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The Influence of Soil Fertilization with Struvite on Water Efficiency – Lysymetric Columns

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1. Introduction

At the end of the twentieth century, among people involved in agricultural production, a discussion began on cultivation technologies for crops. It was found that the existing methods of fertilization do not fulfill their role, because the barrier of effectiveness of the doses of nutrients was achieved. The rapid physical and chemical degradation of the soil affected the physiological condition of the plants, resulting in a decrease in yields and their quality. First of all, you should take care of the right condition of the soil as the basic and only source of nutrients, water, and plant growth substances.

Soil additives, consisting of specific mixtures of mineral compounds, should affect the activation of cellular metabolism processes, soil microflora, best adapted to the environment. Applied proper fertilization stimulates the processes occurring in the humus in a gentle way. This triggers a number of reactions favoring the development of soil and plants, allowing to compensate for the degrading effect of intensive agricultural production. Works on fertilizers enriched with microelements, growth regulators or amino acids with extended release of biogenic elements have begun. An important element in the application of fertilizers is their dose, which is closely related to the previously determined soil parameters.

Due to the high rate of exploitation of phosphate rock, from which fertilizers are produced, other sources of this element are sought for. Therefore, there is growing interest in the field of effective recovery of nutrients from waste. The bioavailable forms in which we can recover phosphorus are calcium phosphates, as well as struvite – $(NH_4)Mg[PO_4] \cdot 6H_2O$ – containing 58% P_2O_5 (Doyle & Parsons 2002). Struvite is a mineral, inorganic chemical compound, having a crystalline form, quickly becoming weathered in the form of a white powder. Struvite crystals contain two important macroelements necessary for the growth and development of plants - phosphorus and nitrogen. Struvite is characterized by low solubility, thanks to which fertilizer components are released slowly, which reduces the need for frequent fertilization. Struvite can be used directly in agriculture as a mineral fertilizer (de Bashan & Bashan 2004). The phosphorus recycling from waste including sewage sludge is favored by the development of other more efficient wastewater treatment technologies. It is estimated that one inhabitant of Europe discharges about 2 g of phosphorus per day (on average) mainly in the form of sewage, from which subsequently in the purification process significant amounts of sludge containing various impurities, including biogenic compounds, are obtained. While biogenic compounds in the aquatic environment are part of its rapid eutrophication, in the case of field crops the presence of these components is a necessary soil component in order to obtain sufficiently high yields. The problem is that the waste containing these compounds also contain many other elements and undesirable components that prevent their direct use as a fertilizer. So in order to properly use the components contained in the waste and get a good fertilizer, it is necessary to isolate them. However, the problem of proper processing and waste management as well as recovery of valuable components is still waiting for a solution, not only in Poland but also in the world. At present, economically, struvite production is still unprofitable, but in the near future when fertilizer prices start to grow, the profitability of the process will become a reality. Struvite is an almost perfect fertilizer – in addition to containing two basic macroelements necessary for plant growth, it also exhibits correspondingly low solubility. So is the so-called organic fertilizer or in other words slow-acting fertilizer because it dissolves slowly in the soil and the plants themselves stimulate its intensity. In connection with the above, there is no leaching element for both its surface water and deeper soil layers, where it may become inaccessible to plants. As you can see, this mineral can significantly contribute to solving selected problems of environmental protection.

This work focuses on the analysis of the effect of struvite soil fertilization on the quality of effluent and the physical and chemical properties of soil.

2. Material and methods

The research was carried out in lysimeter columns, reflecting the top layer of the soil profile. The columns were filled with soil with appropriate doses of struvite. Struvite used in the tests was obtained in laboratory conditions.

2.1. Substrates for research

The soil for research according to the classification of Polish Society of Soil Science, the 2008 and USDA (United States Department of Agriculture) after drying to dry air and sieving through a 2 mm sieve, they were classified as loamy sand. The material was taken from the backyard garden. The effectiveness of fertilization on acidic soils is very low, therefore high pH soil was selected for testing.

This initial material was used to obtain 3 mixtures with different weight ratio, for 250 g of soil:

- mixture with content of 0.1 g struvite, denoted as M/0.1(53.2 kg/ha),
- mixture with content of 0.5 g struvite, denoted as M/0.5 (266.2 kg/ha),
- mixture with content of 1 g struvite, denoted as M/1.0 (533.5 kg/ha).

