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Struvite—An Innovative Fertilizer from Anaerobic Digestate Produced in a Bio-Refinery

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Abstract: This paper presents the results of a pot experiment aimed at the assessment of the fertilizer value of struvite, a precipitation product obtained from a liquid fraction of the digestate. The effects of struvite (STR), struvite + ammonium sulphate (STR + N) and ammonium phosphate (AP) treatments were examined on maize and grass cultivation on silty loam and loamy sand soil. The crop yields were found to depend on both the soil type and experimental treatment. Crop yields produced under STR and STR + N exceeded those under the control treatments by respectively 66% and 108% for maize, and 94% and 110% for grass. Crop yields under STR + N were similar or greater than those under the AP treatment. The nitrogen recovery by maize and grass reached respectively 68% and 62% from the struvite and 78% and 52% from AP. The phosphorus recovery by maize and grass reached 7.3% and 4.8%, respectively, from struvite (i.e., STR and STR + N), which was lower than that from the AP (18.4% by maize and 8.1% by grass).

Keywords: struvite precipitation; biogas plant; farm bio-refinery; P and N recovery; fertilizer value

1. Introduction

Intensive animal production generates large amounts of liquid manure. Application of the manure to croplands could lead to contamination of groundwater with N and P [1–3]. Production of biogas through anaerobic digestion constitutes an alternative way of utilizing the manure from farm livestock. However, utilization of the remaining digestate is problematic due to a low content of dry matter in the waste [4]. In the light of circular bioeconomy, various solutions are studied in order to convert digestate into valuable products. Among the different commercial options for digestate treatment and nutrient recovery, the most relevant are drying, struvite precipitation, stripping, evaporation and membranes technology [5]. Recovery of nitrogen (N) and phosphorus (P) by precipitation of struvite ($MgNH_4PO_4{\cdot}6H_2O$) can improve N and P management, because they may be exported from farms over large distances at relatively low cost. Magnesium-ammonium-phosphate products can contain 12.65% P in pure compound, while struvite precipitated from organic waste contain from 6 to 12% P [6]. Depending on the raw material, recovered product except pure struvite may contain organic matter and heavy metal pollutants. Due to the fact that struvite is a slow-release multi-nutrient fertilizer [7], released P can be more efficiently used by crops, because it meets nutritional demands of crops in a better way. Struvite can limit the soil phosphorus losses that typically occur under treatment with fast-release artificial fertilizers. However, low solubility of struvite may result in an insufficient supply of phosphorus to crops, particularly during the early phase of growth, which may reduce the fertilizer value of struvite [8]. Several studies have proven that struvite is an effective water-soluble phosphorus fertilizer in neutral and slightly acidic soils [9,10]. The literature also provides information that the solubility and P uptake by plants from struvite is comparable to that for artificial phosphorus fertilizers, e.g., triple superphosphate (TSP) or potassium phosphate (KH_2PO_4) [8]. Incomplete dissolution of struvite in the first year after application suggests that struvite has a residual value for succeeding plants [7]. The application of struvite should be recommended after evidencing that the residual value of struvite is higher than the residual value of traditional phosphorus fertilizers [8]. Struvite is known to be appropriate for use on turf, tree seedlings, ornamentals, vegetables and flower boards as fertilizer [11]. A struvite would be also effective in grasslands and forests, where fertilizers are applied once every several years. However, the agronomic value of struvite was not fully examined [12]. Therefore, in this study we report on a pot experiment that aimed at an evaluation of the fertilizer value of struvite obtained from a liquid fraction of anaerobic digested slurry in a dairy farm bio-refinery.

