

RESIDUAL EFFECT OF ACID RAIN ON THE SOIL

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A b s t r a c t. Research into the mechanism of soil degradation as affected by excessive immission of sulphur from man-made sources indicates unequivocally that the process is by no means ended once the inflow of pollutant to the soil is discontinued. The aim of the investigations was to look into the residual effect of prolonged sulphur contamination of the soil with diluted H_2SO_4 that simulated an acid rain of the pH of 2.8-3.5 on soil physical properties after the excess of sulphates was washed away.

In the experiment with loamy soil (particle size fraction of <0.02 mm accounting for 25-30 %) 5 sulphur contamination treatments were considered equivalent to the following levels of sulphur immission: 0, 62.5, 125, 250 and $500 \text{ kg S ha}^{-1}\text{year}^{-1}$. The treatments were superimposed on two series with and without 1 Hh $CaCO_3$ addition.

The study showed that after the input of non-native sulphur was cut off and excess sulphur washed out the pH of the studied soil continued to decline and its potential acidity continued to rise. Another effect was a substantial decrease in the saturation of the sorption complex with bases, mainly as a result of further losses of calcium and magnesium from the soil. Both as the effect of direct and residual acidification of soils due to sulphur contamination, liming slowed down the rate of soil degradation and, hence, alleviated the negative effects of that phenomenon.

Key words: simulated acid rain, sulphur contamination of soil

INTRODUCTION

Changes in the chemical properties of soils contaminated with sulphur compounds are related to acidification that builds up from the surface [1,2,5]. Excessive sulphur immission through the soil both as acid rain and dry deposition triggers off many processes and the result

is the reduction in soil base cations, mainly Ca^{2+} and Mg^{2+} , and the release of phytotoxic elements, i.e., Al^{3+} and Mn^{2+} [1,4,6]. As a result, degradation of soil environment comes about and its effects, as indicated by the mechanism of the process, do not disappear once the inflow of sulphur compounds to the soil is discontinued [4]. That is why Stigliani [7] thinks that because of the heavy sulphur contaminations of Central European soils even a cut down in sulphur emission rate by as much as 30 % against the level of 1980 will have little effect on the checking of the progress of their acidification-related degradation.

The undertaking of this study was promoted by the relevance of the problem due to the known international agreements [9,10] and by the absence of data regarding the residual effect of excessive sulphur immission in the soil.

MATERIALS

The laboratory experiment with a brown soil developed from light loam (particle size fraction of <0.02 mm accounting for 25-30 % of its granulometric composition) was conducted in PCV tubes 10 cm in diameter and 50 cm high. The restored model of that soil consisted of layers A_1 - 25 cm thick and B - 20 cm thick. The soil pH in those layers was 5.4 and 7.2, respectively. Five treatments were included in

the experiment that corresponded to the following rates of sulphur contamination: 0, 62.5, 125, 250 and 500 kg S ha⁻¹ year⁻¹. Two series without and with an addition to the soil of 1 Hh CaCO₃ were also included.

Sulphur additions to the soil were made once a week. A single dose, equivalent to 1/12 of annual application, was applied as diluted H₂SO₄ to simulate 'acid rain' the pH of which, depending on sulphur rate, corresponded to 3.5, 3.2, 3.0 and 2.8. After 15 months, the length of time equivalent to a 5-year acid rain impact at 500 mm of annual precipitation, the first cycle of study was completed by discontinuing one of two replication of the experiment and collecting soil samples for chemical analyses. In the second replication, systematic washing of columns with distilled water was started just as in the first cycle. The washing was continued until similar amounts of SO₄²⁻ ions were found in the filtrates from individual treatments. The concentration of those ions, along with other constituents, was measured successively in 1-liter aliquots of soil filtrates. Once the effect had been reached, the experiment was brought to an end by collecting soil samples at depths of 0-20 and 21-40 cm. Those samples were analysed for chemical properties using methods applied by Agrochemical Stations [3].

