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LEACHING OF ELEMENTS FROM SOIL IN GRASSLAND FIELD CROPS TREATED WITH RAW AND ACIDIFIED SLURRY

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ABSTRACT

The state of soils was presented in the aspect of environmental protection when using acidified slurry was used as fertilizer to protect ammonia from escaping into the atmosphere. The use of concentrated sulfuric acid to lower the pH of the slurry and thus retain nitrogen in the soil and then use it by crops gives a double benefit, reduces nitrogen losses, and reduces the cost

Keywords:
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of mineral fertilizers that should be purchased. Injecting raw slurry below the surface of the soil has some benefits in the form of reducing ammonia emissions, but it does not affect the use of fertilizers with the addition of sulfur, which is ensured in the case of acidification of the slurry. Additional benefit is to obtain environment protection. Leaching of elements from grassland and corn crop soil treated with raw cattle slurry and acidified cattle slurry ($m^3 \cdot ha^{-1}$) was presented. The K content was highest in the leachate collected after the application of the last batch of acidified slurry. Yield tests were conducted on similar soils as presented in the tables for grass, using six 500 m^2 plots with corn, cultivar *ES Cirrus*, with acidified slurry and one test plot with non-acidified slurry. Analysis of variance and significant difference among the treatment means were separated using Duncan's Multiple Range Test (DMRT) at a probability level of 0.05. Based on statistical analysis, it was demonstrated that crop yields of corn grain increased when fertilized with acidified slurry, at an average of 4 $t \cdot ha^{-1}$. During field tests corn crop yield varied from 14 $t \cdot ha^{-1}$ to 18 $t \cdot ha^{-1}$ when non-acidified and acidified slurry were used. The yield on the grassland was approx. 30 $t \cdot ha^{-1}$. The soil sorption complex, in combination with its buffer properties and acidification, did not affected the pH value. This makes the acidification process safe for plants and for the soil environment.

Introduction

The acidity of soils is closely related to their granulometric composition. This assessment takes into account its simplified form known as the soil agronomics. Historical data shows that the most acidic soils in Poland were identified in the formations with the smallest proportion of particles, with dimensions below 0.02 mm (Barwicki, 2011a, 2011b). Over 42% of very acidic soils are light soils, whereas medium constitute only 12.4% and heavy soils cover only 6.2% of total agriculture land in Poland (Siebielec et al., 2012). In addition, systematically progressing soil acidification can be observed in Poland. This is due to many factors, both natural and anthropogenic (Borusiewicz, Barwicki 2017).

Natural factors include: low soil content in alkaline components (Fangueiro et al., 2013) (e.g. calcium or magnesium), dissociation of aluminum-bound H_2O, leaching of alkaline ions by rainwater deeper into the soil profile, the release of H^+ and Al^{3+} to the soil by weathering of soil minerals, mineralization of organic matter in the soil, as a result of which non-metal oxides (e.g. NO_3^- or SO_4^2) react with water to form acids, as presented in reactions (1) and (2):

$$N \rightarrow NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O \qquad (1)$$

$$S \rightarrow H_2S + 2O_2 \rightarrow 2H^+ + SO_4^2 \qquad (2)$$

Natural factors of soil acidification also include the uptake of basic cations by plant roots, which causes soil depletion in these components (Ca, Mg, K, Na cation), as well nitrification of NH_4^+ ions by bacteria of the genus *Nitrosomonas* and *Nitrobacter*, as presented in reaction (3):

$$2NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 2H_2O + 4H^+ \qquad (3)$$

Anthropogenic factors of soil acidification include, among others, the use of acidic mineral fertilizers (e.g., single superphosphates), or physiologically acidic fertilizers (e.g., ammonium sulphate), as well as acid rain with pH 3-5. It is the result of the emission of non-metallic oxides into the atmosphere and their reaction with water (wet deposition) and the sulfur and nitrogen oxides in the atmosphere (dry deposition) (Jaggi et al., 2005; Beausang et al., 2021).