The control sample (soil without struvite addition) was denoted as M/0.0. Basic physical and chemical analyses were performed for samples of soil and soil mixtures (see Table 1).

Synthetic struvite was obtained from distilled water, the following ion concentrations were used: 100 mg PO_4^{3-}/L, 500 mg NH_4^+/L, 20 mg Mg^{2+}/L, and pH=10 (Worwąg 2018a; Worwąg 2018b; Worwąg & Kałwak 2018). The resulting sediments were analyzed using a X-ray diffractometer. The results of the analysis demonstrate that the sediments contain 99% of the mixture of struvite, its amorphous forms and trace contents of compounds used for synthesis of the compound, and NaOH used for correction of pH. Confirming the content of 58% P_2O_5 in the resulting sediments. Struwit contains 9.9% Mg, 12.62% P, 6.57% H, 5.71% N and 65.20% O. Amounts N introduced into the soil together with 0.1; 0.5; and 1 g struvite dose was 0.0057g, respectively; 0.02855g, 0.0571g. By contrast, the quantity P 0.01262 g for a dose of 0.1 g struvite; 0.0631 g for the 0.5 g dose and 0.1262 g for the 1 g dose.

2.2. Physical and chemical analysis

Analyses of soil material included:

- organic matter based on the EN 1997-2:2007 standard; Organic matter was determined by dry combustion (% OM determination): organic matter is burned in furnaces muffle furnace. First, the absolutely dry soil mass was determined, the soil sample was dried at 105°C and then, the sample was calcined in a mouflon oven at 500°C for 5 hours,
- pH in H_2O and 1M KCl for the soil was determined using the potentiometric method by means of a multiparameter meter (HANNA INSTRUMENTS HI 9828) according to ISO 10390:2005,
- total alkaline cations (Tac) were evaluated using the Kappen method (Karczewska & Kabała 2005),
- total carbon (TC) content was evaluated by means of the Multi N/C 2100 analyzer (Analytik Jena) according to PN-EN 15936:2013-02E,
- total phosphorus (TP) content was evaluated according to ISO 6878:2004,
- available phosphorus (AP) extraction by the Egner-Riehm method determined on a spectrophotometer (Riehm 1958),

- total nitrogen (TN) was determined by the Kjeldhal method (Horneck & Miller 1998) using the BÜCHI 435 mineralizer and the BÜCHI 355 distillation system.

Furthermore, pH, conductivity and TDS (Total Dissolved Solids) were determined in the leachates from lysimetric columns.

- electrical conductivity and TDS were determined directly in the leachate from lysimetric columns using a mulitparameter meter (HANNA INSTRUMENTS HI 9828),
- total phosphorus content was evaluated according to ISO 6878:2004.

Each evaluation was repeated for three times, and the analysis was based on mean values.

2.3. Research procedure – lysimeter test

The study used a lysimeters with a smooth inner wall made of acrylic glass with the length of 1.0 m and inner diameter of 5 cm. Each column was connected via a valve with a bottle in which the effluents formed were collected. Lysimeter examinations in the columns were carried out in 3 columns modeling 3 levels of soil washing (10, 20 and 30 cm) for each soil mixture with an appropriate dose of struvite and soil without struvite. Each experiment consisted of flushing water through a column filled with a mixture, with an amount modeling the average annual rainfall for the area from which the soil sample was taken, which was assumed at the level of 650 mm. Simulation of the rainfall was performed using deionized water, with its dose calculated according to annual rainfall levels in the area where soil sample was obtained, by converting to the surface of the column (0.001963 m^2).

The dose calculated in this way was divided into 12 portions corresponding to monthly precipitation, which were administered to the column for the next 12 days. Before the experiment began, the material in the columns was watered to similar water content (97.65%).

Leachates from the columns were collected every 2 days and designated as L1 (leachate after 2 days), L2 (leachate after 4 days), L3 (leachate after 6 days), L4 (leachate after 8 days), L5 (leachate after 10 days), L6 (leachate after 12 days). The research stand for the column experiments is shown in Figure 1.

