




Article

Ammonium Sulphate from a Bio-Refinery System as a Fertilizer—Agronomic and Economic Effectiveness on the Farm Scale

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Abstract: This paper presents the results of a pot experiment aimed at the assessment of the agronomic and economic effectiveness of ammonium sulphate from an agro bio-refinery (Bio-AS). The Bio-AS was obtained by means of the ammonia stripping process from effluent after struvite precipitation from a liquid fraction of digestate. The agronomic effectiveness of Bio-AS in a pot experiment with maize and grass in two different soils, silty loam (SL) and loamy sand (LS), was investigated. The fertilising effect of Bio-AS was compared to commercial ammonium sulphate fertilizer (Com-AS) and control treatment (without fertilisation). The crop yields were found to depend on both soil type and nitrogen treatment. Crop yields produced under Bio-AS and Com-AS exceeded those under control treatments, respectively for SL and LS soils, by 88% and 125% for maize and 73% and 94% for grass. Crop yields under Bio-AS were similar to those under the Com-AS treatment. The fertilizer use of Bio-AS affected the chemical composition of plants and soil properties similarly as Com-AS. This suggests that Bio-AS from a bio-refinery can replace industrial ammonium sulphate, resulting in both economic and environmental benefits.

Keywords: digestate; nitrogen removal; ammonia stripping; agro bio-refinery; ammonium sulphate; fertilizer value; crop yield; environmental sustainability

1. Introduction

According to the International Energy Agency (IEA), biorefining is sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, heat) [1,2]. Moncada et al. [3] define bio-refinery as a complex system where biomass is integrally processed to obtain more than one product including bioenergy. The concept of bio-refinery results from the necessity of sustainable management of resources and promotion of efficient use of biomass. Bio-refineries correspond with the idea of the circular economy and bioeconomy [4], permitting recovery of various substances and energy from waste used for production of value-added bioproducts. Recovery of such value-added bioproducts aims at the replacement or reduction of the use of fossil fuels and excavation of natural resources necessary for their conventional production [5]. Bio-refineries can function at various agricultural-food processing plants as well as in agricultural farms with intensive animal production. Intensive organic fertilisation applied there causes pollution of drainage waters with nutrients [6,7], as well as the emission of odours, volatile organic compounds,

ammonia (NH₃), nitrous oxide (N₂O), and hydrogen sulphide (H₂S) to the atmosphere [8,9]. Due to intensification of animal production observed in EU agriculture, the European Commission regulated the use of organic fertilizers in the Nitrates Directive adopted on 12 December 1991. It aimed at water quality protection across Europe by prevention of pollution of the ground and surface waters with nitrates from agricultural sources and by promoting the use of good farming practices. One of the major restrictions was the limitation of the amount of nitrogen applied, taking into account the crop needs, all nitrogen inputs and soil nitrogen supply, as well as the maximum amount of livestock manure to be applied (corresponding to 170 kg nitrogen per hectare per year) [10]. The Dutch government negotiated special derogation allowing use of 250 kg·N·ha⁻¹ in organic fertilizers under the condition of more efficient use of nitrogen from animal sources, which is included in the Dutch Manure Policy [11] and also encompasses regulations limiting the use of P from organic fertilizers. Many studies report considerable farm-gate N surplus for dairy farms per unit area, for example 138 kg N ha⁻¹ year⁻¹ in Sweden, 223 kg·N·ha⁻¹·year⁻¹ in the Netherlands, and 240 kg·N·ha⁻¹·year⁻¹ in Denmark [12]. So far, the dominant method of processing of animal waste has been anaerobic digestion. The process results in the production of biogas and digestate [13]. Biological conversion of organic compounds during anaerobic digestion considerably reduces the odour as compared to untreated manures [14–16]. Both the nitrogen and phosphorus content in the digestate are comparable with untreated manure; however, in contrast to livestock manures, the digestate is characterized by the presence of the nutrients in soluble mineral forms. It forces the development of N and P recovery technology from the digestate [17]. Excess nitrogen can be removed from anaerobic digestate by means of nitrification and denitrification [18]. Nutrient removal and recovery from organic products such as untreated and anaerobic digested livestock manure by struvite precipitation [19], membrane filtration [20], and ammonia stripping [21] is more justified. The aforementioned processes of recovery of N and P, resulting in obtaining value-added fertilizers, have recently become popular in bio-refineries [22]. Precipitation of struvite crystals (MgNH₄PO₄·6H₂O) occurs in accordance with Reaction 1 [23]:



The factor limiting the efficiency of struvite precipitation from the digestate product is magnesium deficit. For the purpose of improvement of the efficiency of N and P recovery, it is necessary to use a large amount of magnesium salts. It considerably increases the operational costs and limits the possibilities of the broad application of the technology in small agricultural farms [24]. Due to this, various low-cost materials such as seawater [25], bittern [26], and magnesite (MgCO₃) [27] are considered as a cheap alternative source of Mg⁺² ions. The molar ratio of N : P in digestate varies from 2 : 1 to 4 : 1 [28], and in struvite it is 1:1. Therefore, the leachate after struvite precipitation still contains a large number of ammonium ions [19,29]. The combination of a struvite precipitation installation with ammonia stripping installation permits more efficient nitrogen removal from digestate. The ammonia stripping process occurs in several stages: (1) conversion of ammonium ions (NH₄⁺) to ammonia gas (NH₃), (2) diffusion of NH₃ to the air–water interface, (3) release of NH₃ to the air at the interface, and (4) diffusion of NH₃ from the air–water interface into the air above [28]. Released NH₃ is absorbed by sulphuric acid to (NH₄)₂SO₄. The efficiency of the process depends on the pH, temperature, and mass transfer area [30]. Recovered ammonium sulphate can be applied in agriculture as mineral fertilizer. Next to nitrogen, it contains sulphur, the deficit of which in soil may cause a considerable decrease in the plant production yield [31]. According to Jamal et al. [32], in order to produce 1 t of biomass, grain crops need to take up 3–4 kg·S·ha⁻¹ (at a variation of 1–6), leguminous crops 8 kg·S·ha⁻¹ (at a variation of 5–13), and oilseed crops 12 kg·S·ha⁻¹ (at a variation of 5–20). Recovery of ammonium sulphate potentially permits a decrease in energy expenditure in the production of commercial nitrogen fertilizers via the Haber–Bosch process. Industrial synthesis of 1 t of NH₃ requires the expenditure of 37 GJ of energy [33].