The main source of ammonium nitrogen emissions in the Baltic Sea region is slurry. Atmospheric emissions constitute a significant part of the nitrogen entering the Baltic Sea. In relation to the natural environment, the Slurry Acidification Technology (SAT) also bring measurable benefits as it reduces ammonia emissions by 40-70% depending on the system. SAT also reduces the emissions of nitrogen oxides and methane. Ammonia emissions from eight EU Member States of the Baltic Sea amounted to 1 227 000 t of nitrogen in 2014 (Baltic Slurry Acidification, 2017) and have increased in recent years, with the exception of Finland, Lithuania and Poland. Most countries of the region will have a problem meeting their ammonia emission reduction targets.

There are three main techniques for acidifying slurry: in farm buildings, in slurry tanks, and during spreading slurry onto fields. The use of slurry acidified with sulfuric acid is beneficial for farmers as it helps retain nitrogen in the slurry and thus obtain higher yields. It also enriches the slurry with sulfur (Fangueiro et al., 2014). As a result, it leads to cost savings on mineral fertilizers, at a better yield ratio. The disadvantages are the costs of sulfuric acid and the investment in acidification equipment, or the costs of hiring acidification services.

Depot application of raw slurry using the slurry tank, tiller and nozzles for subsurface slurry injection is shown in Figure 1.

Figure 1. Subsurface injection of raw slurry using a slurry tank, tiller and nozzles.

Source: Private collection.

The use of the field set for spreading acidified slurry in the field with trailing hoses is shown in Figure 2.

Figure 2. Use of the field set for spreading acidified slurry on the field with trailing hoses.

Source: Private collection.

Slurry acidification with concentrated sulfuric acid in a tank is shown in Figure 3.

Figure 3. Acidification of slurry in a tank

Source: Private collection.

Methodology of slurry treatment

In the research, two replications of permanent grassland fertilization with slurry were carried out. Soil samples were taken according to the standard, at a depth of 0-30 cm, which is directly accessible to grasses for permanent green use, throughout the soil profile. During the research period, the experimental plots of permanent grasslands were covered in 65 to 85% by the following grass species: cocksfoot, meadow grass, meadow fescue, perennial ryegrass, and timothy grass. Soil pH value on selected plots ranged from 6.4 (in plots without acidification) to 6.5 (in plots subjected to application with acidified liquid slurry. Statistically, these differences were not significant. Acidification did not significantly affect the level of this parameter, and despite research on mineral soils, the soil sorption complex in combination with its buffer properties did not affect the acidification process (Skwierawska, 2008). The results of the soil analysis are presented in the following tables. The tests conducted as part of field trials were performed under real conditions. In 2017, precipitation was higher than the long-term average, while in 2018 precipitation was below the long-term average.

In the research, two replications of permanent grassland fertilization with slurry were carried out. In June 2017, after the first swath and preparation of research facilities, fertilization was carried out on an area of 500 m^2 of permanent grasslands in the variant, fertilization with cattle slurry and cattle slurry acidified with sulfuric acid, previously obtaining a pH value of 5.5 during the initial storage of slurry in a sealed concrete tank on the farm for two weeks.

Repetition of fertilization in other research facilities as another field test was carried out on permanent grassland in July, after the second swath and preparation of further research facilities. The treatment was carried out on 500 m^2 of permanent grasslands in the variant with raw cattle slurry and cattle slurry acidified with sulfuric acid. The slurry used was cured for two weeks to obtain a pH value of 5.5 during the initial storage of liquid slurry in a concrete, airtight tank located at the farm.

The test treatments are presented in Table 1. The experiment was conducted in 4 replications. The slurry was applied to the grass bottles 1–2 week after cutting of grass. Slurry was acidified with H_2SO_4. Chemical composition of untreated and acidified slurries is presented in Table 2 [Borowski et al. 2020]. The temperature during the 5 days after slurry application was: in 2017 average – 13.0°C, maximum 24.0°C, minimum 2°C and in 2018: average 16.1°C, maximum 30.5°C, and minimum 1.8°C.

