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# Anaerobic Digestate from Biogas Plants—Nuisance Waste or Valuable Product?

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**Abstract:** Biogas production in waste-to-energy plants will support the decarbonization of the energy sector and enhance the EU's energy transformation efforts. Digestates (DG) formed during the anaerobic digestion of organic wastes contain large amounts of nutrients. Their use for plant fertilization allows for diversifying and increasing the economic efficiency of farming activities. However, to avoid regional production surpluses, processing technologies allowing the acquisition of products that can be transported over long distances are required. This study therefore aimed at determining the effect of applied methods of DG treatment on the chemical composition of the resulting products and their effect on the yields and chemical composition of plants. The following digestate-based products (DGBPs) were tested: two different digestates (DGs), their liquid (LF) and solid fractions (SF) and pellets from DGs (PDG), and pellets form SFs (PSF). Results from the experiment show that during SF/LF separation of DGs, >80% of nitrogen and 87% of potassium flows to LFs, whereas >60% of phosphorus and 70% of magnesium flows to SFs. The highest yields were obtained using untreated DGs and LFs. The application of DGs and LFs was not associated with a leaching of nutrients to the environment (apparent nutrients recovery from these products exceeded 100%). Pelletized DG and SF forms can be used as slow-release fertilizer, although their production leads to significant nitrogen losses (>95%) by ammonia volatilization.

**Keywords:** digestate-based products; alternative fertilizers from biogas plants; bioeconomy

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## 1. Introduction

The European Union (EU) has promoted a waste-to-energy (WTW) initiative to minimize waste and greenhouse gas (GHG) emissions, and increase renewable energy production [1]. Examples of WTW technology are thermal treatment (incineration), pyrolysis, gasification, mechanical biological treatment, the biological drying process as a source of refuse-derived fuel or solid-recovered fuel, and anaerobic digestion (AD) [1]. Among the technologies mentioned, AD is very promising and has many advantages. AD is a biological process for converting organic waste into biogas [2], which has recently become a promising source of renewable energy. The key advantage of AD is that it can handle a wide range of organic waste forms, especially wastes with high moisture content (60–99%) [1]. These types of waste are particularly difficult to manage and recover energy from with the use of other technologies. In biogas plants, manure, slurry, agricultural residues, energy crops, by-products from the agri-food industry or wastewater treatment plants, and other organic wastes are subject to anaerobic digestion. Most biogas production in the EU (76%) comes from plants grouped under the term "methanation of non-hazardous waste or raw plant matter ("other biogas")" [3]. Biogas is currently most often utilized in Combined Heat and Power (CHP) units consisting of gas engines co-generating heat and electricity.

The electrical efficiency of such systems is rather low, reaching 35−43% [4]. Biogas can also be upgraded to biomethane by $CO_2$ extraction. Biomethane can be injected into gas distribution grids, and stored and distributed as biofuel for vehicles [3]. A recent outlook on the future of biogas applications indicated that biogas may be used for the production of high-purity hydrogen [5].

Increasing biogas production is part of the European Commission's medium-term strategies. An acceleration of this development is currently expected due to political tensions in the Eastern European region [6]. The European Green Deal stipulates obtaining climate neutrality in the EU by 2050, and reduction in GHG emissions in the EU by 50% by 2030. These ambitious objectives require the implementation of a strategy of low-emission management of organic waste. Landfilling of such waste results in the emissions of GHGs, particularly $CH_4$ and $CO_2$ [7]. The European Commission has also developed the EU Methane Strategy, which focuses on three main sources of $CH_4$ emissions: energy (coal, oil, gas), agriculture, and waste. According to the estimates of the International Energy Agency [8], approximately 570 million tonnes of methane is emitted to the atmosphere annually. A share of 25% of anthropogenic emissions arises from agriculture (among others animal production and rice cultivation). The introduction of fees for methane emission from agriculture will be particularly unfavorable for farms with animal production. Methane is produced both as a result of enteric fermentation, and at the stage of storage and application of manure. In the years 2016−2019, in the European Union (EU-27) and UK, animal farming generated more than 1.4 billion tonnes of manure annually [9]. This is an immense source of potential methane emission that may be mitigated by the use of BP. The analyses of the European Commission show that biogas input could increase from 16.6 Mtoe in 2019 to 30 Mtoe by 2030, and to 45–79 Mtoe by 2050 [1,3].

Considerations regarding the possibility of increasing biogas production conducted in the context of the EU energy policy usually do not take into account the management of the digestate (DG). Furthermore, biogas production is related to generating considerable amounts of DG constituting a mixture of organic and mineral compounds with high moisture content [10]. A biogas plant with power of 1 MW (megawatt) can produce approximately 40,000 tonnes of DG annually. Promoting biomethane and hydrogen production from biogas will require the construction of larger biogas plants (approximately 3 MW). Such installations will produce substantial amounts of DG. Further, the management (i.e., recycling) of the large amount of liquid digestate derived from the AD becomes an important issue.

Digestate is commonly applied to soils as an organic fertilizer [11]. DG is characterized by a high level of hydration. This limits the possibilities of its transport over large distances. Biogas plants attempt to solve the problem through the application of different techniques of DG treatment. DG is usually subject to mechanical separation, resulting in the liquid and solid fraction (LF and SF, respectively) [12]. LF can be applied to fields or in cultivation of aquatic plants and algae [13,14]. Nitrogen and phosphorus recovery from LF is also practiced through struvite precipitation and ammonia stripping [15]. Although many authors confirmed a high fertilizer value of struvite and ammonium sulphate [16–18], the recovery methods have limited practical application. This results from the fact that the alkaline effluent remaining after these processes is characterized by considerable salinity. Study results by Sońta et al. [13] show that the effluent (EFL) after struvite precipitation and ammonia stripping from LF had a pH value of 12.2, and potassium and sodium content of 3.8 and 9.2 g $kg^{-1}$ FM (fresh matter), respectively. Management of this effluent as a medium for cultivating *Lemna minuta* required very high dilution of EFL with water to create conditions suitable for duckweed growth. SF resulting from separation can be applied to fields [11], composted [19], dried by heat energy generated by the biogas plant, or pelletized. Pelletized SF (PSF) can be applied to fields or burned in energy production [20]. Research is also being conducted on the pyrolysis of SF leading to the production of gas and biochar [21]. As a very durable carbon compound, biochar is considered to be a $CO_2$ sink [22]. In summary, manifold technologies for processing DG into products with added value currently exist. However, most emerging technologies require significant financial investments and are thus not always economically viable. Due to these and other technical challenges, the predominant treatment of DG is still its use as fertilizer.