2. Materials and Methods

2.1. Pot Experiment

The pot experiment was conducted in the experimental greenhouse of the Warsaw University of Life Sciences. The experiment was arranged as a completely randomized design with three replications. The location of the pots was randomized daily. We examined two types of soil, i.e., loamy sand (LS) and silty loam (SL). The samples (0–25 cm soil layer) were collected in Skierniewice (51°96′ N, 20°15′ E) and Obory (52°08′ N, 21°17′ E), respectively. Each pot contained 15 kg of soil. The pots were irrigated with distilled water up to a constant moisture at 60% water-filled pore space. Water was applied to the entire surface of the pots, in order to allow surface casts to deconstruct and let the nutrients they contained leach into the soil. The experiment was conducted in controlled growth conditions that included a day/night cycle of 16/8 h, with a day/night temperature of 25/19 °C and artificial lighting to complement daylight. Struvite (STR) used in the experiment was precipitated from a liquid fraction of anaerobic digested slurry (LFDS) obtained at a farm-scale bio-refinery located at the Experimental Dairy Farm 'De Marke' in Hengelo (Gld), the Netherlands (52°03″ N, 6°18″ E) (the scheme and description of the bio-refinery are presented in another authors' work [13]). The content of N, P and Mg in STR was 23.1, 39.4, 32.3 g kg^{-1} respectively. The chemical properties of the struvite have been analyzed in our previous publications [13]. In the recovered product except pure struvite the content of monohydroxycalcite ($CaCO_3 \cdot H_2O$) and quartz (SiO_2) were detected. The fertilizer value of struvite was evaluated in comparison with the agronomic commercial ammonium phosphate fertilizer (AP). To account for the differences in the N:P ratio between STR and AP, we included the STR + N treatment in the study design, where the insufficient N supply from the STR and AP fertilizers was supplemented with commercial ammonium sulphate (AS). The examined substances were applied to each pot at the following rates:

STR treatment: 2.0 g P, 1.17 g N, 1.6 g Mg;

STR + N treatment: 2.0 g P, 1.8 g N (1.17 g N as STR and 0.63 g N as AS);

AP treatment: 2.0 g P, 1.8 g N.

Control treatments (without N and P fertilization) were established. Potassium was applied into all pots at a dose of 1.0 g K per each pot (potassium chloride 50%). Maize plants (*Zea mays,*) and grass *(Lolium multiflorum)* were cultivated for 90 and 140 days, respectively. Three grass mowings were collected (this article presents combined results). Soil and plant samples were taken from each pot once, after harvesting.

2.2. Analytical Procedures

The dried plant material was mineralized in HNO_3, H_2O_2, and HCl using a DK 20 digestion unit Model (VELP Scientifica, Usmate, Italy). Magnesium (Mg) content in the crops was measured using the atomic absorption spectrometer (AAS) SOLAAR (Thermo Elemental, Cambridge, UK). The P content in the crops was determined by the vanadomolybdophosphoric method using the Genesys 10 UV-VIS (ultraviolet and visible light region) spectrophotometer (Thermo Electron Corporation, Madison, USA). The total N content (N_{tot}) in the crops was measured with the Vapodest analyzer model VAP 30 (Gerhardt, Bonn, Germany). Soil pH in 1 mol dm^{-3} KCl was determined using a pH meter (Schott, Mainz, Germany); the content of the available phosphorus and magnesium forms (P_{M3}, Mg_{M3}) was assessed by the means of the Mehlich-3 method. The content of active forms of phosphorus (P_{CaCl_2}) and magnesium (Mg_{CaCl_2}) was examined after soil extraction in 0.01 mol·dm^{-3} $CaCl_2$ with the soil/extractant ratio of 1:10. The P_{CaCl_2} concentration and Mg_{CaCl_2} content were determined using molybdenum-blue ascorbic and AAS methods, respectively.

2.3. Estimation of Phosphorus and Nitrogen Use Efficiency

An apparent fertilizer nutrient (P and N) recovery (APR and ANR, respectively) was calculated as follows according to the formulae by Cavalli et al. [14]:

$$AP(N)R\ (\%) = (P(N)_{\text{uptake on STR, STR + N or AP}} - P(N)_{\text{uptake control}})/P(N)_{\text{dose per pot}} \times 100$$

The related fertilizer efficiency (RFE_P and RFE_N) was taken as a parameter to rank P or N sources with respect to ammonium phosphate (AP). The indicators were calculated as follows:

$$RFE_{P(N)}\ (\%) = [(P(N)_{\text{uptake on STR or STR + N}} - P(N)_{\text{uptake control}})/(P(N)_{\text{uptake AP}} - P(N)_{\text{uptake control}})] \times 100$$

The coefficient of potential release of soil reserves of P (phosphorus release coefficient—PRC) was calculated according to the following formula:

$$PRC = (P_{M3}tr - P_{M3}ctr)/(P_{dose} - P_{up})$$

where: $P_{M3}tr - P_{M3}$ content in the soil under the fertilizer treatments; $P_{M3}ctr - P_{M3}$ content in soil under the control treatments; P_{up}—P uptake by the crops. All values were set in mg P·kg^{-1} of soil.