Table 1.
Test treatments in 2017 and 2018

Treatments, 2017		Treatments, 2018
Barley	Annual ryegrass	Corn
1. Control (unfertilised)	1. Control (unfertilised)	1. Control (unfertilised)
2. 15 $m^3 \cdot ha^{-1}$PS (pig slurry) 25.05	2. 15 $m^3 \cdot ha^{-1}$CS (cattle slurry) 25.05	2. 45 $m^3 \cdot ha^{-1}$PS+Bacter 15 cm (PSbac·)
3. 15 $m^3 \cdot ha^{-1}$PAS (acidified)	3. 15 $m^3 \cdot ha^{-1}$CAS (acidified)	3. 45 $m^3 \cdot ha^{-1}$PS 15cm (PS·)
4. 45 $m^3 \cdot ha^{-1}$PS	4. 3x 15 $m^3 \cdot ha^{-1}$CS 25.05; 11.07;15.09	4. 45 $m^3 \cdot ha^{-1}$PS+Bacter 0 cm (PSbac)
5. 45 $m^3 \cdot ha^{-1}$PAS	5. 3x 15 $m^3 \cdot ha^{-1}$CAS	5. 45 $m^3 \cdot ha^{-1}$PS 0 cm (PS)
	6. 45 $m^3 \cdot ha^{-1}$CS	6. 45 $m^3 \cdot ha^{-1}$PAS 0 cm (PAS)
	7. 45 $m^3 \cdot ha^{-1}$CAS	

- slurry was injected into the soil at a depth of 15 cm.

Source: Own elaboration

Table 2.

Chemical composition of slurry

Chemical composition	Cattle slurry	
	Untreated slurry	Acidified slurry
	2017	2017
Total C, %	40.1	36.7
pH	7.9	5.0
Total N, kg·m^3	3.8	3.8
NH_4, kg·m^3	2.3	2.4
Total P kg·m^3	0.59	0.6
Total K kg·m^3	2.2	2.3
Ca, kg·m^3	0.112	0.146
S, %	0.029	0.257
DM, %	8.0	7.7

Methods: dry matter, gravimetria; N_{tot} – Kjeldahl method; pH - straight from the sample; NO_3-N – Foss Tecator AN 5232; NH_4-N – Foss Tecator AN 5226; P_{tot}, K_{tot}, Ca – wet ashes+ICP/OES[6];C_{tot}ISO 10694; 1995; S – PMK-JJ-4C.

Source: Own elaboration

The yield tests were conducted on similar soils as presented in the tables, using for grass: six 500 m^2 plots with corn *ES Cirrus* and adding acidified slurry, as well as one test plot with nonacidified slurry. All tests on grass plots and corn plots were provided in 4 replicates.

Results and discussion

The effect of slurry acidification on the leaching of the elements with ryegrass and its dynamics was quite different for different elements (Table 3, Fig. 1). The use of an acidified slurry resulted in a higher leaching of S and Ca two months after slurry application. The K content was highest in the leachate collected after last slurry application.

The P content in the leachate decreased with the use of acidified slurry at a later stage, while the use of nonacidified slurry increased the amount of water-soluble P in the leachate. The leaching of Mg increased and leaching of N_{tot} decreased with the use of acidified slurry. Statistically, the leaching of Ca, S, K, and Mg from grassland trial soils increased as a result of acidification of 45 m^3 and 3x15 m^3 ha^{-1} of cattle slurry, but the leaching of P (Riley, 2002) and N_{tot} decreased (Table 3).

Data collected were subjected to variance analysis and the significant difference among the treatment means were separated using Duncan's multiple range test (DMRT) at 0.05 level of probability.