The use of DG for crop nutrition gains from the rapid increase in mineral fertilizer prices. These lead to an increase in the cost of cultivation and, consequently, food prices. Farmers are dependent on alternative sources of nutrients for their crops. This increases the demand for DG and the products resulting from DG treatment. Accordingly, there is still a need for research on the fertilizer efficiency of the different products obtained from DG. Most of the publications on biogas production focus on the evaluation of the effectiveness of anaerobic digestion, ignoring the issue of digestate management. Furthermore, the search for methods for the rational use of digestate is as important as the search for methods to increase the efficiency of biogas production. Due to the considerable amount of available digestate, its treatment must be optimized to avoid negative effects on the environment, such as excessive ammonia emission, leaching of N and P to waterbodies, or an increase in the content of heavy metals in plants. This study therefore aimed to determine the effect of different methods of DG treatment on the chemical composition of the resulting products, and their resulting effect on the yields and chemical composition of plants. Additionally, the article presents a methodology for calculating the flow of nutrients to the liquid and solid fractions during the separation of raw digestate, which should be considered as a significant added value of the work. This is especially important from an engineering point of view. Estimating the chemical composition of the LF of the DG is important at the stage of selecting the technology and designing the biogas plant. The LF can be returned to the fermenter in order to dilute the solid substrates. The inflow of an excessive amount of potassium ions contained in the LF of the DG may lead to salinity and inhibition of the biological process of methane fermentation. The calculation formulas proposed in the work will allow the assessment of the chemical composition of the LF without its laboratory analysis. This will enable quick balancing and selection of the volume of the LF that can be returned to the fermenter, and the volume that should be utilized by other methods.

## 2. Materials and Methods

### *2.1. Collection of Digestate-Based Produtcts*

The study was conducted using digestate obtained from anaerobic digestion conducted in two fermenters with a volume of 140 L. In the first fermenter (F1), stillage (rye) and maize silage were used as substrates, and in the second (F2), pig slurry and maize silage were used. A detailed description of the fermentation and substrates is presented in [23]. The obtained digestate samples were separated into the solid and liquid fraction. The solid fraction was dried on an oil drying floor up to 85% dry weight, and pelletized on a 30 kW matrix pelletizer (Testmer, Reguły, Poland) (Figure 1). The obtained pellets were approximately 10–20 mm long and 0.6 mm in diameter (Figure 2). Due to the partition of nutrients during digestate separation affecting the fertilizer value of the obtained products, the study also involved drying and pelletizing digestate.

The following digestate-based products (DGBPs) were obtained: liquid digestate from fermenters F1 and F2 (DG1, DG2), solid fraction from DG1 and DG2 (SF1, SF2), liquid fraction from DG1 and DG2 (LF1, LF2), pellets from DG1 and DG2 (PDG1, PDG2), and pellets from SF1 and SF2 (PSF1, PSF2) (Figure 2).

**Figure 1.** Matrix pelletizer (Testmer, Reguły, Poland).

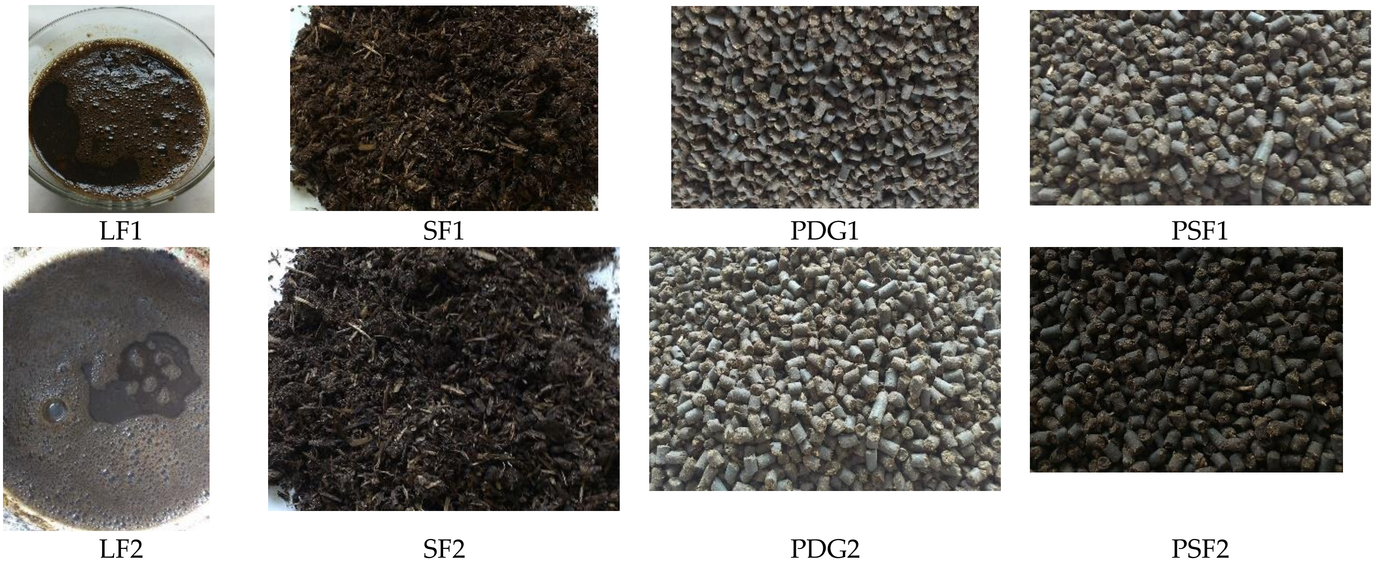


**Figure 2.** The digestate-based products (DGBPs): liquid fraction from DG1 and DG2 (LF1, LF2), solid fraction from DG1 and DG2 (SF1, SF2), pellets from DG1 and DG2 (PDG1, PDG2), and pellets from SF1 and SF2 (PSF1, PSF2).