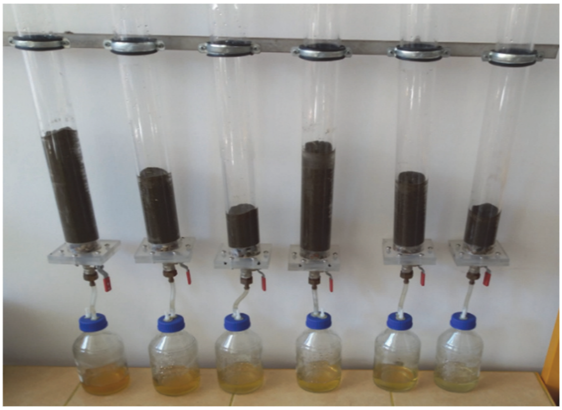

Fig. 1. Stand for column experiments

3. Results and discussion

3.1. Analysis of the soil before and after completion of the experiment

Table 1 presents overall characterization of soil and mixtures of soil with various doses of struvite before and after 12 days of running the experiment. After completion of the experiments, the soil was removed from the columns, averaged (3 columns with different height of soil profile were connected) for each combination and subjected to the analysis. Percentage of the organic fraction for the soil was 3.65%, whereas for the mixtures, it ranged from 3.30% to 3.35%. The content of organic matter after completion of the experiment was not significantly changed (OM: 3.18-3.32%)

Addition of struvite to soil led to the increase in the content of biogenic elements: total nitrogen and phosphorus, especially in the mixture of soil with 1g struvite. Total phosphorus content and available forms before experiment in the mixtures increased with the increasing struvite percentage. A noticeable increase in the content of available forms of phosphorus was observed for the mixtures with addition of 0.5 g and 1.0 g struvite. The total carbon content in the soil and mixtures was at a similar level, ranging from 15.01 to 15.2 mg/g. At the end of the experiment an increase in the tested parameter was observed for all combinations. A similar tendency was observed for total nitrogen.

Reducing the content of organic matter and at the same time increasing the content of total carbon in the soil after the experiment can be associated with the transformation of individual fractions included in the organic matter, the process of humification. In addition, some of the substance can be washed away and pass into the effluent. The high pH of the soil helps reduce the leaching of total carbon.

Table 1. Physical and chemical properties of test substrates: soil and soil mixtures (before and after experiment)

Parameters	Substrates			
	(M/0.0)	(M/0.1)	(M/0.5)	(M/1.0)
OM, %	3.65^b 3.32^a	3.30^b 3.10^a	3.33^b 3.20^a	3.35^b 3.18^a
pH, (-)	H_2O: 7.58^b 7.80^a	H_2O: 7.65b 7.75^a	H_2O: 7.68^b 7.84^a	H_2O: 7.71^b 7.81^a
	KCl: 7.45^b 7.38^a	KCl: 7.42^b 7.31^a	KCl: 7.44b 7.30^a	KCl: 7.48^b 7.28^a
Total alkaline cations, mmol (+) /100 g	0.20^b 0.22^a	0.22^b 0.24^a	0.23^b 0.25^a	0.23^b 0.25^a
Total carbon, mg/ g	15.01^b 17.00^a	15.18^b 17.44^a	15.20^b 17.25^a	15.17^b 17.93^a
Total phosphorus, mg P_2O_5/ 100 g soil	425.1^b 401.4^a	451.4^b 421.0^a	565.7^b 510.1^a	841.4^b 675.5^a
Available phosphorus, mg P/ kg	265.0^b 228.0^a	289.0^b 274.0^a	489.0^b 417.0^a	645.0^b 488.0^a
Total nitrogen, mg/g	0.79^b 0.87^a	0.80^b 0.90^a	0.89^b 1.01^a	1.01^b 1.22^a

b – before experiment
a – after experiment

Acidity is the basic indicator of soil fertility. It has a positive effect on the structure, determines the activity of microorganisms, the dynamics of the processes of mineralization and humification of organic matter, the absorption of macro- and microelements, and thus significantly affects the efficiency of fertilization. Optimal pH is the foundation of effective fertilization. The high pH of the studied soil had a beneficial effect on fertilization efficiency.

All the substrates were characterized by an alkaline reaction. Analysis of these parameters showed that the sample is alkaline mineral soil with high phosphorus content. After experiment, an insignificant reduction in the pH (KCl) value was found with the increase in struvite content in the soil. Availability of nutrients for plants depends on acidity of soil they grow in (Mocek 2015; Zawadzki 1999). According to Handzel, availability of some nutrients is reduced in acidic soils, eg. molybdenum, boron or phosphorus (Handzel et al. 2017).