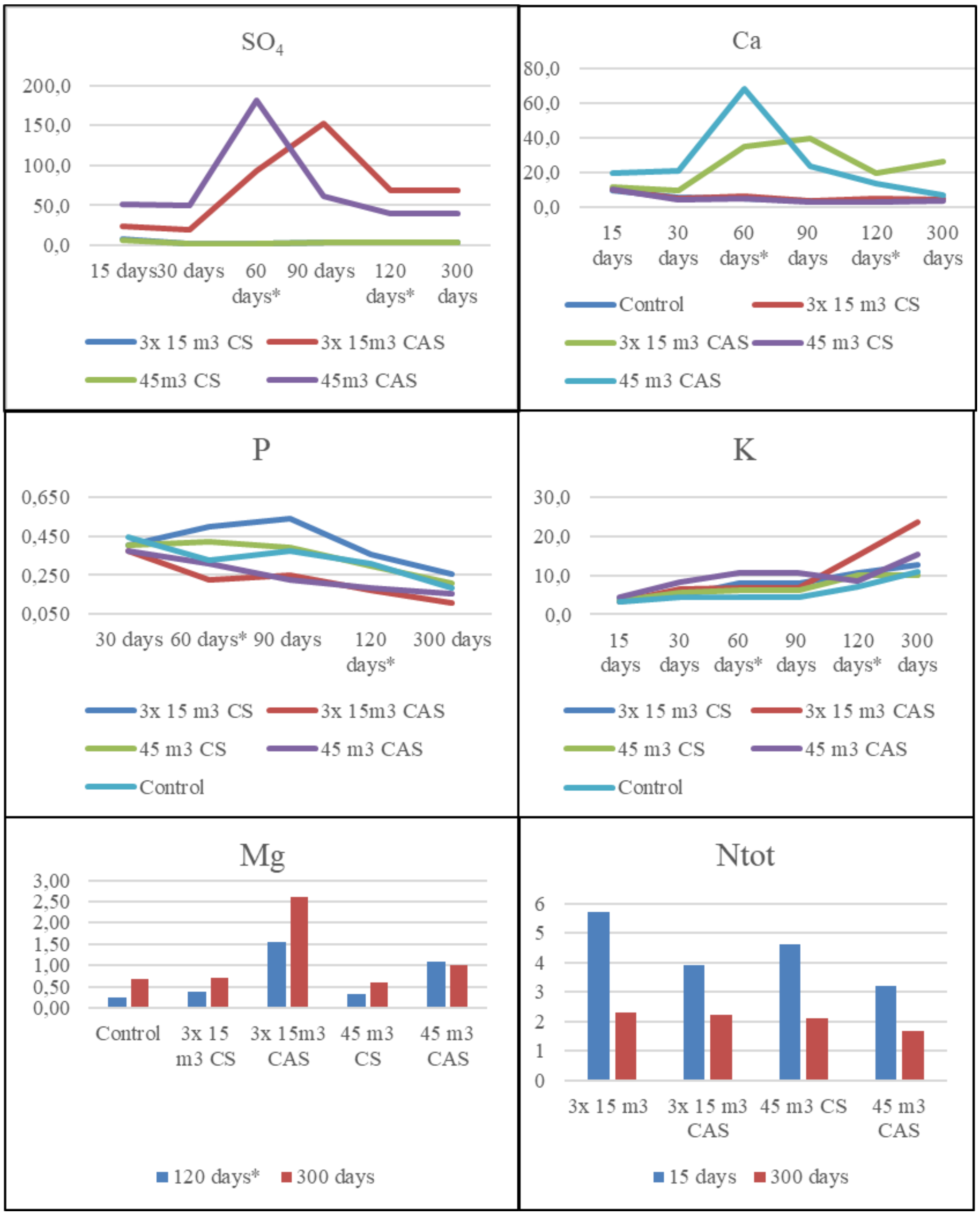
The soil properties were significantly affected by the use of 45 m^3 of slurry. The acidified slurry decreased soil pH_{KCl} by 0.1 units, which was also in a plausible correlation (r = 0.768) with soil S content (Table 4). The second most influential element was K, which increased in leachate when slurry was used. With acidified slurry, the increase in soil was somewhat lower due to leaching of K (Singleton, 2000).

Table 3.
Leaching of elements from the soil treated with cattle slurry (m^3·ha^{-1}) on grassland

Treatments	Elemental content in leachate, mg·L^{-1}					
	Ca	SO_4	P	K	Mg	N_{tot}
Control	31.6	18.1	1.64	34.7	0.94	7.96
15 m^3 CS	27.8	18.3	1.44	35.5	0.71	8.65
15 m^3 CAS	53.0	**140.4**	**1.25**	45.1	1.45	**6.50**
3x 15 m^3 CS	35.0	21.9	2.06	47.7	1.09	8.00
3x 15 m^3 CAS	**142.3**	**424.6**	**1.13**	**61.9**	**4.15**	**6.12**
45 m^3 CS	29.5	20.7	1.72	41.8	0.92	6.71
45 m^3 CAS	**154.1**	**423.1**	**1.25**	**58.0**	**2.10**	**4.87**
LSD 95%	51.6	176.3	0.30	9.7	1.12	0.74

·Red – statistically significant negative effect.
Green – statistically significant positive effect

Source: Own elaboration



- Before the sample was taken, 2 and 3 times the liquid slurry was applied 15 $m^3 \cdot ha^{-1}$.

