

# Reaction of Degraded Chernozem to Acidification

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## Abstract

Soil acidification in top layers (measured as its intensity and range in soil profile) is related to the value of acid rainfall and causes particular changes in chemical and physicochemical features.

The model research presents reaction of degraded chernozem to acidification. Determining the level of soil acidification, in which strong chemical degradation occurs, was an aim of our investigation.

A model study upon the degraded chernozem reaction toward the acidifying action of simulated acid rain was performed in columns of 1 m height and 7 cm diameter. The acid rain was divided into 20 doses of 80 ml per each column and was applied daily in six doses equivalent to 25%, up to 150% of the sorption capacity of Ap horizon.

The surface application of hydrogen ions within Ap horizon of reconstructed chernozem profile invokes the decrease of pH value of the soil solution and hydrolytic acidity till the complete saturation of the sorption complex with hydrogen cations at concentration equivalent to 150% of sorption capacity of Ap horizon (level VI), proportional to the acid concentration. Reaction toward acidifying gradually weakens in deeper layers. The basic cations eliminated out of the surface horizons at low amounts were removed along with filtrates out of the soil profile in the following sequence: Ca>Na>Mg>K; they were retained mainly in deeper horizons.

Acid rain application in a dose equivalent to 50% of the sorption capacity of Ap horizon of degraded chernozem provokes substantial deterioration of chemical and physicochemical features, while in deeper layers it is less visible. Strengthening the acid rain (over 50% of the sorption capacity of Ap horizon) increases the negative effect and enlarges its range in soil profile.

**Keywords:** acid rain, soil profile, filtrate, buffering capacity

## Introduction

Under conditions of leaching type of water balance, the soil acidification occurs through its top layers. The process is intensified due to farming and, sometimes, atmospheric contamination, which leads to chemical, biological, and physical degradation of soils. Balance between H<sup>+</sup> and Ca<sup>+2</sup> ions plays an important role not only from a point of view of farming culture, but also in a global C $\rightleftharpoons$ CO<sub>2</sub> cycle, which is particularly significant in Mollisols. One gram of

decomposed CaCO<sub>3</sub> releases about 224 ml CO<sub>2</sub>. Calcium compounds present in a soil can have lithologic origin from a mother rock, where they occur most often as calcite [1], or dolomite, aragonite, and siderite in some other soils, or may be secondarily created resulting from soil-evolution processes [2]. A necessity to reduce the CO<sub>2</sub> concentration in air requires recognizing factors and mechanisms that cause carbonate and organic matter decomposition in various soil types, depending on their management system.

Chernozems, as common zonal soils, cover about 7% of worldwide soils and are present in natural habitats beneath grassy ecosystems that are characterized by producing a

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Table 1. Basic properties of the investigated soil (before treatment).

Horizon	Depth (cm)	Soil particles, $\Phi$ mm			Bulk density	$C_{org}$	$N_{tot}$	pH		$H_w^*$	$Al^{+3*}$	$H_h^*$	SEB*	CEC*	BS* %
		1-0.1	0.1-0.02	<0.02				H <sub>2</sub> O	KCl						
		%			$g \cdot cm^{-3}$	%	mmol (+) $\cdot 100 g^{-1}$								
Ap	0-26	2	62	36	1.18	1.15	0.101	7.01	6.46	0.08	0.03	0.90	14.04	14.94	94.0
A	26-37	1	53	46	1.25	0.59	0.054	7.42	6.40	0.09	0.02	0.75	14.33	15.08	95.0
AC	37-65	6	47	47	1.20	0.20	0.022	7.21	6.18	0.08	0.01	0.75	14.62	15.37	95.1
C1	65-77	0	52	48	1.21	0.09	0.011	6.73	5.90	0.08	0.02	1.12	13.44	14.56	92.3
C2	77-89	2	51	47	1.16	n.d.	n.d.	6.47	5.77	0.09	0.02	1.42	12.56	13.98	89.8
C3	89-100	0	56	44	1.15	n.d.	n.d.	6.04	5.48	0.10	0.02	2.02	11.85	13.87	85.4

$H_w$  – Exchangeable acidity,  $Al^{+3}$  – Exchangeable aluminum,  $H_h$  – Hydrolytic acidity, SEB – Sum of exchangeable bases, CEC – Cation exchange capacity, BS – Base saturation, n.d. – not determined

large biomass abundant in nutrients, namely  $Ca^{+2}$ . They have been developed from different parent materials abundant in carbonates and have accumulated large amounts of calcium carbonate in the profile [3].