3.2. Analysis of the leachate from lysimeter columns

Migration of phosphorus in the soil profile is connected with physicochemical properties of the soil solution. The following parameters were evaluated to find changes in chemical composition of waters that wash the soil profile in eluates from lysimetric columns: reaction (pH), electrical conductivity (EC) and total dissolved solids (TDS), which is the indicator of water mineralization. Table 2 presents the results of the analysis of leachates from lysimetric columns sampled 6 times over the period of the experiment.

The first analyzed parameter was reaction of leachates from lysimetric columns. In all leachates from soil samples with addition of struvite, regardless of the sample height, a decline in pH was observed compared to pH of the leachate from the control sample (M/0.0 – soil without struvite addition). The highest differences were found for the 10 cm samples, with maximal decline in pH of 1.83 for addition of 1.0 g of struvite. For the samples with height of 20 and 30 cm, the reduction in the value was lower (max. 0.89). A general tendency for a gradual reduction in pH with the increase in struvite content in the sample was found, especially noticeable for the samples with height of 10 cm. This suggests that the most important changes occur in the upper part of the soil profile. Addition of struvite leads to an insignificant increase in acidity of leachates. However, pH determined for the soil samples and its mixtures after completion of the experiment (Table 2) confirms that they remain to have an alkaline character.

Electrical conductivity (EC) and TDS are the parameters which are closely correlated with each other and depend on each other. For most of the analyzed leachates, the increase in the content of struvite in the soil sample led to the increase in the value of both parameters. The biggest increase was found for the samples with content of struvite of 1.0 g, regardless of the sample height. They ranged from 143 $\mu S\ cm^{-1}$ and 0.07 ppb for the 10 cm samples to 404 $\mu S\ cm^{-1}$ and 0.2 ppb, and 597 $\mu S\ cm^{-1}$ and 0.3 ppb for the 20 cm and 30 cm samples, respectively. This means an increase at the level of 54.2-122.3% for EC and 53.8-183.3% for TDS. The increase in the content of struvite applied to the soil translated directly into mineralization of the soil solution. The analysis of the dynamics of soil profile leaching by consecutive doses that modelled the atmospheric precipitation showed a decline in salinity of the soil solution as a result of leaching the soluble forms, which is consistent with the commonly observed tendency (Roy 2017). Solutions with EC lower than 25,000 $\mu S\ cm^{-1}$ are considered as little saline. Therefore, the analyzed leachates belong to very little saline, whereas adding the used struvite doses did not lead to the increase in salination that would have a negative effect on plants by making it difficult to collect water or inhibiting root growth (Balemil & Negisho 2012).

Table 2. Analysis of the leachates from lysimetric columns

No leachate [1]	Parameters	Unit	Type of sample [2] – height of the soil profile, cm											
			M/0.0 –10	M/0.0 -20	M/0.0 -30	M/0.1 –10	M/0.1 -20	M/0.1 -30	M/0.5 –10	M/0.5 -20	M/0.5 -30	M/1.0 –10	M/1.0 -20	M/1.0 -30
L1	pH	(-)	8.25	8.19	*0	7.93	8.11	7.95	8.01	8.14	8.29	7.91	7.92	8.03
	COND	µS/cm	821	1842	*0	528	873	1301	575	1596	2491	694	2052	2238
	TDS	ppb	0.41	0.92	*0	0.26	0.44	0.65	0.29	0.80	1.20	0.35	1.03	1.22
L2	pH	(-)	8.16	8.18	7.97	7.63	7.64	7.73	7.80	8.02	8.05	7.26	7.71	7.82
	COND	µS/cm	331	505	1488	314	677	1008	357	581	899	418	909	1294
	TDS	ppb	0.16	0.25	0.74	0.16	0.34	0.50	0.18	0.29	0.44	0.21	0.45	0.64
L3	pH	(-)	8.39	8.14	8.11	8.49	8.02	7.85	7.55	7.60	7.76	7.02	7.45	7.68
	COND	µS/cm	193	285	488	332	410	550	194	360	680	276	590	1085
	TDS	ppb	0.10	0.14	0.24	0.16	0.21	0.28	0.1	0.18	0.34	0.14	0.29	0.54
L4	pH	(-)	8.33	8.24	8.21	7.43	7.26	7.43	7.51	7.49	7.64	7.14	7.35	7.37
	COND	µS/cm	264	241	482	223	351	223	262	289	545	407	414	692
	TDS	ppb	0.13	0.17	0.24	0.12	0.17	0.11	0.13	0.19	0.27	0.20	0.21	0.35
L5	pH	(-)	8.07	7.68	7.78	7.98	7.28	7.24	7.03	7.08	7.2	6.24	6.90	6.97
	COND	µS/cm	228	283	238	212	311	190	238	172	239	233	288	659
	TDS	ppb	0.11	0.14	0.12	0.11	0.16	0.10	0.12	0.09	0.12	0.12	0.14	0.34
L6	pH	(-)	8.25	8.09	8.05	7.56	7.29	7.42	7.52	7.51	7.49	6.82	7.73	7.71
	COND	µS/cm	127	145	210	139	164	196	111	154	206	111	241	367
	TDS	ppb	0.06	0.07	0.11	0.07	0.08	0.10	0.06	0.08	0.10	0.06	0.12	0.18