### *2.2. Pot Experiment*

The pot experiment was conducted in an experimental greenhouse of the Warsaw University of Life Sciences. Soil samples (0–25 cm soil layer) were collected in Skierniewice (51°96′48″ N, 20°15′92″ E). The research covered soil fertilized with nitrogen, phosphorus, and potassium fertilizers without liming since 1923. The soil can be described as Luvisol (FAO 2006). The pots were filled with 15 kg of soil and mixed with different DGBPs. DGBPs were applied in a dose corresponding to 170 kg N ha$^{-1}$ (0.68 g N pot$^{-1}$). Doses of particular nutrients and heavy metals introduced to the soil with DGBPs are presented in Table 1.

**Table 1.** Doses of macronutrients (g $pot^{-1}$) and heavy metals (mg $pot^{-1}$) used in the experiment (C = carbon, N = Nitrogen, P = Phosphorus, K = Potassium, Mg = Magnesium, Ca = Calcium, Zn = Zinc, Cu = Copper, Mn = Manganese).

| Fertilization * | g C | g N | g P | g K | g Mg | g Ca | mg Zn | mg Cu | mg Mn |
|---|---|---|---|---|---|---|---|---|---|
| DG 1 | 2.57 | 0.68 | 0.06 | 0.69 | 0.03 | 0.05 | 3.30 | 0.88 | 1.22 |
| DG 2 | 4.42 | 0.68 | 0.16 | 0.46 | 0.12 | 0.12 | 4.26 | 1.33 | 2.09 |
| LF 1 | 1.71 | 0.68 | 0.03 | 0.68 | 0.01 | 0.05 | 2.51 | 0.52 | 0.97 |
| LF 2 | 2.44 | 0.68 | 0.07 | 0.40 | 0.02 | 0.10 | 3.04 | 0.88 | 1.48 |
| SF 1 | 6.93 | 0.68 | 0.17 | 0.35 | 0.10 | 0.12 | 4.70 | 2.45 | 1.95 |
| SF 2 | 16.43 | 0.68 | 0.60 | 0.82 | 0.45 | 0.25 | 10.69 | 3.40 | 5.62 |
| PSF 1 | 12.24 | 0.68 | 0.31 | 0.68 | 0.19 | 0.21 | 11.01 | 6.11 | 3.98 |
| PSF 2 | 12.86 | 0.68 | 0.43 | 0.88 | 0.33 | 0.29 | 13.52 | 3.87 | 7.12 |
| PDG 1 | 9.79 | 0.68 | 0.27 | 1.02 | 0.15 | 0.25 | 13.57 | 4.62 | 4.79 |
| PDG 2 | 11.04 | 0.68 | 0.41 | 1.09 | 0.35 | 0.31 | 14.25 | 5.93 | 5.15 |

* DG 1–digestate from fermenter 1, LF 1–liquid fraction of DG 1, SF 1–solid fraction of DG 1, PSF 1–pellet from SF 1, PDG 1–pellet from DG 1, DG 2–digestate from fermenter 2, LF 2–liquid fraction of DG 2, SF 2–solid fraction of DG 2, PSF 2–pellet from SF 2, PDG 2–pellet from DG 2.

The fertilizer effect of the analyzed DGBPs was compared to that on control objects, which were not subject to fertilization. The experiment was arranged as a completely randomized design with four replications. The location of the pots was randomized daily. The test plant was maize of the Bosman cultivar cultivated for green forage. 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. 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. After biomass harvest of maize, samples were weighed before and after drying (in an oven set at 60 °C) to determine their fresh and dry matter.

### *2.3. Estimation of the Distribution of DM, FM, and Nutrients Flowing from Digestates into Solid Fraction (SF) and Liquid Fraction (LF)*

The distribution of dry matter (DM), fresh matter (FM), and nutrients flowing from digestates into solid fraction (SF) and liquid fraction (LF) were calculated as fol-lows according to the formulas:

$$DM_{dstLF} = \frac{FS_{DM} - DG_{DM}}{\left(\frac{FS_{DM}}{LF_{DM}}\right) - 1} \quad (1)$$

$$DM_{dstSF} = DG_{DM} - DM_{dstLF} \quad (2)$$

$$FM_{dst(LF\ or SF)} = \frac{DM_{dst(LF\ or SF)}}{DM_{cont(LF\ or SF)}} \quad (3)$$

$$N_{dst(LF\ or SF)} = FM_{dst(LF\ or SF)} \times N_{cont} \quad (4)$$

where:

$DM_{dstLF}$—distribution of DM (dry matter) into LF; $DM_{dstSF}$—distribution of DM into SF; $FM_{dst(LF\ or\ SF)}$—distribution of FM into LF or SF; $N_{dst(LF\ or\ SF)}$—nutrients flow into LF or SF; $N_{cont}$—nutrient content in LF or SF; $FS_{DM}$—DM content in FS; $DG_{DM}$—DM content in DG; $LF_{DM}$—DM content in LF.

### *2.4. Estimation of Nutrients Use Efficiency*

Apparent fertilizer nutrient recovery was calculated as follows according to the formula by Cavalli et al. [24]:

$$ANR\ (\%) = \frac{\text{Nutrient uptake on FO} - \text{Nutrient uptake on CTR}}{\text{Nutrient dose on pot}} \times 100 \quad (5)$$

where: FO—fertilized object; CTR—control object.