The literature broadly describes the processes of removal of N and P from sewage sludge [34]. Less attention is paid to the removal of N and P from untreated and anaerobic digested livestock manure.

Research frequently exclusively focuses on the assessment of the efficiency of various component recovery technologies, but data concerning the assessment of the agronomic value of the obtained products, differing in composition from commercial mineral fertilizers, are scarce. Promotion of technologies of recovery of nutrients from different organic materials requires confirmed knowledge that the obtained products will fulfill the ascribed fertilizer function and find recipients.

Considering the aforementioned current trends and challenges of the modern world, interdisciplinary research was conducted aimed at the assessment of the agronomic value of ammonium sulphate solution (Bio-AS) obtained as a result of processing of livestock manure in a bio-refinery located at a Dutch farm with dairy cattle production.

2. Materials and Methods

2.1. Collection of Ammonium Sulphate (Bio-AS)

The bio-refinery was located at the experimental dairy farm 'De Marke' in Hengelo (Gld), the Netherlands (52°03" N, 6°18" E) [35]. At the biorefinery, cattle manure was subject to anaerobic digestion (the diagram and description of the bio-refinery are presented in another authors' work [36]). The obtained biogas was used for the production of electricity and heat. After sanitation, digestate was fractionated. The solid fraction was applied on fields of the farm as organic fertilizer. The liquid fraction (LFDS) was subject to the processes of P and N removal. Struvite (STR) was precipitated from the liquid fraction in a struvite installation (the fertilizer value of struvite obtained in the bio-refinery was presented in our previous work [22]). Effluent after struvite precipitation was used for the production of ammonium sulphate solution (Bio-AS) in an ammonia stripping installation. The adopted technology should theoretically permit high, approximately 93%, N removal from LFDS [37]. In the stripping tower, effluent after struvite precipitation was alkalisied to pH 10.5 using 5 N NaOH. Air was used to separate the gaseous NH₃ from the liquid phase at a temperature of 54 °C. The released ammonia was bound by sulphuric acid forming Bio-AS. Leachate after nitrogen stripping was further directed to a duck weed lake, where duckweed was cultivated for the production of animal fodder. The said article focused only on the assessment of the agronomic and economic value of Bio-AS produced in the bio-refinery.

2.2. Pot Experiment

The pot experiment involved the assessment of the agronomic value of Bio-AS in comparison to commercial ammonium sulphate fertilizer (Com-AS). The pot experiment was conducted in the experimental greenhouse of the Warsaw University of Life Sciences (WULS-SGGW). The research was conducted on two soils: loamy sand (LS) and silty loam (SL). LS was collected from the 0–25 cm soil layer of the long-term fertilisation experiment carried out since 1923 in Skierniewice (Central Poland). SL was collected from the 0–25 cm soil layer in Wilanów-Obory (Central Poland). The soil properties are presented in Table 1.

Table 1. Chemical properties of soils.

Soil	pH	N total (g·kg ⁻¹)	Active Forms of Nutrients (mg·kg ⁻¹)			Available Forms of Nutrients (mg·kg ⁻¹)		
			P _{CaCl2}	K _{CaCl2}	Mg _{CaCl2}	P _{M3}	K _{M3}	Mg _{M3}
Silty loam (SL)	6.3	2.6	14.6	27.7	187.9	87.2	87.3	306.2
Loamy sand (LS)	6.3	0.8	19.1	45.9	20.0	95.7	97.5	65.0

Each pot consisted of 15 kg of sieved soil. Bio-AS and Com-AS were applied in doses, with which 2.0 g·N was introduced to each pot. The chemical compositions of Bio-AS and commercial fertilizers are provided in Table 2. Control objects, without fertilisation with nitrogen, were designated in the experiment (control). One gram K in the form of potassium chloride (KCl) was applied to each pot. Each treatment had 3 replications. Maize (*Zea mays*, cv CH4) plants and grass (*Lolium multiflorum*)

were cultivated in the experiment. Ten seeds of maize and 3 g of grass seeds were planted on the top (4 cm and 1.5 cm, respectively, for maize and grass) of soil in each pot. The plants were watered regularly in order to keep the soil water content at 60% of the soils' water holding capacity by adding deionised water. Maize and grass were cultivated for 90 and 140 d, respectively (i.e., from May to July 2017 and from May to September 2017). Three grass swaths were performed (the article provides total results). After cut down of plants, samples were weighed before and after drying (in oven set at 60 °C) to determine their fresh and dry matter. Soil samples were collected from each pot after maize harvesting or the last grass swath.

Table 2. Composition of ammonium sulphate from the bio-refinery (Bio-AS), and commercial fertilizer used in the pot experiment.

Fertilizer	Total N Content (TKN; %)	S _T (%)	Pure (NH ₄) ₂ SO ₄ (%)	Free H ₂ SO ₄ (%)	pH	K _T (%)
Bio-AS	1.41	1.68	6.6	0.22	2.1	-
Com-AS ^a	20.8	24.0	98.1	max 0.1	-	-
KCl ^a	-	-	-	-	-	50.0

^a Data from manufacturer information, not experimentally determined.

2.3. Analytical Procedures

The total N content (TKN) in Bio-AS, soils, and plants was measured by means of the Kjeldahl method with a Vapodest analyser model VAP 30 (Gerhardt, Bonn, Germany). The total content of sulphur (S_T) in Bio-AS was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRYS Advantage ThermoElementar, Cambridge, UK). The pH value of Bio-AS was measured by the potentiometric method using a pH meter (Schott, Mainz, Germany). Dry samples of plants were homogenised and mineralised with HNO₃, H₂O₂, and HCl using a Model DK 20 digestion unit (VELP Scientifica, Usmate, Italy). The P content in the plants was determined by the vanadomolybdophosphoric method using a Genesys 10 UV-VIS (ultraviolet and visible light region) spectrophotometer (Thermo Electron Corporation, Madison, USA). Magnesium (Mg) and potassium (K) content in the plants was measured by means of an atomic absorption spectrometer (AAS) SOLAAR (Thermo Elemental, Cambridge, UK).