Figure 4. The dynamics of leached nutrient content in leachate, mg·l^{-1}. Source: Own elaboration

Table 4.
The effect of acidified cattle slurry ($m^3 \cdot ha^{-1}$) on the soil with grassland after leaching of elements. Source: Own elaboration

Treatments	Elemental content in soil, $mg \cdot kg^{-1}$						
	pH_{KCl}	P	K	Ca	Mg	SO_4	N_{tot}
Control	5.0	93	93	1177	54	2.6	0.19
15 m^3CS	5.0	91	99	1170	53	2.2	0.18
15 m^3CAS	5.0	92	95	1182	54	**5.0**	0.19
3x 15 m^3CS	5.0	**100**	**123**	**1219**	**64**	2.6	0.20
3x 15 m^3CAS	5.0	96	**116**	**1209**	**64**	**10.0**	0.19
45 m^3CS	5.0	94	**115**	**1203**	58	2.5	0.19
45 m^3CAS	**4.9·**	95	**107**	**1179**	58	**6.2**	0.19
LSD 95%	0.03	3	11	17	4	2.6	0.01

·Red – statistically significant negative effect,
Green – statistically significant positive effect

In 2016, preceding the field trials, the meadows were fertilized in spring with cattle slurry at a dose of approx. 50 $m^3 \cdot ha^{-1}$, which, in terms of nitrogen content, ranged from 100 to 120 kg $N \cdot ha^{-1}$. The yield achieved after three applications was approx. 30 $t \cdot ha^{-1}$. After the application of carbonate lime in the first decade of November 2016 in an amount of 1.8 to 2.5 $t \cdot ha^{-1}$ and fertilization on 500 m^2 plots in doses of approx. 96 kg $N \cdot ha^{-1}$, 43.2 kg $P \cdot ha^{-1}$ and 129.6 kg $K \cdot ha^{-1}$ yield at a level of approx. 45 $t \cdot ha^{-1}$. In 2017, the yield after the second application on unfertilized plots was approx. 8 $t \cdot ha^{-1}$, while on fertilized slurry it was approx. 16 $t \cdot ha^{-1}$. The lowest yields after applying acidified cattle slurry were 17 $t \cdot ha^{-1}$, and the highest were as much as 20 $t \cdot ha^{-1}$.

The soil pH value was 6.4 on plots without acidification and 6.5 on plots treated with acidified slurry. In statistical terms, these were not significant differences. Despite testing on mineral soils, the soil sorption complex in combination with its buffer properties, acidification did not affect the pH value. This makes the acidification process safe for plants and the soil environment. It should be noted that one-point decrease in pH, below 6.0, released phosphorus contained in soil which was previously unavailable to plants.

In turn, the content of total nitrogen on the discussed research facilities ranged from 0.2 to 0.3% in the case of plots, where cattle slurry without acidification was used and in the range from 0.3 to 0.4%. Facilities subjected to fertilization with cattle slurry were characterized by a very similar content of other nutrients. The phosphorus content, expressed as the pure component, ranged from 0.3 to 0.4 mg $P \cdot kg^{-1}$ for plots not subjected to acidified liquid slurry and in the range of 0.2-0.3 $mg \cdot kg^{-1}$ for plots where acidified slurry was used.

The content of potassium (K) in the soil before fertilization was average for the experimental conditions and ranged from 0.45 to 0.48 $mg \cdot kg^{-1}$ for plots intended for the application of non-acidified slurry and 0.4 to 0.45 $mg \cdot kg^{-1}$ for slurry acidified with sulfuric acid. The results of soil analysis are presented in the tables.