2.4. Statistical Analysis

One-way analysis of variance (ANOVA) was carried out to determine statistically significant differences between treatments (at $P < 0.05$). Homogeneous groups for the examined treatments were determined by Tukey's (HSD) multiple-comparison test. Statistical analyses were carried out using the Statistica PL 13.1 software (Tulsa, USA).

3. Results and Discussion

3.1. Crops Yields

Plant yields are depicted in Figure 1. Grass yields from under STR exceeded those from under the control treatment by respectively 62% and 126% for the SL and LS soil. For the same treatments, the differences in the maize crop yields reached 37% and almost 100%, respectively. As expected, the impact of STR + N on the crop yields was even higher. Grass yields produced on the SL soil under STR + N were similar to those under the AP fertilization; however, on the LS soil, the grass yields under STR + N were greater by 20% than those under the AP treatment. Different reactions of grass and maize on struvite treatment resulted probably from different needs of plants for nutrients, different abilities to uptake them by the roots and different nutrient availability during the growing season. Talboys et al. [7] evidenced similar yields of crops fertilized with struvite and triple superphosphate. Degryse et al. [15] demonstrated similar yields of wheat treated with a dusty form of struvite and ammonium phosphate; however, they showed that struvite granulation reduced the yield efficiency, which is consistent with our previous results [16].