The following was determined in air-dried soil samples sieved through 2 mm mesh: soil pH in 1 mol·dm⁻³ KCl; content of available phosphorus (P_{M3}), potassium (K_{M3}), and magnesium (Mg_{M3}) by the Mehlich-3 method; content of active phosphorus (P_{CaCl2}), potassium (K_{CaCl2}), and magnesium (Mg_{CaCl2}) in 0.01 mol dm⁻³ CaCl₂ (1:10 soil:extractant ratio). P_{M3} and P_{CaCl2} concentrations were determined using the colorimetric method, and K_{M3}, K_{CaCl2}, Mg_{M3}, and Mg_{CaCl2} were determined by the atomic absorption spectroscopy method (AAS).

2.4. Indicator Calculation

Apparent fertilizer N recovery (ANR) was calculated with the following Formula (2):

$$\text{ANR (\%)} = (\text{N}_{\text{up treatment}} - \text{N}_{\text{up control}}) / \text{N}_{\text{dose}} \times 100, \quad (2)$$

where N_{up treatment} refers to N uptake per pot on Bio-AS or Com-AS, and N_{up control} refers to N uptake per pot on control treatments. N_{dose} refers to mg N per pot. N uptake was calculated from aboveground dry matter yield (DM) and N concentration.

Related fertilizer efficiency (REF) was adopted as a parameter to rank the N sources (Bio-AS) with respect to Com-AS. The indicator was calculated by means of the following Formula (3):

$$\text{REF (\%)} = [(\text{N}_{\text{up Bio-AS}} - \text{N}_{\text{up control}}) / (\text{N}_{\text{up Com-AS}} - \text{N}_{\text{up control}})] \times 100, \quad (3)$$

where $N_{\text{up Bio-AS}}$ refers to N uptake per pot fertilised with Bio-AS; $N_{\text{up Com-AS}}$ refers to N uptake per pot fertilised with Bio-AS.

Nitrogen use efficiency, NUE ($\text{g}\cdot\text{DM}\cdot\text{g}\cdot\text{N}^{-1}$), was calculated based on the following Formula (4):

$$\text{NUE} = (Y_{\text{treatment}} - Y_{\text{control}}) / N_{\text{dose}} \quad (4)$$

where $Y_{\text{treatment}}$ is maize or grass yields ($\text{g}\cdot\text{DM}\cdot\text{pot}^{-1}$) on Bio-AS or Com-AS treatments, Y_{control} is maize or grass yields ($\text{g}\cdot\text{DM}\cdot\text{pot}^{-1}$) on control treatments.

2.5. Statistical Analysis

Statistical analyses were carried out with the application of the Statistica PL 13.1 software (Tulsa, USA). The data were subject to ANOVA, and the differences between means were determined by means of a Tukey's test ($P \leq 0.05$).

2.6. Analysis of Economic Performance

To assess the economic performance of the investment, the authors analysed values of investment and operational costs. The economic performance was estimated for the cost and price conditions of the Netherlands, Poland, and Great Britain. The value of investment included the construction of a biogas plant in a co-generation system combined with an ammonium sulphate recovery. The data for the analysis were collected by CCS (Cornelissen Consulting Services, NL), who were responsible for launching an experimental bio-refinery in the Netherlands. Due to the specificity of the agricultural bio-refinery production cycle, the ammonium sulphate produced there that can be used as fertilizer is only one of the co-products; therefore, the profitability assessment was carried out on the scale of the entire farm, assuming obtaining revenues from the sale of electricity generated from biogas combustion in the CHP (Combined Heat and Power) system, revenues from the sale of ammonium sulphate (including sales and consumption for own needs on the farm), and revenues from the replacement of part of the feed with duckweed, produced on the basis of unused nutrients from digestate, and also public support for environmentally friendly practices and savings on cost of utilization of excess of manure (Netherlands only). The investment effectiveness was assessed using NPV (net present value) [38] and IRR (internal return rate) [39].

3. Results

3.1. Characteristic of Bio-AS from the Bio-Refinery

The Bio-AS solution contained 1.41% TKN and 1.68% S_T (Table 2). In comparison to similar fertilizers obtained by Lauren et al. [21] from pig manure and containing 40–60% $(\text{NH}_4)_2\text{SO}_4$, the solution obtained by us was characterised by a very low (6.6%) content of ammonium sulphate. Ammonia stripping was the second stage of N recovery (after struvite precipitation), potentially causing a decrease in the concentration of $(\text{NH}_4)_2\text{SO}_4$ in the produced solution. Content of H_2SO_4 in the Bio-AS solution was 0.22%; therefore, it was characterised by a strong acidity. The obtained results suggest the necessity to introduce changes in the ammonia-stripping technology applied in the discussed bio-refinery. The N recovery efficiency was 43.2% [36], whereas according to Törnwall [33], total ammonia removal from the digestate might reach 42–80%.

3.2. Agronomic Value of Bio-AS from the Bio-Refinery—Crop Characteristics

The crop yields of maize and grass treated with Bio-AS and Com-AS fertilizers were considerably larger than on control objects. At the same dose of nitrogen in Bio-AS and Com-AS, the yield-forming efficiency of both fertilizers was similar (Figure 1). This confirms the high usefulness of Bio-AS for plant fertilisation. A factor considerably differentiating the plant yields was the type of soil. Substantially larger yields of maize were obtained on loamy sand (LS) than on silty loam (SL). Maize is known to

better use nitrates than ammonia cations. In aerobic conditions, NH_4^+ is rapidly nitrified in soil to NO_3^- [40]. In well-aerated LS soil, the nitrification process could have occurred faster than on SL soil. Probably due to this, maize on loamy sand was better nourished with nitrogen and provided a larger yield than on silty loam. On the contrary, the yield of grass cultivated on SL soil was larger than on LS soil. Nonetheless, a higher increase in yields of grass under nitrogen fertilisation was recorded on LS soil (approximately 94%) than on SL soil (approximately 73%). This means that better conditions for growth of grass occurred on SL soil (yields on control in such conditions were significantly larger than on LS soil).