RESULTS

The comparison of the data from the 1st and the 2nd cycles of study (Table 1) unambiguously suggests that the process of soil acidification did not stop with the cessation of sulphur immission in the soil. It is evidenced by the changes in values of pH indicators found on completion of the experiment. Those changes signified further decline in pH, proportional to sulphur rate, and a rise in the potential acidity indicators such as Hh, He and Al mobile in the surface soil layer (0-20 cm). The residual effect of 'acid rain' was particularly adverse on the unlimed soil. On that soil, especially with higher sulphur rates, a nearly twofold increase in mobile aluminium was found. The amount of that constituent in the unlimed sulphur-contaminated soil reached, in extreme cases, values

that were highly toxic to plants (1.5-3.8 mol(+)/100 g of soil). The residual effect of simulated 'acid rain' consisted in the increase of soil acidification in the subhumus layer. In the treatments involving the highest sulphur rate the fall in soil pH_{KCl} at 21-40 cm was 1 unit (Table 1).

The residual effect of sulphur-contamination of the soil with 'acid rain' also involved further deterioration of its sorption complex (Table 2). In the 2nd cycle of study, there was a substantial decrease in the percentage of calcium, magnesium and potassium in the sorption complex of the humus layer and a reduction in its saturation with bases. Those changes were accompanied by a progressive increase in the percentage of hydrogen ions that occurred along with the rise in sulphur-contamination of the soil. All those adverse effects came as a result of intensified leaching of base cations, especially of Ca²⁺ and Mg²⁺ as sulfates. It was manifested by the concentrations of those ions in soil filtrates that were found at the beginning of washing of sulphur-treated soil.

DISCUSSION

The results of chemical degradation of soil obtained in the study pointed to a significant effect, both direct and residual, of 'acid rain'. It is related to the mechanism of that phenomenon that consists in the launching of processes that speed up the decomposition of soil minerals [2,5,6,8]. The result was a time-progressing increase in acidification, intensified leaching of base cations and release of excessive amounts of aluminium. The suppression of buffering systems of the soil by H₂SO₄, a particularly aggressive constituent of 'acid rain', both natural and simulated, led to a highly toxic, sulphur contamination-related concentration of mobile Al. In both the limed and unlimed soil an excessive increase of mobile Al was related to the decrease of pH_{KCl} down to the pH of the aluminium buffer. According to Prusinkiewicz's [6] and Dechnik's [1] citations of Ulrich the aluminium buffer while stabilizing soil pH within a range of 4.2-2.8 at the same time causes Al³⁺ ions to be released by dissolving basic aluminium

Table 1. Residual effect of simulated 'acid rain' on the acidification of a loamy soil

Treatment (dose of S in kg ha ⁻¹ year ⁻¹)	Depth (cm)	1st cycle-sulphur contamination					2nd cycle-washing with H ₂ O					1st cycle-sulphur contamination					2nd cycle-washing with H ₂ O				
		pH _{Ca}	Hh	He	Mob. Al	mmol(+)100 g ⁻¹	pH _{Ca}	Hh	He	Mob. Al	mmol(+)100 g ⁻¹	pH _{Ca}	Hh	He	Mob. Al	mmol(+)100 g ⁻¹	pH _{Ca}	Hh	He	Mob. Al	mmol(+)100 g ⁻¹
		Unlimed soil										Limed soil									
0	0-20	5.3	2.95				5.2	2.96				6.0	2.47				5.8	2.47			
	21-40	7.0	0.56				7.0	0.60				6.8	0.60				6.4	0.60			
62.5	0-20	4.3	3.75	0.33	0.21		4.1	4.10	0.64	0.58		5.4	2.70	0.26	0.17		5.6	2.45			
	21-40	7.0	0.60				6.3	0.56				7.0	0.48				6.2	0.78			
125.0	0-20	4.0	3.97	0.52	0.39		3.9	4.58	1.00	0.87		5.4	2.85	0.51	0.45		5.6	2.85			
	21-40	6.9	0.64				6.2	0.63				6.5	0.63				6.2	0.84			
250.0	0-20	4.0	4.51	1.04	0.79		3.9	5.44	2.15	1.51		4.6	4.54	0.88	0.70		4.4	4.54	0.52	0.36	
	21-40	7.0	0.71				6.2	0.75				6.4	0.63				6.3	0.75			
500.0	0-20	3.5	5.66	2.46	2.21		3.5	7.05	4.06	3.84		3.3	6.39	2.17	1.86		3.8	6.04	2.87	2.64	
	21-40	7.1	0.71				5.9	0.98				5.8	0.56				6.1	0.79			