### 2.5. Analytical Procedures

All analytical tests were carried out in a laboratory belonging to the Division of Agricultural and Environmental Chemistry, Agricultural Institute, Warsaw University of Life Sciences–SGGW. Sampled DGBPs were dried at 60 °C using drier PREMED (Marki, Poland) to estimate Total Solids content (TS). The dried and ground plant material and DGBPs were mineralized in $HNO_3$, $H_2O_2$, and HCl using a DK 20 digestion unit Model (VELP Scientifica, Usmate, Italy). K, Mg, Ca, Cu, Zn, and Mn content in the samples was measured using an atomic absorption spectrometer (AAS) SOLAAR (Thermo Elemental, Cambridge, UK) (PN-EN ISO 6869:2002). P content in the samples was determined by means of the vanadomolybdophosphoric method using a Genesys 10 UV-VIS (ultraviolet and visible light region) spectrophotometer (Thermo Electron Corporation, Madison, WI, USA) (PN ISO 6491:2000). The content of organic carbon (C) in DGBPs was measured with a Thermo Electron-C analyzer model TOC-500 (Shimadzu, Kyoto, Japan) (PN-EN 15936:2013-02). Total N content ($N_T$) was measured with a Vapodest analyzer model VAP 30 (Gerhardt, Bonn, Germany). $NH_4^+$-N content was measured using a Skalar San Plus analyzer (Breda, The Netherlands) (PN-EN ISO 5983-1:2006). The pH value of DGBPs was measured by means of the potentiometric method using a pH meter (Schott, Mainz, Germany) (ISO 10390:2021). The analyses employed the AgroMAT Compost 140—25-111, and corn flour INCT-CF-3 Certified Reference Materials.

### 2.6. Statistical Analysis

One-way analysis of variance (ANOVA) was carried out to determine statistically significant differences between treatments (at $p < 0.05$). The mean values were compared in a Tukey's (HSD) multiple-comparison test. Relationships between the nutrient dose and maize yield, and the macronutrients and heavy metal content in maize, were evaluated using multiple regression with backward selection of variables. Statistical analyses were carried out using Statistica PL 13.3 software (Tulsa, OK, USA).

## 3. Results and Discussion

### 3.1. Chemical Characteristics of Digestate and Products Obtained from Its Treatment

All analyzed products obtained from DGs were characterized by alkaline reaction (pH above 7.0). Digestates not subject to processing (DG1, DG2) and liquid fractions (LF1, LF2) were characterized by low content of total solids (TS) (approximately 5.4 and 3.1%, respectively), and relatively low concentration of nutrients per 1 kg FM (fresh matter) (Tables 2 and 3). Due to higher content of TS, the remaining products contained higher amounts of nutrients (mean content of TS in SF1 and SF2 was approximately 16.0%, and in pellets more than 95%). DG1 and DG2 were characterized by low content of C (on average approximately 20 g C $kg^{-1}$ FM). The obtained data showed that during LF/SF separation, the SFs mainly become enriched in carbon (C) (Table 4). The highest C content was determined in pellets obtained from DGs and SFs (on average approximately 332 g C $kg^{-1}$ FM).

$N_T$ content in DG1 and DG2 was approximately 4.85 and 3.35 g $N_T$ $kg^{-1}$ FM, respectively. This indicates that the type of organic materials used for anaerobic digestion affects the chemical composition of the resulting digestate [25]. More than 80% of nitrogen flows from DG to LF, while only 20% flows to the solid fraction. This shows that, in DG, the dominant form of nitrogen was soluble ionic forms ($NH_4^+$-N). The reported results are in agreement with other studies [26,27]. In the analyzed digestates (DG1, DG2), the share of $NH_4^+$-N in $N_T$ reached an average of approximately 70%. As confirmed by other authors [28], this suggests that digestate has a very high fertilizer potential with a high amount of plant-available N. Mechanical separation caused an increase in the $NH_4^+$-N/$N_T$ ratio in the liquid fraction (Table 2), with an average increase of approximately 97%, and a decrease in the solid fraction that averaged approximately 56%. The lowest $NH_4^+$-N/$N_T$

ratio was measured in the pellets, averaging approximately 6.7% (Table 2). The comparison of the content of $NH_4^+$-N in PDG and PSF with DG and SF indicate a decrease of about 96% in the PDG and PSF. This suggests intensive losses of ammonia with water vapor in the course of drying preceding the pelletizing process. The alkaline reaction of digestate-based products (DG and SF) could have favored the release of $NH_3$. The volatilization of $NH_3$ during the processing of digestate to pellets was addressed in the study by Valentinuzzi et al. [29]. Ammonia negatively affects human health and leads to air quality degradation. $NH_3$ emission and its further transformations constitute a significant indirect $N_2O$ emission pathway in agricultural systems [30]. Drying of DG and SF may thus contribute to the global climate warming. According to Pan at al. [31], $NH_3$ emission results in 0.1−0.16 million tons of indirect $N_2O$-N emission per year. A potential solution may be the application of scrubbers with acid that would bond with the released ammonia in the course of processing digestate-based products. Another practice to minimize $NH_3$ emissions is decreasing the pH of SF by adding acid. Such solutions have been successfully used to reduce $NH_3$ emissions from slurry [32].

**Table 2.** Chemical characteristics of the samples (TS = Total Solids).

| Samples * | pH | TS % | C | $N_T$ | N-$NH_4$ | C:N |
|---|---|---|---|---|---|---|
| | | | g kg$^{-1}$ FM | | | |
| DG 1 | 7.74 | 5.11 | 18.32 | 4.85 | 3.67 | 3.8 |
| DG 2 | 7.34 | 5.69 | 21.78 | 3.35 | 2.17 | 6.5 |
| LF 1 | 7.71 | 3.07 | 10.82 | 4.30 | 4.12 | 2.5 |
| LF 2 | 7.40 | 3.12 | 11.58 | 3.23 | 3.19 | 3.6 |
| SF 1 | 7.66 | 16.5 | 67.04 | 6.58 | 3.74 | 10.2 |
| SF 2 | 7.32 | 16.56 | 80.47 | 3.33 | 1.85 | 24.2 |
| PSF 1 | 7.33 | 95.6 | 344.87 | 19.17 | 1.30 | 18.0 |
| PSF 2 | 7.23 | 96.69 | 317.70 | 16.80 | 0.99 | 18.9 |
| PDG 1 | 7.35 | 96.58 | 333.35 | 23.15 | 1.83 | 14.4 |
| PDG 2 | 7.28 | 94.63 | 334.28 | 20.58 | 1.31 | 16.2 |

* Abbreviations as in Table 1.