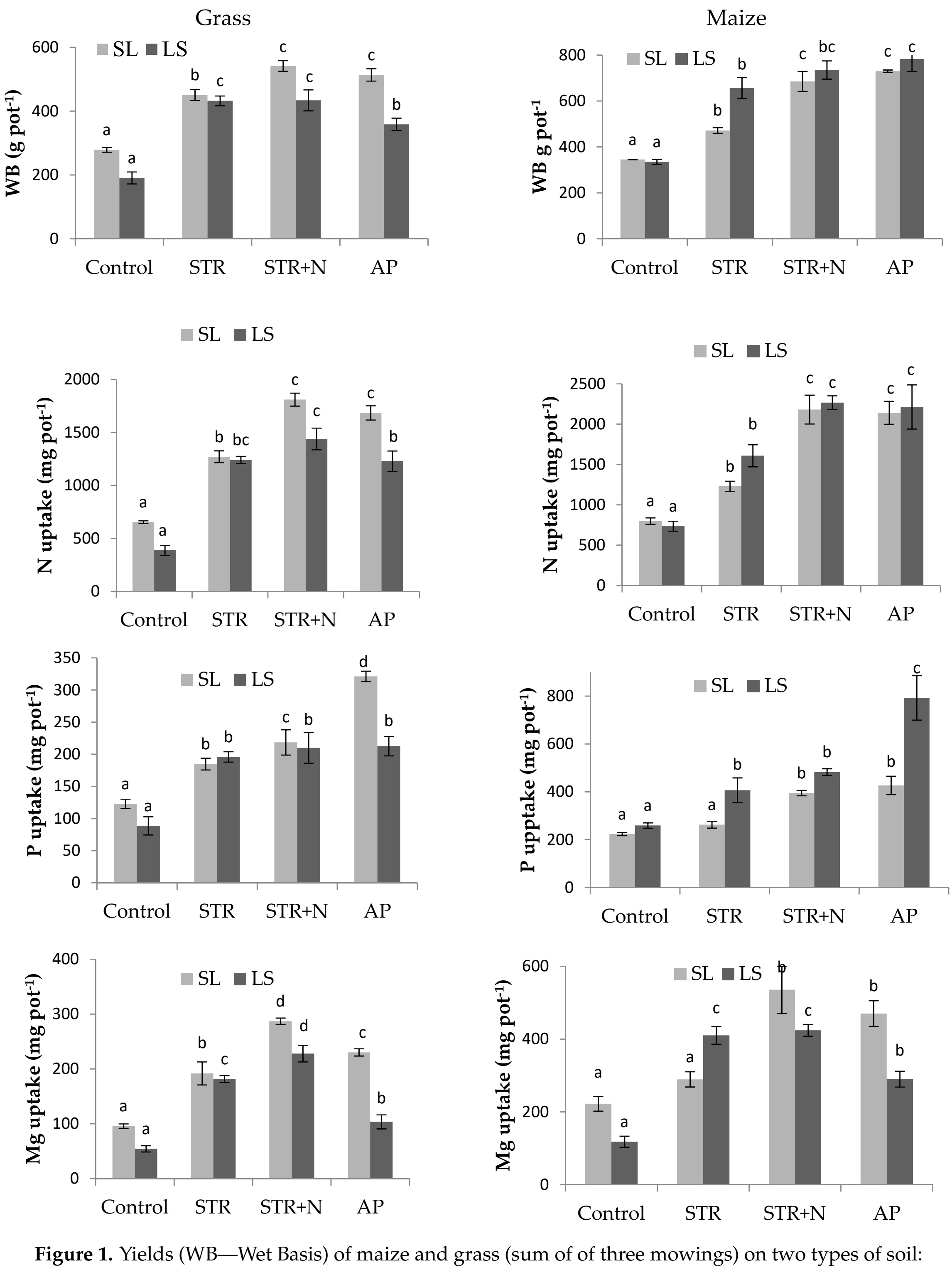

Figure 1. Yields (WB—Wet Basis) of maize and grass (sum of of three mowings) on two types of soil: silty loam (SL) and loamy sand (LS) and N, P, Mg uptake by crops on objects fertilized with: struvite from bio-refinery—STR; struvite from bio-refinery and ammonium sulfate (commercial)—STR + N; ammonium phosphate (commercial)—AP and on control treatment—without fertilization (Control). The standard deviation within each treatment (n = 3) is indicated by the line extending the column. (a–d) Homogeneous groups. Values followed by the same letters in the column (separately for soils: SL and LS) are not statistically different (Tukey HSD multiple range test, 95.0% significance, $P < 0.05$).

3.2. Nutrient Uptake

The uptake of N, P, and Mg by the plants was higher from STR, STR + N, and AP than from the control treatment (Figure 1). The addition of AS to STR significantly increased the nutrient uptake. In the SL soil, the P uptake by grass was greater from AP (321.3 mg P·pot^{-1}) than that from the STR and STR + N treatments (201.6 mg P·pot^{-1}). We made similar observations for the maize cultivation on the LS soil. The P uptake by the maize from the AP treatment (792.3 mg P·pot^{-1}) was greater than that from the STR and STR + N treatments (444.2 mg P·pot^{-1}). Everaert et al. [17] also reported a higher P uptake by the plants from ammonium phosphate than from struvite. Differences in the uptake of nutrients by grass and maize resulted from the different nutritional needs of these species. Grass and maize differed in particular in the amount of phosphorus and magnesium uptake (Figure 1). The rate of nutrient release from struvite is determined by the size of crystals of this substance [15]. Analyzing the effect of using struvite with different grain size (<2 mm, 2–3 mm and 4–8 mm) on yields and chemical composition of ryegrass, Nelson [18] showed an increase in nitrogen uptake with a decrease in the size of crystals. The linear dimension of the experimental struvite was very low and reached 1.4 mm [13]. This means that the release of components from struvite was not rather limited by its physical properties. Therefore, the greater solubility of commercial fertilizer than struvite was most likely the cause of a greater uptake of phosphorus by plants on the treatments with ammonium phosphate than with struvite. This confirms the opinion that struvite is a slow realizing fertilizer [7]. However, Vaneeckhaute et al. [19] report that struvite is a good source of phosphorus at the beginning and in the later part of the growing season. The effect of struvite supplementation with ammonium sulphate on the magnesium uptake by plants is also of particular interest. The obtained results show that struvite can be a valuable source of magnesium for plants, but only under conditions of intensive nitrogen fertilization.

3.3. Phosphorus and Nitrogen Use Efficiency

The apparent nitrogen recovery (ANR) by the plants from the STR, STR + N and AP treatments was very high, notably on the maize cultivation on the LS soil (75%, 85.2%, 82.2% of applied N, respectively) (Figure 2). In the maize cultivation, ANR from the STR + N and AP treatments reached 75.5% and 83.5% on SL and LS, respectively.