Conclusions

The total nitrogen on the discussed research facilities discussed ranged from 0.2 to 0.3% in the case of plots where cattle slurry without acidification was used and was in the range from 0.3 to 0.4%. Facilities subjected to fertilization with cattle slurry were characterized by a very similar content of other nutrients. The phosphorus content, calculated as the pure component, was from 0.3 to 0.4 mg $P·kg^{-1}$, for plots not subjected to the use of acidified liquid slurry and in the range of 0.2-0.3 $mg·kg^{-1}$ for plots where acidified slurry was used.

In 2016, the yield achieved after three applications was approx. 30 $t·ha^{-1}$. After the application of carbonate lime in the first decade of November 2016 in an amount of 1.8 to 2.5 $t·ha^{-1}$ and fertilization on 500 m^2 plots in doses of approx. 96 kg $N·ha^{-1}$, 43.2 kg $P·ha^{-1}$ and 129.6 kg $K·ha^{-1}$ yield was approx. 45 $t·ha^{-1}$. The yield from the second application, in 2017, on unfertilized plots was approx. 8 $t·ha^{-1}$, while on fertilized slurry it was approx. 16 $t·ha^{-1}$. The lowest yields after using acidified cattle slurry were 14 $t·ha^{-1}$, and the highest were as much as 20 $t·ha^{-1}$. The research showed also an increase in crop yields of corn grain when applying fertilization with acidified slurry by average equal 4 $t·ha^{-1}$.

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STOSOWANIE ZAKWASZONEJ GNOJOWICY W ASPEKCIE WYPŁUKIWANIA PIERWIASTKÓW Z GLEBY W UPRAWACH POLOWYCH

Streszczenie. W pracy przedstawiono badania na temat stanu gleby w aspekcie jej ochrony przy stosowaniu zakwaszonej gnojowicy jako nawozu chroniącego przed ulatnianiem się amoniaku do atmosfery. Zastosowanie stężonego kwasu siarkowego w celu obniżenia pH gnojowicy i zatrzymania w ten sposób azotu w glebie, a następnie wykorzystania go przez rośliny uprawne daje podwójną korzyść, zmniejsza straty azotu i obniża koszty zakupu nawozów mineralnych. Wtłaczanie gnojowicy surowej pod powierzchnię gleby przynosi pewne korzyści w postaci ograniczenia emisji amoniaku, ale nie wpływa na ograniczenie stosowania nawozów z dodatkiem siarki, co jest zapewnione w przypadku zakwaszania gnojowicy. Dodatkową korzyścią jest aspekt ochrony środowiska. W badaniach przedstawiono wymywanie pierwiastków z gleby na użytkach zielonych i uprawy kukurydzy przy stosowaniu niezakwaszonej gnojowicy bydlęcej oraz zakwaszonej gnojowicy bydlęcej ($m^3 \cdot ha^{-1}$). Zawartość K była największa w próbie po zastosowaniu ostatniej partii zakwaszonej gnojowicy. Doświadczenie z kukurydzą przeprowadzono na podobnych glebach jak w przypadku doświadczenia z trawami, na sześciu poletkach o powierzchni 500 m^2 z odmianą ES Cirrus z zakwaszoną gnojowicą i poletkiem testowym z niezakwaszoną gnojowicą. Analizę wariancji i istotne różnice między średnimi zabiegów wykonano przy użyciu testu wielozakresowego Duncana (DMRT) na poziomie prawdopodobieństwa 0,05. Na podstawie analizy statystycznej wykazano, że plon ziarna kukurydzy wzrósł przy nawożeniu zakwaszoną gnojowicą średnio o 4 t·ha^{-1}. Podczas badań polowych plon ziarna kukurydzy wahał się od 14 t·ha^{-1} do 18 t·ha^{-1}, przy nawożeniu gnojowicą niezakwaszoną i zakwaszoną. Plon na użytkach zielonych wyniósł ok. 30 t·ha^{-1}. Kompleks sorpcyjny gleby, w połączeniu z jego właściwościami buforowymi i zakwaszeniem, nie wpłynął na wartość pH. Dzięki temu proces zakwaszania jest bezpieczny dla roślin i środowiska glebowego.

Słowa kluczowe: ochrona środowiska, gleba, zakwaszenie gnojowicy, nawozy, uprawy polowe