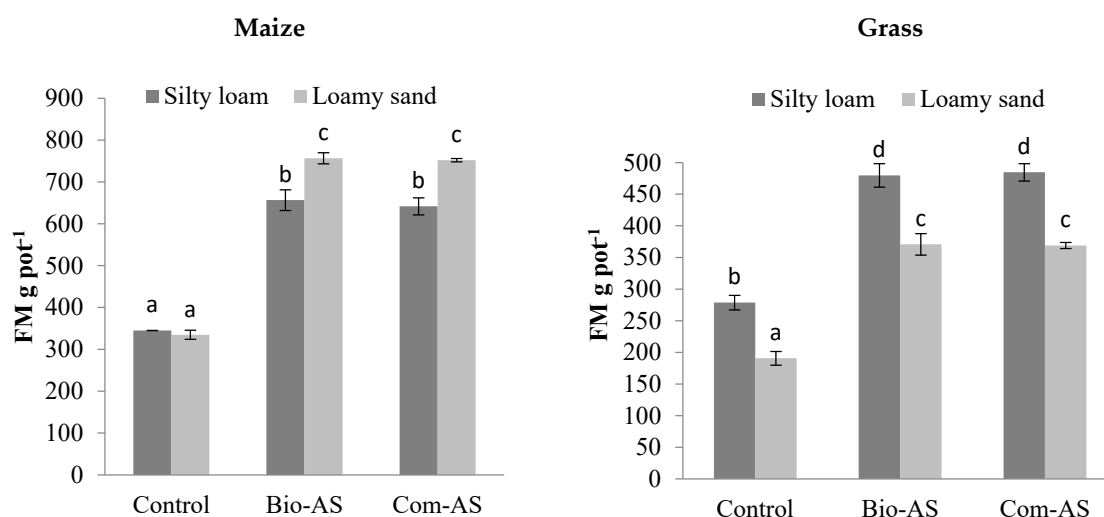


Figure 1. Yields of fresh mass (FM) of maize and grass (total of three swaths) cultivated on two types of soils: SL and LS. The standard deviation within each treatment ($n = 3$) is indicated by the line extending the column. Different letters indicate significant differences ($P \leq 0.05$).

Nitrogen use efficiency (NUE) from Bio-AS and Com-AS measured by the increase in dry matter of maize per 1 g of applied N was almost twice higher on LS soil (on average for Bio-AS and Com-AS $28.3 \text{ g-DM}\cdot\text{g-N}^{-1}$) than on SL soil (on average for Bio-AS and Com-AS, $14.2 \text{ g-DM}\cdot\text{g-N}^{-1}$) (Table 3). Higher NUE values were obtained on objects where tested Bio-AS was applied. The difference between objects fertilised with Bio-AS and Com-AS was 7.4 and $1.4 \text{ g-DM}\cdot\text{g-N}^{-1}$, respectively, for SL and LS soils. The value of the ANR indicator (apparent fertilizer N recovery) suggests that maize cultivated on LS soil utilised nitrogen from Bio-AS and Com-AS fertilised better than on SL soil (Table 3). The ANR by maize fertilised with Bio-AS and Com-AS on LS soil averaged 78.2% , and on SL soil 57.5% . It may be connected to the high mobility of mineral N in sandy soil because of the lack of binding sites [41], potentially contributing to an increase in N uptake by plants.

Table 3. Apparent recovery of applied N (ANR), nitrogen use efficiency (NUE), and related fertilizer efficiency of Bio-AS (REF).

Soil	Fertilization	ANR (%)		NUE (g DM g N^{-1})		REF (%)	
		Maize	Grass	Maize	Grass	Maize	Grass
SL	Bio-AS	58.2	59.8	17.9	10.4	102.4	96.3
	Com-AS	56.8	62.1	10.5	11.5	100.0	100.0
LS	Bio-AS	75.9	51.5	29.0	9.6	94.3	89.2
	Com-AS	80.5	57.7	27.6	9.0	100.0	100.0

Grass utilised N from Bio-AS and Com-AS more efficiently on SL soil than on LS soil. NUE values averaged approximately $11 \text{ g-DM}\cdot\text{g-N}^{-1}$ on SL soil and approximately $9.3 \text{ g-DM}\cdot\text{g-N}^{-1}$ on LS soil (Table 3). The value of the ANR coefficient from Bio-AS and Com-AS on SL soil averaged

approximately 61% and on LS soil approximately 55% (Table 3). On both SL and LS soils, ANR values were higher in objects fertilised with Com-AS than Bio-AS (on SL soil by approximately 2.3% and on LS soil by approximately 6.2%, respectively).

Related fertilizer efficiency (RFE) describes the effectiveness of the analysed product (in this case Bio-AS) and allows for comparisons with commercial fertilizer (Com-AS). The related fertilizer efficiency of Bio-AS was inconsiderably lower than that of Com-AS (Table 3). Only in maize cultivation on SL soil was the REF of Bio-AS higher than the REF of Com-AS.

The applied fertilisation affected the chemical composition of the tested plants (Table 4). The content of nitrogen in maize cultivated on objects fertilised with Bio-AS and Com-AS (average 16.7 g·N·kg·DM⁻¹) was significantly higher than in plants cultivated on the control object (average 8.9 g·N·kg·DM⁻¹). On LS soil, no significant differences were determined in N content between maize fertilised with Bio-AS and Com-AS. On SL soil, higher N content was determined in maize fertilised with Com-AS than Bio-AS. Nitrogen fertilisation applied in the experiment (Bio-AS and Com-AS) affected the content of phosphorus, potassium, and magnesium in the analysed plants in different ways (Table 4). Irrespective of soil conditions, phosphorus content in maize under Bio-AS and Com-AS fertilisation was lower than on the control object. Nitrogen fertilisation applied on LS soil increased, and on SL soil it had no effect on the content of potassium in maize. The content of magnesium in maize cultivated on LS soil was approximate on all objects, and on SL soil an increase in the content of magnesium in comparison to the control object was determined only under fertilisation with Com-AS. Uptake of a nutrient from soil is a function of the yield and content of the nutrient in the plant biomass. Irrespective of nitrogen fertilisation, uptake of phosphorus and potassium by maize cultivated on LS soil was higher than on SL soil. On the contrary, uptake of magnesium by plants cultivated on SL soil was higher than on LS soil. Nitrogen fertilisation predominantly increased uptake of phosphorus, potassium, and magnesium. Only on SL soil it had no effect on uptake of phosphorus by maize.

Table 4. NPKMg content in plants.