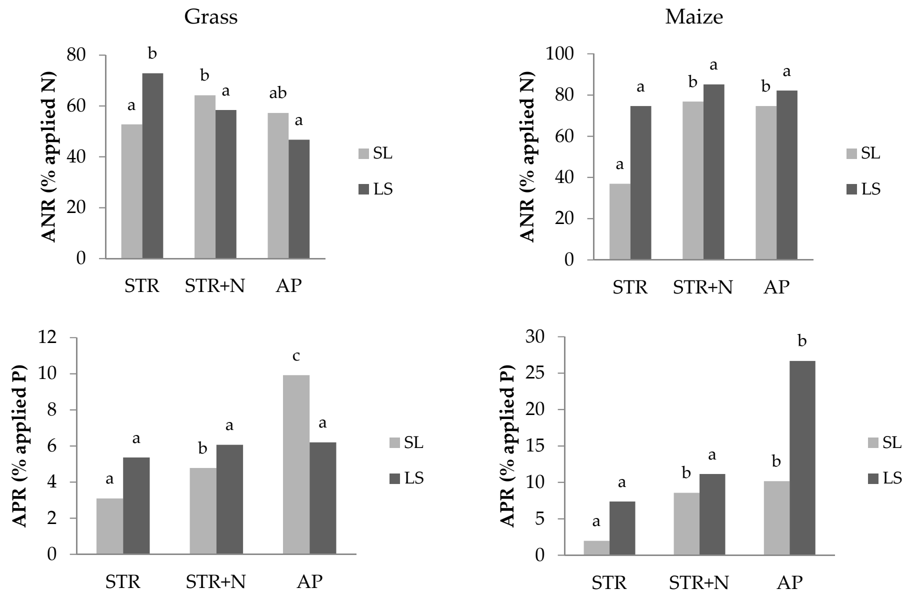

Figure 2. Apparent recovery of applied N (ANR) and P (APR) in maize and grass (%) at SL and LS soils. a, b, c—homogeneous groups. Values followed by the same letters in the column (separately for soils: SL and LS) are not statistically different (Tukey HSD multiple range test, 95.0% significance, P < 0.05).

In the grass cultivation, ANR from struvite (58.5% from STR and STR+N on SL and 66% on LS) was higher than from the AP treatment (57% and 47% on SL and LS, respectively) (Figure 2). This suggests that plants very efficiently use the nitrogen contained in struvite. On the contrary, Corréa et al. [20] obtained only 30 to 35% of apparent nitrogen recovery of the urine-N in the grass cultivation.

Nevertheless, the APR by plants was low, especially from the STR treatment in the SL soil (only 2% and 3.1% of applied P in maize and grass cultivation, respectively) (Figure 2). The highest APR was observed in the maize cultivation on the LS soil (7.4%, 11.2%, and 26.7% of applied P from STR, STR + N and AP, respectively). STR supplementation by the means of AS fertilization increased the APR. For comparison, in the study by Talboys et al. [7], APR reached 1.5% for struvite and 5.5% for ammonium phosphate after 36 days of plant cultivation, and it increased to 11% and 13% for struvite and triple superphosphate, respectively, after 90 days of plant cultivation.

The related fertilizer efficiency (RFE) describes the effectiveness of the analyzed product (in this case struvite), and allows for comparison with commercial fertilizer (AP). The nitrogen relative fertilizer efficiency (RFE_N) of the STR + N and AP treatments did not change considerably in function of the soil type and cultivated plant (Table 1). This suggests that struvite is released to the soil quickly and thus constitutes a form of nitrogen easily available to the crops. By contrast, low RFE_P indicates that struvite phosphorus is used ineffectively by the cultivated crops. This is illustrated by notable differences in REF_P between STR and AP treatments. RFE_P of the STR + N treatment was higher (average for all treatments: 68%) than that of the STR treatment (average for all treatments: 41%), while the differences in RFE_P between STR and STR + N treatments (average 92%) and AP treatment (100%) being negligible only in the grass cultivation on the LS soil.

Table 1. The related fertilizer efficiency (%) of STR and STR + N.