The present research aimed at evaluating the influence of simulated acid rain on select chemical and physico-chemical features within the degraded chernozem profile.

### Material and Methods

The soil for study was collected from an exposed spot on an intensively farmed area in Sietesz (near Łańcut, Podkarpacie region), on terrain culmination (255 m above sea level) with quite good surface waters outflow. The study area (southeastern Poland) lies within an oceanic-type moderately warm climate, and it is temporarily affected by strong influences of continental climate like no other Polish region. Mean annual air temperature is  $7.5^{\circ}C$  (the warmest in July,  $18.2^{\circ}C$ ), while annual rainfall amounts to 665 mm at considerable differences in particular years (from 475 to 987 mm) with maximum rainfalls in July (100 mm, on average).

Considering the soil profile, its morphology was described and samples were collected for laboratory analysis; moreover, the soil material was collected in 5-centimeter thickness layers to simulate its profile in the laboratory. The soil profile was reconstructed in 1 meter high and 7 cm diameter plastic columns and then the soil was adjusted to its full capillary water capacity and allowed for collecting the filtrates.

A total of 350 mm of acid rain was applied by dividing it into 20 portions used once a day for 20 days, which made 80 milliliters of solution per column daily. Hydrogen ions concentration in a dose was a variable factor – 6 levels that were set up on a base of determined sorption capacity of the soil in the Ap horizon and control object (with distilled water). The first acidification level (I) was equivalent to 25% of the capacity, II – 50%, III – 75%, IV – 100%, V – 125%, and VI – 150% of the soil sorption capacity. Every

object was prepared in three replicates. After the experiment was complete, the soil was removed from the columns and its samples were collected from particular levels for laboratory analyses.

The following determinations were performed using the soil material from the profile that were subjected to the simulated acid rain impact: acidity (potentiometry), exchangeable acidity and exchangeable aluminum (Sokolow method), hydrolytic acidity and sum of exchangeable bases (Kappen method), as well as contents of basic cations (Ca, Mg, Na, and K) after their extraction from a sorption complex using 1 M  $NH_4Cl \cdot dm^{-3}$  (AAS technique). Moreover, for soil from the outcropped profile the granulometric composition (sedimentation method according to Cassagrande's with Prószyński's modifications) was determined, soil weight (in 100  $cm^3$  capacity cylinders), organic carbon content (Tiurin method), total nitrogen concentration (Kjeldahl method), buffering capacity within the acidity range up to 16 ml 0.1 M HCl (Arrhenius method with The Soil Science Department staff, UMK in Toruń [4] using 10 g of soil sample), as well as available forms of phosphorus and potassium contents (Egner-Riehm method), and magnesium (Schachtschabel method). Generated filtrates were subject to determine the acidity as well as Ca, Na, Mg, and K concentrations, applying common procedures for water analysis [5].

### Results and Discussion

The soil used for studies was developed from loess maternal formation and showed the granulation of loamy dust within the profile (Table 1). The share of sandy fraction was negligible, while fine dust dominated within the dusty fraction ( $\Phi 0.05-0.02$  mm), amounting to 39% to 49%. The volumetric weight in plough-humus horizon (Ap) of examined soil was  $1.18 g \cdot cm^{-3}$ , while in deeper layers (up to 77 cm), it was larger. The soil contained slight quantities of organic carbon (1.15%) within plough-humus horizon Ap, 0.59% in A, and 0.20% in AC horizon. Therefore, it

Table 2. The soil contents of available P, K, and Mg forms, as well as Ca, Mg, K, and Na forms soluble in 1 mol NH<sub>4</sub>Cl·dm<sup>-3</sup> (before experiment).