**Table 3.** Content of macronutrients and heavy metals in the samples.

| Samples * | P | K | Mg | Ca | Zn | Cu | Mn |
|---|---|---|---|---|---|---|---|
| | g kg$^{-1}$ FM | | | | mg kg$^{-1}$ FM | | |
| DG 1 | 0.44 | 4.94 | 0.22 | 0.34 | 23.52 | 6.25 | 8.73 |
| DG 2 | 0.81 | 2.28 | 0.61 | 0.61 | 20.98 | 6.56 | 10.28 |
| LF 1 | 0.22 | 4.27 | 0.06 | 0.33 | 15.86 | 3.28 | 6.14 |
| LF 2 | 0.31 | 1.90 | 0.08 | 0.46 | 14.46 | 4.20 | 7.05 |
| SF 1 | 1.62 | 3.38 | 0.92 | 1.17 | 45.52 | 23.74 | 18.88 |
| SF 2 | 2.92 | 4.00 | 2.18 | 1.24 | 52.35 | 16.65 | 27.52 |
| PSF 1 | 8.63 | 19.23 | 5.25 | 6.05 | 310.27 | 172.13 | 112.18 |
| PSF 2 | 10.64 | 21.79 | 8.26 | 7.09 | 333.92 | 95.53 | 175.85 |
| PDG 1 | 9.35 | 34.75 | 5.07 | 8.63 | 461.90 | 157.17 | 162.87 |
| PDG 2 | 12.52 | 32.89 | 10.71 | 9.35 | 431.23 | 179.42 | 156.01 |

* Abbreviations as in Table 1.

**Table 4.** Distribution (%) of FM and nutrients in SF and LF after mechanical separation of digestate.

| Samples * | FM | C | N | P | K | Mg | Ca | Zn | Cu | Mn |
|---|---|---|---|---|---|---|---|---|---|---|
| LF 1 | 84.8 | 47.4 | 78.5 | 43.1 | 87.6 | 26.7 | 61.2 | 66.0 | 43.5 | 64.5 |
| LF 2 | 80.9 | 37.8 | 80.4 | 31.0 | 66.8 | 13.4 | 53.9 | 53.9 | 51.6 | 52.0 |
| SF 1 | 15.2 | 52.6 | 21.5 | 56.9 | 12.4 | 73.3 | 38.8 | 34.0 | 56.5 | 35.5 |
| SF 2 | 19.1 | 62.2 | 19.6 | 69.0 | 33.2 | 86.6 | 46.1 | 46.1 | 48.4 | 48.0 |

* Abbreviations as inTable 1.

The rate of nutrients released from organic matter depends on its susceptibility to the processes of mineralization, determined by the ratio of carbon to nitrogen compounds (C:N). Soil N immobilization after anaerobic digestate application has been previously reported for products with the C:N ratio exceeding 25−30 [27]. All the analyzed digestate-based products were characterized by a narrow C:N ratio (ranging from 2.5 for LF 1 to 24.2 for SF 2) (Table 2). Thus, their mineralization in the soil and release of plant nutrients was fast. However, Valentinuzzi et al. [29] reported that the C:N ratio is not an accurate indicator to predict N mineralization in soil treated with anaerobic digestates. According to the authors, that kind of products contain organic matter with lower biodegradability in the soil. In the case of a very narrow C:N ratio, however, higher nitrogen losses are probable, as previously observed by Möller and Müller [33]. According to Sosulski at al. [34], the magnitude of nitrogen losses through leaching corresponds with the fertilization system, and was highest in the mineral-organic system. The application of mineral forms of nitrogen decreased the C:N ratio, increasing leaching of nitrogen.

Phosphorus is a depleting resource. Therefore, great attention is paid to the search for alternative sources [35]. Compared with P contents of wastewater or urine [36], the P content in digestate is relatively high. The N:P ratio is an important indicator for the assessment of the fertilizing properties of digestate-based products. Low N:P ratios (i.e., ≤2) in digestate may indicate P deficiencies that should be supplemented with mineral fertilizers containing P [29]. A high excess of P in relation to N may lead to an increased risk of run-off or leaching of P from soil to surface water bodies. Among the analyzed forms of digestate, in DGs and FCs, the N:P ratio was considerably higher than 2. Due to the lower P content, fertilization with the remaining forms, i.e., SFs, PSFs, and PDGs, did not increase the risk of phosphorus losses from the soil.

In the analyzed digestates DG1 and DG2, P content reached 0.44 and 0.81 g kg$^{-1}$ FM, respectively (Table 3). Thus, during separation of SF/LF, more phosphorus was supplied to SFs (approximately 57% from DG1 and 69% from DG2, Table 4). Literature data [12] indicate that, during SF/LF separation, only 30% of total amount of phosphorus flows to SF. Our results further show a high content of phosphorus in pellets obtained from DGs (9.35 and 12.52 g kg$^{-1}$ FM for PDG1 and PDG2, respectively). Due to the partitioning of P between SF and LF, pellets obtained from SFs contained less P than pellets from DGs (PDG). Pellets PSF1 contained approximately 8% less P than PDG1. In PSF2, P content was approximately 15% lower than in PDG2. Differences in potassium (K) content in the analyzed pellets were even more evident than differences in phosphorus content. K content in PSF1 was more than 44% lower than in PDG1, and in PFS2 approximately 34% lower than in PDG2 (Table 3). In digestate, potassium primarily occurs in an unbound ionic form that during separation mainly flows to the liquid fraction. In our study, 87% of K contained in DG1 flows to LF1 (Table 4). Such large flows of K to LF may disqualify the possibility of returning LF to the fermenter in order to dilute the solid substrates. Such an engineering solution is proposed [37], but as the conducted research shows, it may lead to excessive salinity and inhibition of methane fermentation. Potassium recovery from LF is difficult, because this nutrient forms soluble salts that cannot be precipitated from solution. Moreover, membrane technologies can be used to a limited extent [38]. More advanced treatment methods are too expensive considering the amount of LF produced in the biogas plant [37]. Hence, it can be concluded that LF, as a nitrogen- and potassium-rich, liquid, fast-acting fertilizer, is the best eco-friendly and cost-effective solution. Mg and Ca content in the analyzed digestate-based products was lower than the content of the remaining macroelements (Table 3). Magnesium content was the lowest in LF (averaging 0.07 g kg$^{-1}$ FM) and, as expected, the highest in pellets (from 5.1 g kg$^{-1}$ FM in PDG1 to 10.7 g kg$^{-1}$ FM in PDG2). During LF/SF separation, more magnesium flows to SF (approximately 73% from DG1 and 87% from DG2). The opposite dependency was observed in the case of Ca. During separation, more Ca flows from DGs to LFs (Table 4). Due to this, no considerable differences were recorded between Ca content in DGs and LFs.