Fertilizer	SL				LS			
	Grass		Maize		Grass		Maize	
	RFE_N	RFE_P	RFE_N	RFE_P	RFE_N	RFE_P	RFE_N	RFE_P
STR	59.9a	31.2a	32.2a	19.3a	101.4a	86.4a	59.1a	27.6a
STR + N	112.1b	48.2a	102.9b	84.3b	125.0b	97.7a	103.6b	41.8a
AP	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

RFE_N—nitrogen relative fertilizer efficiency; RFE_P—phosphorus relative fertilizer efficiency. a, b—homogeneous groups. Values followed by the same letters in the column are not statistically different (Tukey HSD multiple range test, 95.0% significance, $P < 0.05$).

3.4. Soil Chemical Properties

The pH and nutrient concentration in soil was affected differently depending on the fertilizer treatment (Table 2). The AP fertilization determined the soil pH decreased in a considerable way. The application of STR to the LS soil caused an increase in the soil pH from 6.1 under the control treatment to 7.2 pH and 7.4 pH in the under grass and maize cultivation, respectively. A change in pH of soil is a frequent effect of struvite application. Talboys et al. [7] determined that an increase in pH occurs already after 2 days from the application of struvite. An additionally alkalizing effect of struvite could be a result of the release of Mg^{2+} ions. On STR + N treatments, no increase in the pH of soil was recorded. This could result from the addition of acidifying ammonium sulphate.

Table 2. Soil pH_{KCl} and nutrient concentration in soil.

Soil	Fertilization	pH_{KCl}	N_{tot} ($g \cdot kg^{-1}$)	P_{CaCl2}	P_{M3} ($mg \cdot kg^{-1}$)	Mg_{CaCl2}	Mg_{M3}
					Soil use in pot experiment		
SL		6.3	2.6	14.6	87.2	187.9	306.2
LS		6.3	0.8	19.1	95.7	20.0	65.0
					After grass harvesting		
SL	Control	6.4 a	2.6 ± 0.1a	11.8 ± 0.2a	81.2 ± 0.9a	133.0 ± 1.9a	312.6 ± 2.7a
	STR	6.6 a	2.6 ± 0.1a	37.6 ± 1.0d	237.4 ± 14.1d	262.8 ± 24.8b	385.4 ± 4.4b
	STR + N	6.2 a	2.4 ± 0.2a	33.1 ± 0.6c	213.3 ± 1.7c	254.6 ± 5.8b	382.1 ± 4.7b
	AP	5.7 b	2.5 ± 0.1a	15.4 ± 1.1b	163.5 ± 4.3b	132.9 ± 0.5a	305.0 ± 3.6a
LS	Control	6.1 b	0.8 ± 0.04a	15.0 ± 0.02a	90.0 ± 0.4a	19.8 ± 0.4a	57.8 ± 3.0a
	STR	7.2 c	0.8 ± 0.02a	43.1 ± 1.8c	287.2 ± 4.1c	59.2 ± 4.1b	145.0 ± 3.3c
	STR + N	6.5 b	0.8 ± 0.02a	34.0 ± 0.6b	266.9 ± 1.5c	55.0 ± 3.6b	112.2 ± 1.6b
	AP	5.4 a	0.7 ± 0.01a	31.8 ± 0.7b	230.3 ± 17.1b	25.7 ± 2.5a	52.0 ± 4.5a
					After maize harvesting		
SL	Control	6.1 a	2.7 ± 0.1a	10.9 ± 0.5a	86.7 ± 1.3a	130.5 ± 7.1a	351.0 ± 1.7b
	STR	6.7 a	2.8 ± 0.1a	31.4 ± 0.4c	242.9 ± 4.9d	179.2 ± 3.4b	423.6 ± 0.5d
	STR + N	6.3 a	2.7 ± 0.1a	28.0 ± 2.3bc	202.1 ± 3.0c	199.6 ± 4.4c	415.2 ± 2.7c
	AP	5.7 b	2.6 ± 0.03a	27.0 ± 1.8b	160.4 ± 4.4b	133.1 ± 0.7a	344.5 ± 2.4a
LS	Control	6.1 b	0.7 ± 0.02a	14.7 ± 0.2a	84.1 ± 2.1a	20.3 ± 1.0a	63.5 ± 0.6a
	STR	7.4 a	0.9 ± 0.03b	36.0 ± 1.1d	264.1 ± 3.3d	94.4 ± 2.9c	135.7 ± 4.7b
	STR + N	6.4 b	0.8 ± 0.04a	29.3 ± 0.5c	228.3 ± 7.1c	77.1 ± 11.9b	122.3 ± 15.6b
	AP	5.6 c	0.7 ± 0.02a	16.9 ± 0.8b	185.2 ± 4.5b	25.3 ± 1.1a	59.5 ± 2.0a