Horizon	Available			Extracted 1 mol NH <sub>4</sub> Cl·dm <sup>-3</sup>			
	P	K	Mg	Ca	Mg	Na	K
	mg·100 g <sup>-1</sup> soil			mmol (+)·100 g <sup>-1</sup> soil			
Ap	8.68	23.60	5.68	13.28	0.23	1.41	1.02
A	3.17	7.12	8.58	11.84	0.27	1.02	0.44
AC	4.42	6.10	11.80	13.75	0.34	0.49	0.47
C1	4.56	6.37	11.53	11.35	0.28	0.51	0.40
C2	4.45	6.18	11.85	10.47	0.32	0.48	0.35
C3	4.57	6.14	11.42	10.09	0.32	0.50	0.37

was not particularly abundant in humus, which is associated with very a long period of agricultural management resulting in its decomposition [6-8] and, on the other hand, with considerable spatial variability of organic carbon content and thickness of humus horizons within degraded chernozems in southeastern Poland [9]. The soil showed slightly acidic reaction to 89 cm (from 6.46 in Ap to 5.77 pH in C2) and acidic up to 100 cm of depth (5.48 pH in C3) in particular genetic horizons. Its exchangeable acidity and content of exchangeable aluminum within the profile were insignificant, while its hydrolytic acidity did not exceed 1 mmol(+)·100 g<sup>-1</sup> soil within horizons with humus (to 65 cm of depth); it was higher in the mother rock (89-100 cm) – 2.02 mmol(+)·100 g<sup>-1</sup> soil.

The field survey revealed the presence of a horizon with numerous precipitates of calcium carbonate (puppets) at depths of 150-160 cm, which should be attributed to anthropological degradation range [10], as well as intensive soil agitation due to HCl addition, which indicates the several per cents of carbonates content. The sum of exchangeable bases in particular genetic horizons was poorly diverse, while in surface levels up to 77 cm of depth, it was higher (from 13.44 to 14.62 mmol (+)·100 g<sup>-1</sup>) as compared to the mother rock (about 12 mmol (+)·100 g<sup>-1</sup> soil). The level of sorption complex saturation with basic cations was high, amounting to 94-95% in surface horizons containing humus to 85% in mother rock.

The percentage of available phosphorus, potassium, and magnesium forms in examined soil was diverse, which depended on their contents in the parent material (Table 2). Loess was characterized by moderate phosphorus and low potassium concentrations; high levels of phosphorus and very high potassium within plough-humus horizon (Ap) may result from intensive nutrition with these components. Considering magnesium, the mother rock contained very large amounts of the element and its exhaustion in surface layers (0-37 cm) can be associated with agrotechnical negligence. Calcium dominated in the soil sorption complex within particular genetic horizons; its content was from 11.84 to 13.75 mmol (+)·100 g<sup>-1</sup> soil in horizons containing humus with a decrease up to 10.09 mmol (+)·100 g<sup>-1</sup> soil in

C3 horizon. Magnesium share was low: from 0.23 in Ap to 0.32 mmol (+)·100 g<sup>-1</sup> soil in C3 horizon (Table 2). Concentrations of exchangeable sodium and potassium within sorption complex were low: 1.41 and 1.02 mmol (+)·100 g<sup>-1</sup> soil in Ap horizon, respectively, with a gradual decrease to 0.50 and 0.37 mmol (+)·100 g<sup>-1</sup> soil.

Buffering capacity of the examined soil within the acidic range were significantly diverse within its profile. Soil of Ap horizon most effectively neutralized the acidification; the pH decrease up to 5 units below was achieved after applying 10 ml 0.1 M HCl; the same effect was observed after adding 8 ml 0.1 M HCl in soils of A and AC horizons. If a buffering surface area within the acidic range of the soil from Ap horizon is assumed as 100%, the buffering capacity for A and AC horizons was 79.5% and 79.4%, respectively, while for parent material horizons from 43.3% to 36.1%. The colloid loam fraction, soil humus [11] and soil-forming processes [12] are most probably responsible for buffering capacity shaping within particular genetic horizons of studied soil.