Soil	Fertilization	Maize				Grass			
		I Cut	II Cut	III Cut	Maize	I Cut	II Cut	III Cut	
		N·g·kg·DM ⁻¹				P·g·kg·DM ⁻¹			
SL	Control	9.4 a	24.1 b	23.8 a	17.3 bc	2.6 c	3.6 ab	5.6 b	3.6 ns
	Bio-AS	16.3 b	39.6 c	41.9 b	19.2 cd	2.1 a	2.6 a	3.6 a	2.8 ns
	Com-AS	18.3 c	39.1 c	40.3 b	20.2 d	2.1 a	2.7 a	4.1 a	2.5 ns
LS	Control	8.5 a	19.4 a	20.7 a	15.5 ab	3.0 d	4.4 b	5.8 b	2.8 ns
	Bio-AS	15.6 b	43.6 d	39.6 b	13.0 a	2.2 ab	3.6 ab	3.7 a	2.8 ns
	Com-AS	16.6 b	45.1 d	47.4 c	17.8 bcd	2.4 b	3.9 ab	3.8 a	3.1 ns
Soil ^a		***	**	**	***	***	**	ns	ns
Fertilizer		***	***	***	***	***	*	***	ns
Soil × Fertilizer		ns	***	***	**	*	ns	ns	ns
		K·g·kg·DM ⁻¹				Mg·g·kg·DM ⁻¹			
SL	Control	7.0 a	12.2 a	12.5 bc	12.1 a	2.6 b	2.6 b	3.2 a	3.7 d
	Bio-AS	7.7 a	13.3 ab	14.0 c	21.5 c	2.5 b	4.1 c	6.0 b	3.1 c
	Com-AS	8.6 ab	14.0 b	10.2 ab	20.1 bc	3.4 c	3.7 c	5.6 b	3.5 d
LS	Control	9.8 b	16.7 c	11.4 abc	28.4 d	1.4 a	2.0 a	2.9 a	3.0 bc
	Bio-AS	14.1 c	15.8 c	9.2 a	20.0 bc	1.6 a	2.2 ab	3.7 a	2.3 a
	Com-AS	12.8 c	17.1 c	14.0 c	18.7 b	1.7 a	2.3 ab	3.2 a	2.6 ab
Soil ^a		***	***	**	**	***	***	***	***
Fertilizer		***	*	*	*	**	***	***	***
Soil × Fertilizer		**	*	***	***	ns	***	***	ns

^a Statistical significance of fertilizer or soil or interaction effect: * $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$; ns: not significant. Different letters in the column indicate significant differences ($P \leq 0.05$) between different fertilizer treatments (together for SL and LS but separate for grass and maize).

Irrespective of soil conditions, nitrogen fertilisation (Bio-AS and Com-AS) significantly increased nitrogen content in grass harvested in the first two swaths. Differences in nitrogen content in plants harvested in the third swath resulting from nitrogen fertilisation or its omission were considerably

smaller and were mostly statistically unproven. This means that a short time after application, ammonium sulphate dissociates, releasing NH_4^+ ions to the soil to be directly available for plants [42], subject to efficient and rapid uptake by grass. Nitrogen uptake by both maize and grass was significantly higher on objects fertilised with Bio-AS and Com-AS than on the control object (Figure 2). Phosphorus content in grass harvested in the first two swaths from control objects on both soils was higher than on objects under nitrogen fertilisation (although the differences were not always statistically proven) (Table 4). The content of the element in grass harvested in the third swath from all objects on both soils was approximate and usually lower than in plants harvested in the first and second swath. No direct effect of nitrogen fertilisation and soil conditions on the content of potassium in the plants was determined. The content of magnesium in grass cultivated on SL soil was higher on objects under nitrogen fertilisation than on the control object, but only in the biomass of plants harvested in the first and second swath. In the biomass of plants harvested in all swaths on LS soil, the content of the nutrient was differentiated by fertilisation applied in the experiment. Grasses took up more phosphorus, potassium, and magnesium from medium soil (SL) than light soil (LS). Irrespective of soil conditions, uptake of components on objects fertilised with nitrogen was higher than on control objects (Figure 2).