T a b e l a 2. Effect of simulated 'acid rain' on sorption properties of a sulphur contaminated loamy soil

Treatment (dose of S in kg ha ⁻¹ year ⁻¹)	Depth (cm)	1st cycle-sulphur contamination					2nd cycle-washing with H ₂ O					1st cycle-sulphur contamination					2nd cycle-washing with H ₂ O				
		Ca	Mg	K	Hh	V (%)	Ca	Mg	K	Hh	V (%)	Ca	Mg	K	Hh	V (%)	Ca	Mg	K	Hh	V (%)
		mmol(+)100 g ⁻¹					mmol(+)100 g ⁻¹					mmol(+)100 g ⁻¹					mmol(+)100 g ⁻¹				
		% relative to T					% relative to T					% relative to T					% relative to T				
		Unlimed soil																			
0	0-20	52	7	4	36	64	47	5	3	44	56	62	7	4	25	75	60	7	3	28	72
	21-40	84	7	3	5	95	81	7	3	7	93	82	8	3	6	94	82	6	2	8	92
62.5	0-20	47	7	3	42	58	46	5	3	45	55	56	6	3	33	67	56	5	3	35	65
	21-40	83	8	2	5	95	81	7	3	7	93	82	9	3	5	95	81	7	3	7	93
125.0	0-20	43	7	3	46	54	40	5	3	50	50	54	6	3	36	64	52	5	3	39	61
	21-40	83	8	2	6	94	82	7	3	7	93	82	8	2	7	93	81	7	3	7	93
250.0	0-20	40	4	3	52	48	32	4	2	61	39	46	5	3	45	55	43	3	3	50	50
	21-40	82	8	2	7	93	81	7	3	7	93	82	8	2	7	93	82	6	3	8	92
500.0	0-20	30	4	3	62	38	20	3	2	75	25	29	3	2	65	35	25	3	2	69	31
	21-40	80	9	3	7	93	80	7	3	8	92	82	8	2	6	94	82	6	3	8	92
		Limed soil																			

Table 3. Concentration* of some cations and anions in soil filtrates (2nd cycle of study)

Treatment (dose of S in kg ha ⁻¹ year ⁻¹)	Unlimed soil				Limed soil			
	Ca ²⁺	Mg ²⁺	SO ₄ ²⁺	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	SO ₄ ²⁺	HCO ₃ ⁻
	mg dcm ⁻³							
0	3.1*	0.5	0.2	2.1	3.0	0.5	0.3	2.0
	3.3-1.5**	0.7-0.2	0.3-0.2	2.5-0.8	3.0-1.8	0.6-0.2	0.3-0.3	2.2-0.9
62.5	2.4	0.4	0.4	1.8	3.0	0.6	0.4	3.0
	3.9-2.0	0.9-0.3	0.6-0.3	2.6-0.6	4.4-2.3	0.9-0.4	0.9-0.4	2.8-1.5
125.0	3.3	0.5	0.4	2.1	3.4	0.6	0.5	2.8
	4.2-2.0	0.8-0.4	1.2-0.2	2.2-1.3	4.4-2.4	1.0-0.4	1.7-0.4	2.2-1.3
250.0	3.5	0.7	0.6	2.9	3.3	0.	0.7	2.0
	4.5-2.5	1.1-0.4	2.5-0.2	2.5-1.5	4.5-3.0	1.0-0.4	2.6-0.4	2.1-1.0
500.0	3.7	0.7	1.0	3.1	3.2	0.6	1.1	2.4
	5.0-2.5	1.2-0.5	5.4-0.3	2.4-2.2	4.8-2.8	1.3-0.4	3.9-0.4	2.1-1.1

* mean concentration;

**initial concentration - end concentration.

compounds of the type $Al(OH)_2(H_2O)_4^+$ arising from the decomposition of clay minerals and has them move directly from the crystal lattice to the solution.