Simulated distilled water rain (control) only slightly affected the properties of examined soil (Table 3), while hydrogen ions introduced along with acid rain evoked specific reactions that were proportional to acid concentration. The low level of hydrogen ions in simulated rainfall (I level) in Ap horizon decreased pH to 4.93 (against 6.49 for control), enhanced the hydrolytic acidity to 4.34 mmol (+)·100 g<sup>-1</sup> soil (against 1.27 mmol (+)·100 g<sup>-1</sup> soil for control), and decreased the level of basic cations saturation to 72.7% (against 92.5% for control); no such prominent reaction was observed in deeper horizons. Applying the hydrogen ions concentration equivalent to the sorption capacity of Ap horizon in simulated rainfall (level IV) decreased the reaction to pH 3.32, increased the hydrolytic acidity to 16.72 mmol (+)·100 g<sup>-1</sup> soil, and decreased the level of saturation with basic cations to 18.4%. The acidification reaction was also transferred to deeper A horizon and decreased its pH to 5.25 (against 6.55 for control), enhanced the hydrolytic acidity to 2.49 (against 1.35 mmol (+)·100 g<sup>-1</sup> soil for control), and decreased the level of sorption complex saturation with basic cations to 84.2% (against 91.8%

Table 3. Influence of hydrogen ions concentration on selected soil properties in particular genetic horizons.

Object	Genetic horizon	pH		H <sub>w</sub>	Al <sup>3+</sup>	H <sub>h</sub>	S	T	V
		KCl	H <sub>2</sub> O						
K	Ap	6.49	6.95	0.08	0.03	1.27	15.76	17.03	92.5
	A	6.55	7.37	0.09	0.02	1.35	15.08	16.43	91.8
	AC	6.23	7.21	0.10	0.02	1.62	14.33	15.95	89.8
	C1	6.09	7.04	0.09	0.03	1.53	13.42	14.95	89.8
	C2	5.94	6.95	0.08	0.04	1.65	13.27	14.92	88.9
	C3	5.87	6.83	0.10	0.03	1.92	12.74	14.66	86.9
I	Ap	4.93	5.83	1.15	0.04	4.34	11.54	15.88	72.7
	A	6.17	6.87	0.18	0.01	1.52	14.88	16.40	90.7
	AC	6.04	7.11	0.09	0.01	1.66	16.92	18.58	91.1
	C1	5.91	6.95	0.10	0.01	1.81	15.54	17.35	89.6
	C2	5.74	6.73	0.09	0.02	1.72	15.31	17.03	89.9
	C3	5.66	6.64	0.09	0.01	1.85	15.85	17.70	89.5
II	Ap	3.97	4.57	3.37	0.07	8.25	8.25	16.50	50.0
	A	5.88	6.62	0.27	0.03	1.49	14.41	15.90	90.6
	AC	6.15	6.49	0.12	0.01	1.82	15.21	17.03	89.3
	C1	5.72	6.56	0.09	0.04	2.07	14.87	16.94	87.8
	C2	5.64	6.42	0.10	0.02	2.19	15.54	16.73	86.9
	C3	5.61	6.31	0.09	0.01	2.10	14.36	16.46	87.2
III	Ap	3.56	4.16	5.61	0.62	11.59	6.17	17.76	34.7
	A	5.77	6.25	0.25	0.17	2.44	14.25	16.69	85.4
	AC	6.20	6.39	0.18	0.08	2.05	13.88	15.93	87.1
	C1	6.04	6.40	0.10	0.02	1.87	15.57	17.44	89.3
	C2	5.93	6.51	0.09	0.01	1.62	14.81	16.43	90.1
	C3	5.81	6.39	0.09	0.01	1.95	14.54	16.49	88.2
IV	Ap	3.32	3.48	7.94	1.38	16.72	3.76	20.48	18.4
	A	5.25	5.86	0.57	0.15	2.49	12.24	15.73	84.2
	AC	5.61	5.94	0.21	0.12	2.66	14.91	17.57	84.7
	C1	5.71	6.27	0.14	0.03	1.99	15.34	17.33	88.5
	C2	5.80	6.33	0.10	0.00	2.24	15.08	17.32	87.1
	C3	5.70	6.22	0.09	0.02	2.00	14.88	16.88	88.1
V	Ap	3.07	3.14	11.12	2.47	18.91	1.85	20.76	8.9
	A	3.84	4.47	0.96	0.33	5.72	11.34	17.06	66.5
	AC	4.83	5.46	0.54	0.12	3.17	13.27	16.44	80.7
	C1	5.27	5.66	0.29	0.08	2.25	12.74	14.99	85.0
	C2	5.65	6.18	0.20	0.04	2.04	13.04	15.08	86.5
	C3	5.58	6.26	0.10	0.03	1.88	13.65	15.33	87.9
VI	Ap	3.01	3.22	13.62	2.78	21.45	0.00	21.45	-
	A	3.57	4.15	3.22	2.11	12.71	5.65	18.36	30.8
	AC	4.25	5.30	0.69	2.13	4.87	11.42	16.29	70.1
	C1	5.54	5.68	0.52	0.19	3.24	13.57	16.81	80.7
	C2	5.62	5.95	0.37	0.03	2.18	14.05	16.23	86.6
	C3	5.70	6.10	0.18	0.05	2.33	14.28	16.61	86