[1] designation as described in point 2.3.

[2] designation as described in point 2.1.

*0 – no leachate

COND – conductivity

Table 3. Analysis of phosphorus of the leachates from lysimetric columns

No leachates	mg P/L											
	Struvite dose g/250g soil											
	0 (control)			0,1			0,5			1,0		
	height of the soil profile (cm)											
	10	20	30	10	20	30	10	20	30	10	20	30
L1	0.62 ±0.08	1.00 ±0.01	0.39 ±0.01	2.32 ±1.02	2.49 ±1.15	1.79 ±1.25	10.55 ±0.16	11.66 ±0.0	11.20 ±0.11	18.75 ±5.71	24.95 ±4.23	13.11 ±2.15
L2	0.42 ±0.02	0.18 ±0.01	0.48 ±0.001	3.80 ±0.07	3.61 ±0.02	3.06 ±0.01	12.92 ±0.27	14.93 ±0.0	10.29 ±0.11	29.15 ±2.53	36.49 ±0.65	23.89 ±0.16
L3	0.35 ±0.02	0.20 ±0.02	0.47 ±0.002	3.49 ±0.09	3.85 ±0.03	3.62 ±0.07	10.32 ±0.05	12.55 ±0.18	10.32 ±0.05	28.27 ±0.11	37.91 ±1.02	39.62 ±0.11
L4	0.50 ±0,0	0.58 ±0.003	0.44 ±0.01	3.94 ±0.96	4.62 ±0.08	4.39 ±0.08	8.38 ±0.54	12.12 ±0.11	12.15 ±0.27	27.59 ±3.02	39.14 ±0.46	45.15 ±0.27
L5	0.82 ±0.04	0.69 ±0.01	0.40 ±0.01	3.92 ±0.001	4.60 ±0.0	3.93 ±0.13	8.27 ±0.05	11.66 ±0.11	13.11 ±0.43	26.71 ±0.16	41.26 ±1.56	57.99 ±0.54
L6	0.62 ±0.01	0.64 ±0.004	0.45 ±0.01	4.16 ±0.45	4.57 ±0.06	3.89 ±0.09	8.68 ±0.11	12.95 ±0.0	12.65 ±0.11	25.87 ±1.56	41.57 ±0.59	46.10 ±0.97

± standard deviation

3.3. Analysis of a phosphorus content in the leachate from columns lysimeter

Table 3 shows the content of P in the effluents registered for individual height of soil profiles in soil samples for subsequent leachate samples. Based on the obtained results, it was found that the mechanism of phosphorus release is similar, regardless of the dose of struvite used. However, the dose has a direct effect on the amount of leached phosphorus in the leachate. In addition, the relationship between pH and the content of leached phosphorus in leachate was confirmed (Busman et al. 2009). During the drop in pH (Table 2) an increase in the phosphorus content in the leachate was noted. Analyzing the phosphorus content in the leachate for individual doses and soil profiles, no regularity was observed. For each dose and individual profiles, the phosphorus leaching proceeded differently and with varying intensity and stability over time.