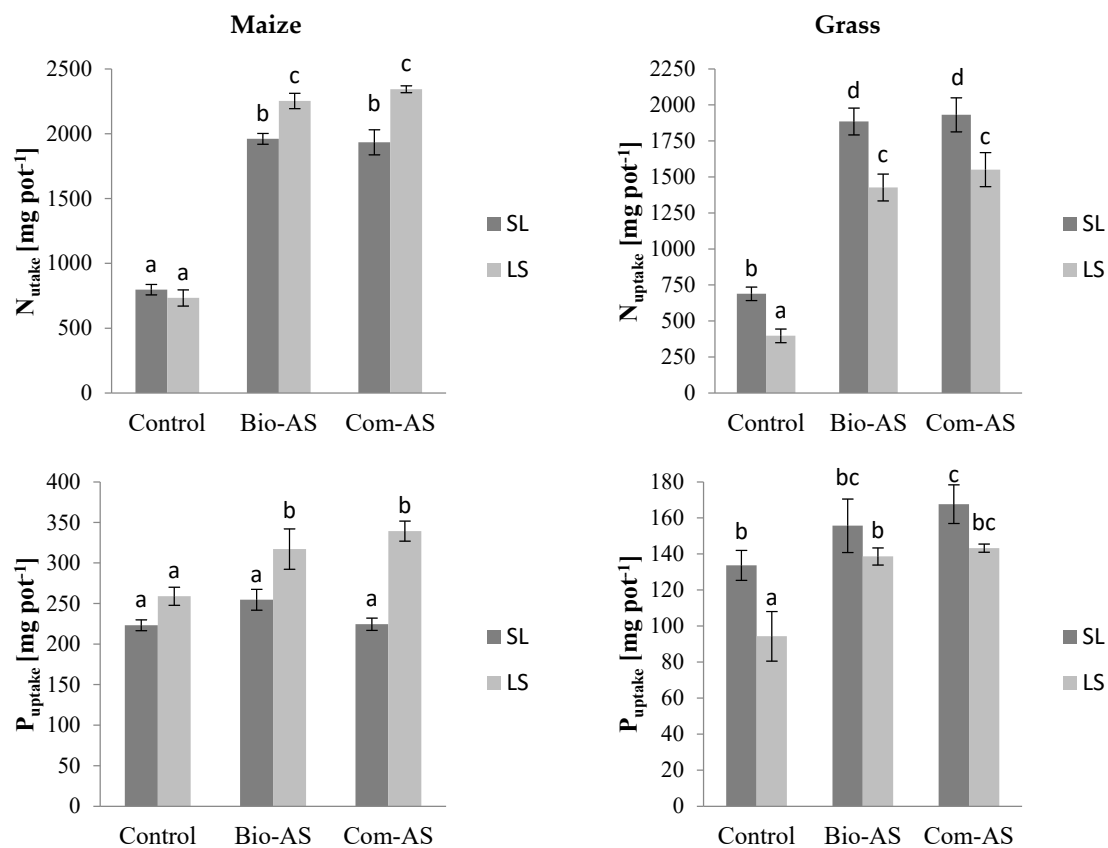


Figure 2. Cont.

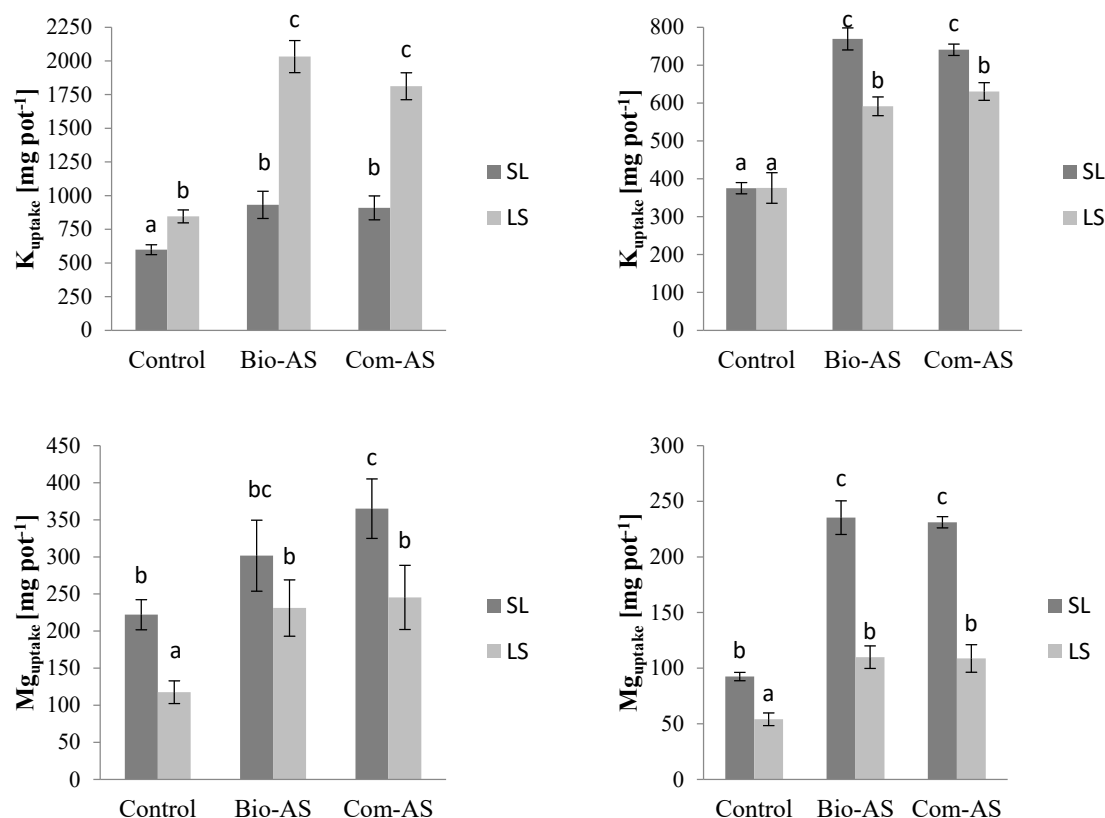


Figure 2. Uptake of NPKMg by maize and grass on objects fertilised with ammonium sulphate from the bio-refinery—Bio-AS, commercial ammonium sulphate—Com-AS, and on control treatment (control, without fertilisation). The standard deviation within each treatment ($n = 3$) is indicated by the line extending the column. Different letters indicate significant differences ($P \leq 0.05$).

3.3. Agronomic Value of Bio-AS from the Bio-Refinery—Soil Characteristics

The applied fertilisation affected the chemical soil properties (Table 5). On control treatment, the pH of the analysed soils was in the range of 6.1–6.4. As a result of fertilisation with Bio-AS and Com-AS, values of soil pH decreased to approximately 5.1–5.4. When uptaking NH_4^+ , plants release H_3O^+ ions, causing soil acidification [40]. The mechanism of soil acidification related to the physiology of NH_4^+ uptake by plant roots was intensified by the presence of free H_2SO_4 in ammonium sulphate (0.22%) (Table 2). Results of our study suggest that the Bio-AS obtained in the bio-refinery rapidly and strongly acidified the soil (Table 5). Notice, however, that the acidifying effect of Bio-AS was similar to the activity of the commercial fertilizer Com-AS. It can be, therefore, concluded that the application of Bio-AS on production fields will not require the implementation of practices aimed at the neutralisation of soil acidification, other than in the case of application of Com-AS fertilizers.

Pursuant to expectations, fertilisation with Bio-AS and Com-AS had no quantifiable effect on the content of total nitrogen in the soil. In comparison to control objects, higher soil acidification and P uptake by maize and grass caused a significant decrease in the content of active (P_{CaCl_2}) and, to a lower degree, available (P_{M_3}) forms of phosphorus in both soils fertilised with Bio-AS and Com-AS. On average, in soils of objects fertilised with nitrogen, the content of P_{CaCl_2} was approximately 77.5%, and P_{M_3} was only approximately 9% lower than in soil on control objects (Table 5). Although the assessment of the possibilities of nourishing plants with phosphorus commonly applies results of soil tests concerning the abundance of available forms of phosphorus in the soil [43], the differences in uptake of the element by plants cultivated on (strongly acidified) objects with nitrogen fertilisation and (weakly acidified) control objects evidenced in our experiment suggest that the availability of P for plants was determined, to a greater degree, by processes limiting the solubility of phosphates

in the soil solution than the content of phosphorus theoretically available for plants in the soil (P_{M3}) measured by the Mehlich-3 method.