Results indicate that the various forms of digestate may be a valuable source of nutrients for plants. The potential of digestate to harm the environment and human health, however, is a matter of concern [29]. An important indicator used to assess the agronomic quality of digestates is the content of heavy metals. Contents of heavy metals (HMs) in the analyzed digestate-based products were low (Table 3). The lowest content of HMs was determined in LFs and DGs. Mean content of HMs in the LFs (averaging LF1 and LF2) was approximately 15.2 mg Zn; 3.7 mg Cu; and 6.6 mg Mn $kg^{-1}$ FM. Mean content of HMs in the DGs (averaging DG1 and DG2) was 22.2 mg Zn; 6.4 mg Cu; and 9.5 mg Mn $kg^{-1}$ FM. Content of Zn and Mn in SFs was more than twice as much, and Cu more than three times higher, than in DGs. The obtained results correspond with the scientific literature. Exemplarily, Tambone et al. [12] report for DG: Zn content of 13.5 mg $kg^{-1}$ FM, Cu 4.2 mg $kg^{-1}$ FM; for the LF: 10.1 mg Zn $kg^{-1}$ FM and 3.0 mg Cu $kg^{-1}$ FM; and for SF: 69.9 mg Zn $kg^{-1}$ FM and 22.1 mg Cu $kg^{-1}$ FM. In our study, during SF/LF separation, more Zn and Mn flowed from DG to LF (Table 4). The distribution of Cu to LF and SF was divided evenly between SF and LF. The highest content of HMs was observed in pellets of both SFs and DGs.

### 3.2. Crop Yields

The results from this study showed that the use of digestate increased maize yields, and the form of digestate was a factor determining their size. Such fertilization effects have been observed in previous research studies with maize and other plants [39,40] (Table 5). The literature provides considerable data on the fertilizer value of digestates. Significant yield potential of digestate had also been demonstrated by Szymańska et al. [41]. According to Riva et al. [28], digestate application resulted in a maize yield as high as that obtained by using urea. Meanwhile, Greenberg et al. [42] reported that the use of digestate from AD resulted in lower aboveground crop biomass production than the application of mineral fertilizer. Lošák et al. [43] reported that the yield potential of digestate is higher when it is used in combination with mineral phosphate fertilizers. The average yield of maize in our study ranged from 252.75 g FM $pot^{-1}$ on the control object to 447.50 g FM $pot^{-1}$ on the object treated with DG2. For maize plants treated with DGBPs, considerably higher yields were obtained than for the control. However, considerably lower maize yields were obtained when fertilized with the pelletized form of DGs and SFs. This suggests that this form of digestate is rather suitable as a slow-nutrient-release (mid- and long-term) organic fertilizer. According to Dahlin et al. [44], pellets from digestate should find application in the private garden sector. A considerably greater (short-term) yield-generating effect was observed after fertilization with PDG1 and PDG2 than with digestate solid fraction pellets (PSF1 and PSF2). It appears unjustified to dry digestate for the purpose of retaining nutrients that easily flow to the liquid fraction during DG separation. The difference in the yields of maize between PSF1 and PSF2, and between PDG1 and PDG2, averaged approximately 38 g FM $pot^{-1}$ (11%). Relatively high crop yields were obtained on soils treated with unprocessed digestate DG2 and liquid fraction obtained from that DG (LF2). On average, the maize yields obtained under these treatments exceeded the control yield by 75%.

In summary, study results highlight that irrespective of substrates used for the production of biogas, an evidently better yield-generating effect is provided by unprocessed digestate and the liquid and solid fraction of digestate than SFs and DGs pellets. Regression analysis (Table 6) showed that among the applied nutrients, only the dose of $NH_4^+$-N has a statistically significant relationship with maize yield, indicating that yields mainly benefitted from these nutrients. This confirms that different forms of DGs containing an active form of nitrogen are a suitable alternative to mineral nitrogen fertilizers. Results suggest that digestate processing techniques should especially consider the retention of mineral N in the fertilizer mass. Heavy metal (HM) contents in the tested products had no significant effect on yields.