The excess of sulphuric acid that occurs in soils subjected to long-time action of 'acid rain' impairs the protective function of the sorption complex against the leaching of mineral constituents, including sulphates. Hence, the residual effect of simulated acid rain consisted in adverse changes in ion composition of the sorption complex thus contributing to further decrease in Ca^{2+} and Mg^{2+} cations and an increase in H^+ ions. Ion composition-related saturation of the sorption complex with bases dropped to 25 % in the heavily sulphur contaminated soil. That extremely low value of the V indicator, the best descriptor of soil deterioration according to Siuta [8], was reached as a result of secondary effects of simulated acid rain.

Summing up the above, the determination of the negative effects of past and present immission of sulphur from SO_2 - contaminated air in the soil is an important task to be carried out as part of conservation and remediation of degradation-threatened agroecosystems.

CONCLUSIONS

1. The study demonstrated that the process of the chemical degradation of soil due to sulphur immission-related acidification proceeding

form soil surface downwards does not cease with the cessation of sulphur deposition.

2. The residual effect of sulphur contamination of a loamy soil subjected to leaching consisted in further adverse changes in soil environment. Proportional to the amount of sulphur dose, they were as follows:

- decrease in pH_{KCl} and increase in the potential forms of acidity and in mobile Al content.

- decrease in the percentage of base cations, especially of Ca^{2+} and Mg^{2+} , and increase of H^+ ions in the sorption complex of the soil.

3. As regards both direct and residual effect, liming of the soil according to 1 Hh failed to prevent its further acidification merely slowing down the process and thus alleviating the negative effects of sulphur-contamination.

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EFEKTY NASTĘPCZE ODDZIAŁYWANIA KWAŚNYCH DESZCZY NA GLEBĘ

Z badań nad mechanizmem degradacji gleb pod wpływem nadmiernej imisji siarki, ze źródeł antropogenicznych

wynika jednoznacznie, że proces ten nie kończy się z dopływem polutanta do gleby. Celem badań było określenie następczego działania długotrwałego zasiarczenia gleby rozcieńczonym roztworem H_2SO_4 , symulującym kwaśny deszcz o pH 2.8-3.5, na kształtowanie się jej właściwości chemicznych, po odmyciu nadmiaru siarczanów. W doświadczeniu z glebą gliniastą (% fr., <0.02 mm = 25-30) uwzględniono 5 obiektów równoważących imisję siarki w ilości: 0, 62.5, 125, 250 i 500 kg S ha⁻¹r⁻¹ oraz 2 serie bez i z dodatkiem CaCO₃ w dawce według 1 Hh.

Badania wykazały, że w glebie zasiarczonej po odcięciu dopływu siarki z zewnątrz i odmyciu nadmiaru jonów SO₄²⁻ nastąpił dalszy spadek pH oraz wzrost kwasowości potencjalnej. Poza tym znacznemu obniżeniu uległ stopień wysycenia kompleksu sorpcyjnego zasadami, głównie wskutek dalszego ubytku wapnia i magnezu z gleby. Zarówno w bezpośrednim, jak i następczym zakwaszaniu się gleby pod wpływem zasiarczenia, wapnowanie opóźniło tempo jej degradacji, łagodząc tym samym negatywne skutki tego zjawiska.

S ł o w a k l u c z o w e: symulowany kwaśny deszcz, zanieczyszczenie gleby siarką.