The content of available and active forms of potassium and magnesium in the analysed soils was generally shaped similarly to the content of available and active forms of phosphorus. Notice, however, that soil acidification resulting from the application of nitrogen fertilizers had a considerably smaller effect on the exchange of potassium ions between the solid phase of soil and soil solution than on the phosphorus compounds in the soil. This is suggested by considerably smaller differences in the content of K_{CaCl2} determined in soils treated with nitrogen fertilizers and control objects (Table 5) in spite of considerably higher uptake of K than P by the plants (Figure 2). In the case of the content of magnesium, soil acidification contributed to an increase in the activity of the element in the soil. In silty loam (SL), in spite of significant differences in uptake of Mg by plants (Figure 2), the differences in the content of Mg_{CaCl2} on strongly acidified objects treated with nitrogen fertilizers and weakly acidified control objects were insignificant (Table 5). This was accompanied by a considerable decrease in the content of Mg_{M3} in the soil, suggesting intensive supplementation of the soil solution with Mg^{2+} ions from the solid phase of the soil. Lower abundance and exhaustion of Mg_{M3} resources in loamy sand as a result of uptake of the element by plants limited the possibility of efficient supplementation of resources of Mg_{CaCl2} (Table 5). Therefore, the content of Mg_{CaCl2} in light soil treated with nitrogen fertilizers was considerably lower than on the control object.

Table 5. Characteristics of the soils collected after plants cut down.

Soil	Fertilization	pH _{KCl}	TKN (g·kg ⁻¹)	P _{CaCl2}	P _{M3}	K _{CaCl2} (mg·kg ⁻¹)	K _{M3}	Mg _{CaCl2}	Mg _{M3}
After Maize Harvesting									
Silty loam SL	Control	6.1 b	2.7 ns	10.9 c	86.7 b	25.2 b	78.6 b	130.5 ns	351.0 b
	Bio-AS	5.4 a	2.8 ns	2.4 a	80.0 a	17.8 a	66.1 a	128.4 ns	246.4 a
	Com-AS Fertilizer	5.3 a **	2.7 ns ns	3.8 b ***	82.3 a **	18.2 a ***	64.4 a ***	129.2 ns ns	252.6 a ***
Loamy sand LS	Control	6.1 b	0.7 ns	14.7 c	84.1 b	50.5 b	94.6 b	20.3 b	63.5 b
	Bio-AS	5.1 a	0.8 ns	1.7 a	73.3 a	26.0 a	64.4 a	15.7 a	48.6 a
	Com-AS Fertilizer	5.2 a ***	0.8 ns ns	3.2 b ***	77.5 a ***	25.7 a ***	67.3 a ***	15.3 a **	46.7 a ***
After Grass Harvesting									
Silty loam SL	Control	6.4 b	2.6 ns	11.8 b	81.2 b	26.0 b	84.6 ns	133.0 ns	312.6 b
	Bio-AS	5.4 a	2.7 ns	3.3 a	78.4 a	21.7 a	82.0 ns	122.3 ns	245.6 a
	Com-AS Fertilizer	5.3 a **	2.7 ns ns	3.5 a ***	78.6 a *	23.0 ab *	80.1 ns ns	127.5 ns ns	254.3 a **
Loamy sand LS	Control	6.1 b	0.8 ns	15.0 c	90.0 b	48.1 b	96.4 b	19.8 b	57.8 b
	Bio-AS	5.1 a	0.8 ns	2.2 a	74.0 a	20.2 a	76.8 a	14.8 a	35.3 a
	Com-AS Fertilizer	5.2 a ***	0.8 ns ns	3.5 b ***	76.1 a ***	25.0 a **	72.7 a ***	15.0 a ***	36.3 a ***

^a Statistical significance of fertilizer: * $P \leq 0.05$; ** $P \leq 0.01$; *** $P \leq 0.001$.

Different letters in the column indicate significant differences ($P \leq 0.05$) between different fertilizer treatments separately for soils (SL and LS) and crops (grass and maize).

3.4. Economic Performance of Installation

Like other sectors, agriculture contributes to a number of negative environmental effects related mainly to the emission of methane to the atmosphere and biogenic elements to the soil and water. Processing agricultural waste products in agricultural bio-refineries can help reduce the negative environmental effects of agriculture. Until now, the evaluation of agricultural waste processing in biogas plants was limited, to a major extent, to the analysis of the environmental benefits and economic profitability. It should be emphasized that the production cycle may be extended by subsequent stages, including the processing of digestate produced in a biogas plant. This study presents the results of analyses that covered an experimental bio-refinery consisting of a biogas plant and a digestate processing plant for recovering unused nutrients as mineral fertilizers. Irrespective of the

fact that the biomass is a renewable raw material, the possibilities of its production remain limited; hence, its processing should be carried out in an economically and energetically efficient way [44–46]. An effective bio-refinery should operate at the lowest possible costs to ensure the cost competitiveness of the end-products. At the current level of the development of the bio-refinery technology, it can be assumed that economically efficient bio-refineries remain still a theoretical concept; however, one can take actions to challenge this status in practice.

The economic effects of ammonium sulphate recovery were assessed on the basis of technical and organizational parameters of the De Marke bio-refinery described above. This installation was located on a farm with an area of 44 ha and dairy cattle population of 85 cows. The parameters of the installation allowed to utilize all organic fertilizers produced on the farm. In the analysis of economic performance of installation, it was assumed that part of the produced ammonium sulphate (with a content of N 1.4%) was used on the farm for substitution of nitrogen fertilizers with purchases. Of the 807 t of ammonium sulphate solution produced, 528 t were intended for the internal needs of a farm, of which 28 tons was UAN (N 27%). The scale of eliminated purchases of UAN at the same time determined the financial benefits generated by processing digestate, increased by the assumed sale of the remaining part of ammonium sulphate (i.e., 46 t). An additional benefit of using the tested installation is produced duckweed, which can substitute for purchased feed. This feed is predestined especially for use in extensive and medium intensive production systems [44]; hence, the benefits of its use in Poland and the United Kingdom are greater than in the Netherlands. Aggregated revenues and costs and the annual financial result (assuming a lifetime of 15 years) for the three countries included in the analysis are presented in Table 6. Definitely the highest value of revenues was recorded in the case of the Netherlands (EUR 77.8 thousand) and the lowest in Poland (EUR 48.7 thousand). In the case of Poland and the United Kingdom, the main share in the structure of revenues was the sale of electricity generated from CHP, while in the Netherlands, savings were due to avoided expenditures on utilization of manure excess (the manure needs to be transported at large distances). The amount of manure produced in Poland and UK could be utilized locally for crop production and does not require additional expenditures. The estimated share of revenues from the production of ammonium sulphate in all cases was at a similar level (13.7% in Poland, 11.8% in the Netherlands, and 12.1% in the United Kingdom). Much smaller differences were observed on the cost side, which ranged between 42–43 thousand EUR per farm. The observed differences in revenues translate into significant differences in the annual financial result, the value of which would be the lowest in Poland and the highest in the Netherlands.