**Table 5.** Yields and chemical composition of maize.

| Fertilization * | Yields | N | P | K | Mg | Ca | Zn | Cu | Mn |
|---|---|---|---|---|---|---|---|---|---|
| | g FM pot$^{-1}$ | | | g kg$^{-1}$ DM | | | | mg kg$^{-1}$ DM | |
| DG 1 | 410.00 $^{d}$ | 16.70 $^{d}$ | 2.03 $^{b}$ | 19.10 $^{d}$ | 0.74 $^{a}$ | 1.86 $^{bc}$ | 15.26 $^{a}$ | 1.96 $^{a}$ | 45.73 $^{a}$ |
| DG 2 | 447.50 $^{g}$ | 17.41 $^{e}$ | 1.86 $^{b}$ | 14.75 $^{a}$ | 1.08 $^{cd}$ | 2.29 $^{de}$ | 15.79 $^{b}$ | 2.31 $^{b}$ | 59.22 $^{e}$ |
| LF 1 | 426.25 $^{ef}$ | 16.36 $^{cd}$ | 1.85 $^{b}$ | 18.24 $^{d}$ | 1.11 $^{cd}$ | 2.97 $^{f}$ | 17.50 $^{d}$ | 2.53 $^{cd}$ | 55.31 $^{d}$ |
| LF 2 | 440.25 $^{fg}$ | 16.21 $^{c}$ | 2.09 $^{bc}$ | 16.77 $^{c}$ | 0.97 $^{bc}$ | 3.12 $^{f}$ | 17.90 $^{e}$ | 2.56 $^{cd}$ | 56.17 $^{d}$ |
| SF 1 | 415.50 $^{de}$ | 17.58 $^{e}$ | 2.05 $^{b}$ | 16.38 $^{bc}$ | 0.84 $^{ab}$ | 1.48 $^{ab}$ | 15.81 $^{b}$ | 2.55 $^{cd}$ | 48.08 $^{b}$ |
| SF 2 | 418.00 $^{de}$ | 18.92 $^{f}$ | 2.34 $^{c}$ | 15.45 $^{ab}$ | 1.22 $^{d}$ | 2.28 $^{de}$ | 16.70 $^{c}$ | 2.24 $^{b}$ | 58.15 $^{e}$ |
| PSF 1 | 347.00 $^{b}$ | 17.44 $^{e}$ | 3.32 $^{f}$ | 24.78 $^{f}$ | 1.03 $^{c}$ | 1.40 $^{a}$ | 17.57 $^{d}$ | 2.32 $^{b}$ | 49.56 $^{b}$ |
| PSF 2 | 349.75 $^{b}$ | 15.68 $^{b}$ | 3.01 $^{e}$ | 25.46 $^{fg}$ | 0.75 $^{a}$ | 1.89 $^{cd}$ | 15.47 $^{a}$ | 2.66 $^{cd}$ | 48.65 $^{b}$ |
| PDG 1 | 384.75 $^{c}$ | 15.98 $^{bc}$ | 2.74 $^{d}$ | 25.51 $^{fg}$ | 0.76 $^{a}$ | 1.45 $^{a}$ | 17.59 $^{d}$ | 2.73 $^{e}$ | 49.45 $^{b}$ |
| PDG 2 | 388.25 $^{c}$ | 15.75$^{b}$ | 3.00 $^{de}$ | 26.64 $^{g}$ | 0.98 $^{bc}$ | 2.30 $^{e}$ | 16.66 $^{c}$ | 3.23 $^{f}$ | 51.84 $^{c}$ |
| Control | 252.75 $^{a}$ | 14.57 $^{a}$ | 1.40 $^{a}$ | 20.39 $^{e}$ | 0.86 $^{ab}$ | 2.35 $^{e}$ | 24.56 $^{f}$ | 2.50 $^{c}$ | 58.65 $^{e}$ |

* Abbreviations as in Table 1. Different letters in the column indicate significant differences ($p < 0.05$) between different fertilizer treatments.

**Table 6.** Results of linear regression analyses describing the relationship between maize yields and nutrient dose in the pot experiment.

| | Intercept | Slope | *p*-Value | $R^2$ |
|---|---|---|---|---|
| N-$NH_4$ | **341.25** | **163.14** | **<0.0000** | **58.03** |
| C | 386.99 | 0.29 | <0.86 | 0.77 |
| P | 385.51 | 15.67 | <0.73 | 0.28 |
| K | 356.98 | 49.97 | <0.06 | 8.08 |
| Mg | 387.42 | 10.51 | <0.85 | 2.90 |
| Ca | 383.62 | 34.20 | <0.67 | 0.43 |
| Zn | 390.84 | −0.24 | <0.88 | 0.05 |
| Cu | 395.35 | −2.30 | <0.56 | 0.80 |
| Mn | 389.05 | 0.01 | <0.99 | - |

Boldface types indicate statistically significant correlations ($p < 0.05$).

### *3.3. Chemical Composition of Crops*

The application of digestates and digestate-based products affects the chemical composition of crops [33]. The lowest nitrogen content was found in plants growing on the control object (14.57 g N kg$^{-1}$ DM) (Table 5). Nitrogen content in plants growing on objects fertilized with LFs was more than 11% higher than on the control object. Higher nitrogen content was determined in plants fertilized with DGs and SFs than those fertilized with other forms of digestate. Nitrogen content in plants on these objects was 17% and 25% higher in comparison to nitrogen content in plants from the control object. Fertilization with digestate pellets increased nitrogen content in the plants to the lowest degree (by approximately 8% in comparison to control).

Similar to our results on the nitrogen content, the phosphorus content in plants was lowest for the control (1.40 g P kg$^{-1}$ DM). The highest P content was determined in plants fertilized with pellets (PDG1, PDG2, PSF2, and PSF1). It was approximately twice as high as on the control object. P content in plants on objects DGs, LFs, and SFs was significantly higher (by approximately 33−50%) than on the control object.

As expected, mean potassium content (20.31 g K kg$^{-1}$ DM) in maize was higher than that of nitrogen, phosphorus, calcium, and magnesium (16.60 g N, 2.33 g P, 2.13 g Ca, 0.94 g Mg kg$^{-1}$ DM, respectively). Potassium contents strongly depended on the form of the applied digestate (Table 5). The lowest potassium content was determined for plants growing in the soil fertilized with DG2 (14.75 g K kg$^{-1}$ DM). Potassium content in maize on objects fertilized with DGs, LFs, and SFs was significantly lower than that on the control object. Fertilization with PSFs and PDGs considerably increased potassium content in plants by approximately 22–31% in comparison to the control object.

The magnesium content in plants varied from 0.73 to 1.22 g Mg $kg^{-1}$ DM. Only fertilization with DG2, LF1, and SF2 significantly increased Mg content in maize. On the remaining experimental objects, Mg content in maize was approximate to that on the control object.

The calcium content in plants varied from 1.40 to 3.12 g Ca $kg^{-1}$ DM. Only on objects fertilized with LFs, was significantly higher Ca content in maize in comparison to the control object determined.