for control). As a consequence of applying the highest concentration of acid rain (level VI), the soil sorption complex within Ap horizon became completely saturated with hydrogen cations and a prominent increase of hydrogen ions was also recorded in deeper layers, including the ceiling of the mother rock – level C1. The sorption complex occupation was strongly changed due to simulated acid rain (Fig. 1). The largest desorption occurred within plough-humus horizon, which referred to calcium, the amount of which decreased to 0.35 mmol (+)·100 g<sup>-1</sup> soil after the highest hydrogen ions application as compared to 11.5 mmol (+)·100 g<sup>-1</sup> soil for control. In A and AC horizons, acidification had a weaker

influence on calcium desorption and transferred calcium was partially retained within the mother rock. Sodium, potassium, and magnesium were present at much lower quantities in the sorption complex, subject to desorption to the lower extent due to acidification, and they were not retained within the examined profile. Concentration of a simulated acid rain also affected the proportions between basic cations in sorption complex. It was found that the percentage of sodium increased from 10.6% to 23.4%, potassium from 7.7% to 36.6%, while that of magnesium decreased from 80.2% to 40.0% within sorption complex of Ap horizon due to increasing acidification (Fig. 2).

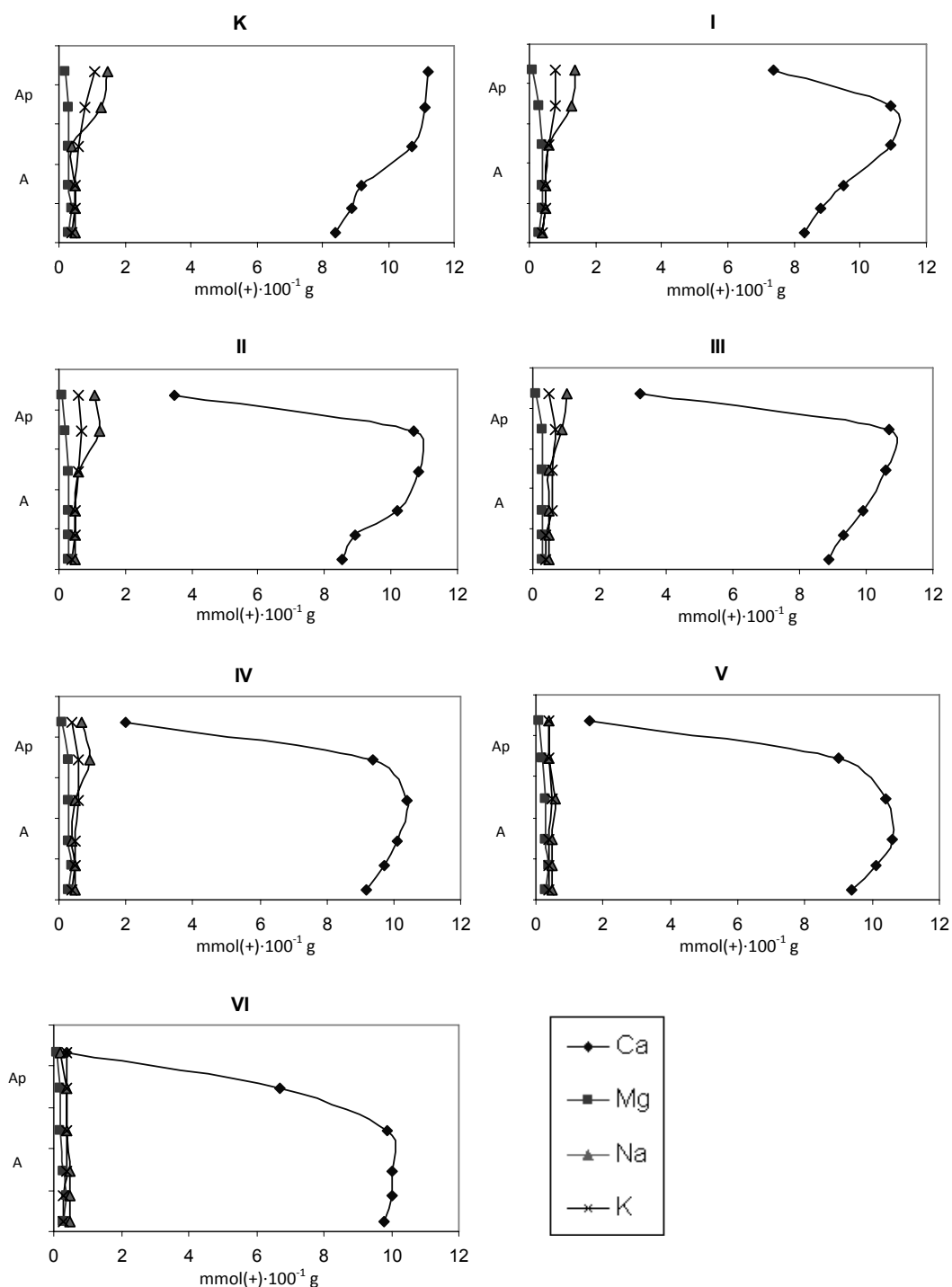


Fig. 1. Contents of exchangeable Ca, Mg, Na, and K in soil sorption complex of particular genetic horizons.

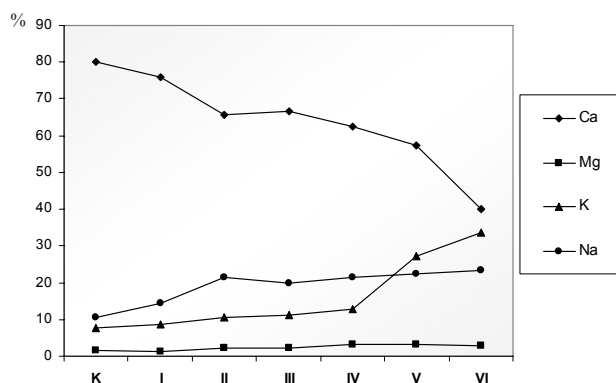


Fig. 2. Percentage of cations in the soil sorption complex of Ap horizon.

The pH values of filtrates achieved from the soil profile was above 7.0 and diverse concentrations of cations contained was associated with the concentration of simulated acid rainfall (Table 4). Low contents of elements in achieved filtrates from degraded chernozem – as compared to much higher ones in other studies (on sandy soils) – result mainly from different physicochemical properties (sorptive and buffering) of used soils [13].

