication for forests in Central Europe. *Water, Air and Soil Pollution* 85 (1995) 63–76.
- [7] Filipek, T.; Badora, A.: An evaluation of magnesium content in soils nutrition of plants by magnesium under strongly acid condition, (in Polish). In: *Scientific papers IV. Magnesiological Symposium* (1996) 93–97.
- [8] Prusinkiewicz, Z.; Pokojka, U.; Frank, U.; Kwiatkowska, A.: The effect of simulated acid rain on the chemical composition of soil solutions. *Ekol. Pol.* 40, 3 (1992) 401–415.
- [9] Rustad, L.E.; Fernandez, I.J.; Fuller, R.D.; David, M.B.; Nodvin, S.C.; Halterman, W.A.: Soil solution response to acidic deposition in a northern hardwood forest. *Agriculture, Ecosystems and Environment* 47 (1993) 117–134.
- [10] Liljeville, A.; Bredemeier, M.; Ulrich, B.: Input-output relations of major ions in European forest ecosystem. *Agriculture, Ecosystems and Environment* 47 (1993) 175–184.
- [11] Tamm, C.O.; Hallbacken, L.: Changes in soil acidity in two forest areas with different acid deposition 1920s to 1980s. *Ambio* 17 (1988) 56–61.
- [12] Koptsik, G.; Mukhina, I.: Effects of acid deposition on acidity and exchangeable cations in podzols of the Kola peninsula. *Water, Air and Soil Pollution* 85, 3 (1995) 1209–1214.
- [13] Motowicka-Terelak, T.: Model-scale investigations on the mechanism and effects of degradation of sulfur – contaminated soils. (in Polish). *Pam. Pul.* 94 (1989) 11–27.
- [14] Schulze, E.D.: Air pollution and forest decline in a spruce (*Picea abies*) forest. *Science* 244 (1989) 776–782.

Correspondence to:

B. Walna  
Adam Mickiewicz University  
Jezioro Ecological Station  
P.O. Box 40  
62-050 Mosina  
Poland