Table 6. Estimated value of revenues, costs, and annual financial result of ammonium sulphate production facility at the farm level.

Specification	Country			
	Poland	The Netherlands	United Kingdom	
Revenues (EUR farm ⁻¹)	Electricity	30,715	30,341	41,348
	Sales of ammonium sulphate solution (1.4% N)	6700	9200	7258
	Avoided expenditures on utilization of manure excess		33,995	
	Savings due to using duckweed as a feed for animals (based on value of saved feed).	11,314	1632	11,314
	Total (EUR farm ⁻¹)	48,729	75,168	59,920
Operational costs (EUR farm ⁻¹)	Materials (active carbon, sulphur acid, natrium hydroxide, water)	6618	6618	6618
	labour costs	4550	9100	9100
	insurances	2215	2606	2606
	Equipment maintenance cost (4% value—digester, CHP, stripping unit facilities)	17,721	20,848	20,848
	Financial costs (interest on loans)	11,296	2870	4417
	Total	42,400	42,042	43,589
Annual operational income (EUR farm ⁻¹)	6329	33,126	16,331	

Source: own results.

The analysis was complemented with an assessment of investment effectiveness using indicators such as NPV (net present value), IRR (internal return rate), and a simple return on invested equity. Results of the economic performance of investment are presented in Table 7.

Table 7. Investment effectiveness analysis.

Specification	Country		
	Poland	The Netherlands	United Kingdom
Total investments costs (EUR)	443,023	521,203	521,203
Public support (investment grant) (EUR)	69,767	331,034	208,481
NPV (EUR)	−291,238	230,862	−100,865
IRR (%)	−14%	15.4%	−3%
Simple payback period (year)	58.98	5.74	19.15

Source: own results.

The results of the investment effectiveness analysis show that with the assumed interest rate for alternative investment (at 4% in PL and 2% in NL and UK) and 15 years of operation, only in the Netherlands would the investment be profitable. In this case, the internal rate of return would be 14%, and the payback period would be less than 6 years, while in the case of Poland and the UK the investment would result in a loss. A simple payback period for Poland would reach almost 60 years, and for the UK almost 20 years. The observed differences in the level of investment efficiency are primarily a consequence of the differences in the level of public financial support that can be received, which is particularly high in the Netherlands. The need to dispose of surplus liquid manure in the Netherlands is significant because of the high concentration of animal production, which makes it impossible to use all available liquid manure for the needs of plant production. The possibility of processing part of the nitrogen from organic fertilizers into a mineral form allows for significant savings, which, apart from the subsidies obtained, exaggerate the positive economic result of the project in Dutch conditions.

4. Conclusions

The ammonium sulphate solution can be used as a valuable nitrogen fertilizer. Bio-AS is obtained as a result of the ammonia-stripping process from effluent after struvite precipitation from the liquid fraction of digestate in a farm-scale bio-refinery. The study shows that Bio-AS impacts the yields of plants, uptake of nitrogen, phosphorus, potassium, and magnesium from the soil by plants, as well as soil properties similarly as commercial ammonium sulphate. Bio-AS does not require additional practices aimed at neutralisation of soil acidification different from those necessary in the case of application of industrial ammonium sulphate. This leads to the conclusion that recovered ammonium sulphate can successfully replace commercial ammonium sulphate in the plant production. Moreover, removal of nitrogen from organic waste and the accompanying production of valuable nitrogen fertilizer contributes to a number of environmental benefits related to both limiting greenhouse emissions and decreasing the use of fossil fuels, in particular the natural gas used by the fertilizer industry in the synthesis of ammonia. Research results indicate that the economic results of the ammonia-stripping unit installation at the farm level are strongly influenced by the local market conditions and public support. In Dutch conditions, characterized by a very high concentration of animal production, the ammonia-stripping unit installation can be profitable. This is due both to the specific forms of public support for farmers seeking to mitigate the negative impact of agriculture on the environment and the high costs of liquid manure disposal resulting from the applicable restrictions in the Netherlands. In the United Kingdom, the economic results of the ammonia-stripping unit installation are only marginally negative, while in Poland, because of the much lower public support rate, the facility will generate loss. However, the problem is more complex because, by financing investments for the environment, taxpayers can contribute to reducing the negative impact of agriculture on the environment by bearing part of the costs associated with food production. Valuation of the effects of

investment in proenvironmental solutions is, however, very difficult. It is worth remembering that the bill covering the profitability of individual solutions at the farm level is incomplete, and, despite the fact that it can be useful in individual assessments, it does not determine the economic legitimacy from a social point of view.

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Abbreviations

DM	Dry matter weight
FM	Fresh matter weight
Bio-AS	Ammonium sulphate from bio-refinery
Com-AS	Ammonium sulphate – commercial mineral fertilizer
LS	Soil—loamy sand
SL	Soil—silty loam
ANR	The apparent fertilizer N recovery
REF	The related fertilizer efficiency
NUE	The nitrogen use efficiency
$P_{CaCl_2}, K_{CaCl_2}, Mg_{CaCl_2}$	Active forms of phosphorus, potassium, and magnesium in soil
$P_{M_3}, K_{M_3}, Mg_{M_3}$	Available forms of phosphorus, potassium, and magnesium in soil
UAN	Urea ammonium nitrate solution
NPV	Net present value
IRR	Internal return rate

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