### Conclusions

1. The surface application of hydrogen ions within Ap horizon of reconstructed chernozem profile causes a decrease of pH value of the soil solution and hydrolytic acidity till the complete saturation of the sorption complex with hydrogen cations at concentration equivalent to 150% of sorption capacity of Ap horizon, proportional to the acid concentration.
2. Reactions toward acidification are weaker, though prominent in deeper soil horizons (up to the ceiling of the mother rock).
3. Buffering properties within the acidic range are much stronger in the part of the chernozem profile containing humus compounds as compared to the parent material.
4. Applied hydrogen ions most strongly eliminated calcium cations from the Ap horizon of soil sorption complex. Higher hydrogen ions concentrations led to the decrease of calcium ions percentage, while that of potassium, sodium, and magnesium increased.
5. Low levels of Ca, Na, Mg, and K in achieved filtrates indicate that these elements when eliminated out of the surface layers, were retained in deeper horizons.

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Table 4. Influence of acid rain concentrations on amounts of elements eluted from the soil profile.

Object	Ca	Na	Mg	K
	mg·dm <sup>-3</sup>			
K	0.34	0.74	0.31	0.04
I	0.81	1.45	0.32	0.04
II	1.50	2.07	0.32	0.05
III	2.00	2.15	0.33	0.05
IV	2.46	2.37	0.40	0.09
V	3.22	2.55	0.48	0.08
VI	4.14	2.99	0.56	0.07

### References

1. AMUNDSON R.G., LUND L.J. The stable isotope chemistry of a native and irrigated Typic Natrargid in the San Joaquin Valley of California. *Soil Sci. Soc. Am. J.* **51**, 761, **1987**.
2. MING D.W. Carbonates. In Lal R. (Ed) *Encyclopedia of soil science*. Marcel Dekker, New York, pp. 139-141, **2002**.
3. BELL J.C., MCDANIEL P.A. Mollisols. In Summer M.E. (Ed) *Handbook of soil science*. CRC Press, Boca Raton, FL, pp. 286-307, **2000**.
4. BEDNAREK R., DZIADOWIEC H., POKOJSKA K., PRUSINKIEWICZ Z. *Ecological and soil-scientific studies*, PWN, pp. 344, **2005** [In Polish].
5. GOMUŁKA B., GOMUŁKA E. *Laboratory practices on water chemistry*, Oficyna Wydaw. Polit. Wrocławskiej, pp. 177, **1996** [In Polish].
6. DAVIDSON E.A., ACKERMAN I.K. Changes in soil carbon inventories following cultivation of previously untilled soils. *Biogeochemistry*. **20**, 161, **1993**.
7. XU J.G., JUMA N.G. Carbon kinetics in a Black Chernozem with roots in situ. *Can. Journ. of Soil Sci.* **75**, 299, **1995**.
8. MIKHAILOVA E.A., BRYANT R.B., VASSENEV I.I., SCHWAGER S.J., POST C.J. Cultivation effects on soil carbon and nitrogen contents at depth in the Russian Chernozem. *Soil Sci. Soc. Am. J.* **64**, 738, **2000**.
9. GĄSIOR J. Variability in chernozemes using the example of profile in Buszkowice (Podkarpacie Ice-marginal Valley). *Wiśnik Lwowskiego Dierż. Uniw. Agrar., ser Agron.* **7**, 398, **2003** [In Polish].
10. MIKHAILOVA E.A., POST C.J. Effects of land use on soil inorganic carbon stocks in the Russian Chernozem. *J. of Environ. Qual.* **35**, 1384, **2006**.
11. NGATUNGA E.L., COOLS N., DONDEYNE S., DECKERS J.A., MERCKX R. Buffering capacity of cashew soils in south eastern Tanzania. *Soil use and management*. **17**, (3), 155, **2001**.
12. MIECHÓWKA A., MAZUREK R., CIARKOWSKA K. Resistance of south Polish soils to acidity changes. *Zesz. Probl. Post. Nauk Rol. z.* **421a**, 285, **1995** [In Polish].
13. WALNA B., DRZYMAŁA S., SIEPAK J. The impact of acid rain on potassium and sodium status in typical soils of the Wielkopolski National Park (Poland). *Water, Air and Soil Pollution*. **121**, 31, **2000**.