N_{tot}—Total nitrogen; P_{CaCl2}, Mg_{CaCl2}—active forms of P, Mg in soil; P_{M3}, Mg_{M3}—available forms of P, Mg in soil. (a–d) Homogeneous groups. Values followed by the same letters in the column (for each plant, separately for soils: SL and LS) are not statistically different (Tukey HSD multiple range test, 95.0% significance, $P < 0.05$).

The nitrogen content in the soil was determined by the type of soil but not by a single application of the examined treatments. The content of N_{tot} was higher in SL (averaging for all objects 2.6 g $N_{tot} \cdot kg^{-1}$) in comparison to LS (averaging for all objects 0.78 $g \cdot N_{tot} \cdot kg^{-1}$).

The average P_{M3} content in the soil increased from 85.5 mg $P_{M3} \cdot kg^{-1}$ under the control treatments to 257.9, 227.6, and 184.8 mg $P_{M3} \cdot kg^{-1}$ under the STR, STR + N, and AP treatments, respectively (Table 2). Likewise, the content of P_{CaCl2} in the soil increased from 13.1 mg P_{CaCl2} under the control treatments to 37.0, 31.1, and 22.8 mg $P_{CaCl2} \cdot kg^{-1}$ under the STR, STR + N, and AP treatments, respectively. An increase in the phosphorus content in the soil following struvite application was also observed by Plaza et al. [9], Massey et al. [10] and Cabeza et al. [6].

Our results suggest a possible release of phosphorus from the soil at a remote time point. This was illustrated by the phosphorus release coefficient (PRC), which depended on the soil type to a greater degree than crop cultivation. In the SL soil, the average PRC reached 1.22, 0.99 and 0.65 under the STR, STR + N, and AP treatments, respectively, whereas, in the LS soil values this coefficient under the STR, STR + N, and AP treatments were 1.51, 1.31, and 1.08, respectively, indicating a quicker release of phosphorus to the soil. Several processes can explain the obtained results. Physical composition has a major influence on the P solubility for slow release fertilizers such as struvite [21]. In this pot experiment, we applied a dusty form of struvite, which is more soluble than the granular one [16], that can be explained by a greater surface of the area of contact between the particles of the fertilizer and the soil. Moreover, the increased soil pH after the struvite application could affect the solubility of phosphorus compounds in soil [22–24]. A combination of those factors could lead to a considerable accumulation of available active forms of phosphorus in the analyzed soils as a result of struvite application. However, the specific mechanism of P release from soil after struvite application still remains unclear. So, further investigation should be conducted.

4. Conclusions

Struvite—precipitate obtained from a liquid fraction of a digestate in a farm scale bio-refinery can be used as a valuable multi-nutrient fertilizer. Low nitrogen content in relation to phosphorus (N:P ratio 0.59:1) requires supplementation of struvite with nitrogen fertilizers. The addition of nitrogen to struvite up to the content of N in commercial ammonium phosphate increases the yield effect of struvite up to the level obtained for the artificial fertilizer. The P uptake by crops from struvite can be lower than from commercial ammonium phosphate. In this case, a majority of the struvite phosphorus remains in the soil as an available form of the nutrient. Contrary to this, the nitrogen uptake and recovery from struvite and commercial ammonium phosphate are generally similar. In conclusion, our results and the literature review prove the value of struvite supplemented with appropriate nitrogen treatment as a substitute for commercial ammonium phosphate.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

STR	Struvite from bio-refinery
STR + N	Struvite from bio-refinery + ammonium sulphate
AP	Ammonium phosphate fertilizer
APR	Apparent Phosphorus Recovery
ANR	Apparent Nitrogen Recovery
RFE_P	Related Phosphorus Efficiency
RFE_N	Related Nitrogen Efficiency
SL	Silty loam soil
LS	Loamy sand soil

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