4. Conclusions

The amount of leached phosphorus is directly related to the dose of struvite in the mixture. As the dose increases, the content of leached into the phosphorus eluate increases. The highest levels of phosphorus concentrations per 20 cm of soil profile height are observed, for a 0.1 g struvite dose. For higher struvite doses, i.e. 1.0 the highest concentrations were recorded for the level of 30 cm. After the 6th intake of the eluate, which was the result of washing the soil profile with simulated annual precipitation, the concentration of leached phosphorus is decreased. It is to be expected that further washing of the bed will leach lower doses of soluble phosphorus until its soluble forms are exhausted.

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Abstract

The rapid physical and chemical degradation of the soil affected the physiological condition of the plants, resulting in a decrease in yields and their quality. Soil additives, consisting of specific mixtures of mineral compounds, should affect the activation of cellular metabolism processes, soil microflora, best adapted to the environment. An important element in the application of fertilizers is their dose, which is closely related to the previously determined soil parameters. This work focuses on the analysis of the impact of struvite soil fertilization on the quality of seepage water, the experiment was carried out in lysimeter columns. Different doses (0.1; 0.5; 1.0 g) of struvite obtained under laboratory conditions by chemical synthesis were used in the study. Three levels of soil wash (10, 20, 30 cm) were analyzed for each dose. For washing, distilled water was used in the amount corresponding to the average annual rainfall for the areas from which the soil was taken for testing. The experiment simulated the monthly precipitation each day, and the resulting effluents analyzed: phosphorus content, pH, conductivity, resistance and sum of dissolved substances Total Dissolved Solids (TDS).

Based on the obtained results, it was found that the amount of phosphorus leached is directly related to the dose of struvite in the mixture. The dependence between the amount of phosphorus in the leachate and the pH value was confirmed. Analyzing the effect of struvite fertilization on the soil, an increase in the content of biogenic elements with increasing doses, especially of available forms of phosphorus, has been noted. Despite the soil flushing, the phosphorus content in the soil was still high at the end of the experiment, confirming the low solubility of struvite and the slow release of the constituents.

Keywords:
struvite, soil, leachate waters, lysimeter, leaching

Wpływ nawożenia gleby struwitem na jakość wód odciekowych – kolumny lizymetryczne

Streszczenie

Postępująca szybko degradacja fizyczna i chemiczna gleby, wpłynęła na stan fizjologiczny roślin skutkując spadkiem plonów i ich jakości. Dodatki doglebowe, składające się z specyficznych mieszanin związków mineralnych powinny wpływać na aktywację procesów metabolizmu komórkowego, mikroflory gleby, najlepiej przystosowanej do środowiska. Istotnym elementem przy stosowaniu nawozów jest ich dawka, która ściśle powiązana jest z określonymi wcześniej parametrami gleby. Niniejsza praca skupiała się na analizie wpływu nawożenia gleby struwitem na jakość wód odciekowych, doświadczenie przeprowadzono w kolumnach lizymetrycznych. W badaniach zastosowano różne dawki (0.1; 0.5; 1.0 g) struwitu uzyskanego w warunkach laboratoryjnych na drodze syntezy chemicznej. Dla każdej dawki analizowano trzy poziomy przemywania gleby (10, 20, 30 cm). Do przemywania zastosowano wodę destylowaną w ilości odpowiadającej średnim rocznym opadom dla terenów z których pobrano glebę do badań. W eksperymencie symulowano miesięczny opad każdego dnia, a w powstających odciekach analizowano: zawartości fosforu, pH, przewodnictwo, oporność i suma substancji rozpuszczonych Total Dissolved Solids (TDS).

Na podstawie uzyskanych wyników stwierdzono, że ilość wyługowanego fosforu jest bezpośrednio związana z dawką struwitu w mieszaninie. Potwierdzono również zależność między ilością otrzymanego fosforu w odcieku a wartością pH. Analizując wpływ nawożenia struwitem na glebę, odnotowano wzrost zawartości pierwiastków biogennych wraz ze wzrostem dawki, zwłaszcza dostępnych form fosforu. Mimo przepłukiwania gleby, po zakończeniu doświadczenia zawartość fosforu w glebie była wciąż na wysokim poziomie, potwierdzając niską rozpuszczalność struwitu i powolne uwalnianie składników.

Słowa kluczowe:
struwit, gleba, wody odciekowe, lizymetr, ługowanie