The use of digestate and digestate-based products for fertilization raises concerns about the deterioration of the quality of biomass, especially in the context of the content of heavy metals (HMs) [45,46]. Among the analyzed HMs, Mn amounts in plants were highest. The average content of manganese in plants was higher than zinc and copper content (52.80 mg Mn, 17.34 mg Zn, and 2.51 mg Cu $kg^{-1}$ DM, respectively). On all objects treated with DGBPs, Zn content in maize was significantly lower than the content of that HM in maize sampled from the control object (Table 5). Moreover, Mn content in maize on the majority of fertilizer objects was lower than on the control object. Only in maize fertilized with DG2 and SF2, was the Mn content approximately similar to that in plants growing on the control object. Copper content in plants varied from 1.96 mg Cu $kg^{-1}$ DM on object DG1 to 3.22 mg Cu $kg^{-1}$ DM on object PDG2. Only the application of pellets obtained from DGs (PDG1, PDG2) significantly increased Cu content in maize in comparison to control. On the remaining objects, Cu content in plants did not significantly differ, or was even significantly lower than in plants from the control object (Table 5).

In summary, study results show that fertilization with digestates and digestate-based products mostly decreased the content of manganese, zinc, and copper in fertilized plants in comparison to the content of these elements in the control object. This may be caused by the chelating effect of organic matter contained in tested products, thereby decreasing the bioavailability of HMs for plants. Only fertilization with pellets from unprocessed digestate increased copper content in plants.

Our experiment suggests that, among the analyzed macronutrients (N, P, K, Mg, Ca) and heavy metals (Zn, Cu, Mn), only the concentrations of Mg and Mn in plants did not show a significant linear relation with the dose of these components provided by the different forms of digestate (Table 7).

**Table 7.** Results of linear regression analyses describing the relationship between nutrient contents in maize and nutrient dose in different forms of digestate.

| | **Intercept** | **Slope** | ***p*-Value** | **$R^2$** |
|---|---|---|---|---|
| N-$NH_4$ dose on N content | **16.10** | **1.71** | **0.01** | **12.1** |
| P dose on P content | **1.84** | **2.16** | **0.00** | **45.5** |
| K dose on K content | **15.18** | **7.98** | **0.00** | **30.3** |
| Mg dose on Mg content | 0.89 | 0.29 | 0.09 | 4.2 |
| Ca dose on Ca content | **2.45** | **−2.01** | **0.01** | **11.1** |
| Zn dose on Zn content | **18.80** | **−0.20** | **0.01** | **14.4** |
| Cu dose on Cu content | **2.33** | **0.07** | **0.00** | **18.1** |
| Mn dose on Mn content | 54.59 | −0.57 | 0.08 | 5.1 |

Boldface types indicate statistically significant correlations ($p < 0.05$).

### *3.4. Apparent Macronutrients and Heavy Metals Recovery*

The apparent macronutrients recovery (ANR) by plants from the tested products were dependent on their form and the type of nutrients (Figure 3). Highest ANR values were determined on objects fertilized with LFs. This results from the fact that this digestate fraction primarily contains soluble forms of nutrients readily available for plants. For the majority of macronutrients, ANR on these objects considerably exceeded 100%. This points to intensive uptake of nutrients from the soil resources by a greater mass of plants than that obtained on the control object. High ANR values were also recorded on objects fertilized with DGs (approximately 100% or higher). It can therefore be concluded that the fertilizer use of DGs and LFs will not be associated with a leaching of nutrients to the environment. However, results from this pot experiment in field trials require further validation in field experiments.

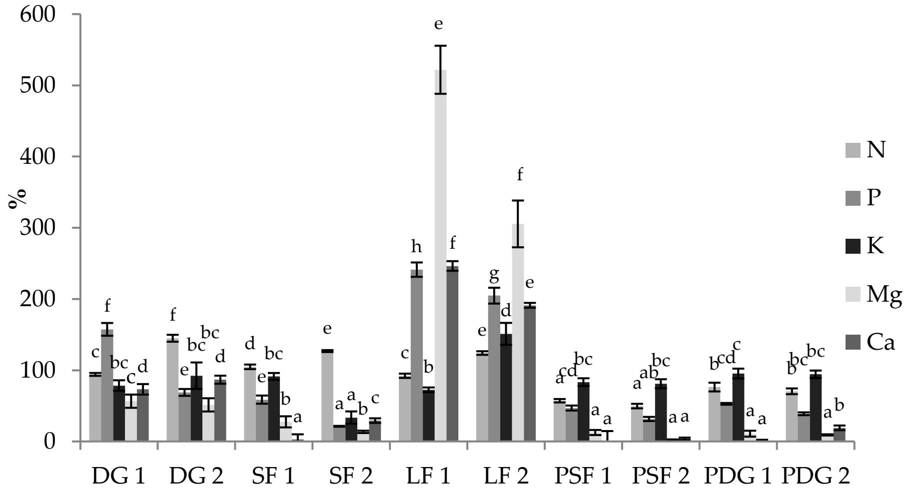


**Figure 3.** Apparent macronutrients recovery (ANR) from different forms of digestate. The standard deviation within each treatment ($n = 3$) is indicated by the line extending the column. Values followed by the same letters in the column (separately for nutrients) are not statistically different ($p < 0.05$).

Considerably lower ANR was recorded on objects fertilized with pellets, i.e., PDGs and PSFs, particularly in reference to Ca and Mg. On these objects, the highest values were reached by apparent potassium recovery (approximately 90%). This was similar to that obtained on objects fertilized with DGs. Apparent N recovery reached 73.3% and 53.4%, respectively, for PDG and PSF treatments. This suggests that maize uses nitrogen contained in these products very efficiently. Corréa et al. [47] obtained only 30 to 35% of apparent nitrogen recovery of urine-N in grass cultivation. P recovery form fertilizers is usually low. It is one of the causes of its accumulation in the soil and run-off, or leaching of P from the soil to surface waterbodies. In the conducted experiment, very high values of apparent P recovery from PDGs (45%) and PSFs (40%) were obtained. In studies conducted by Sarvi et al. [48], apparent P recovery was lower than in our research, reaching approximately 23%.

Apparent Zn and Cu recovery from different forms of digestate was very low (Figure 4). Only on objects fertilized with LFs did the A*HMs*R value exceeded 10%. Only apparent Mn recovery was high, particularly on objects fertilized with LFs and DGs.

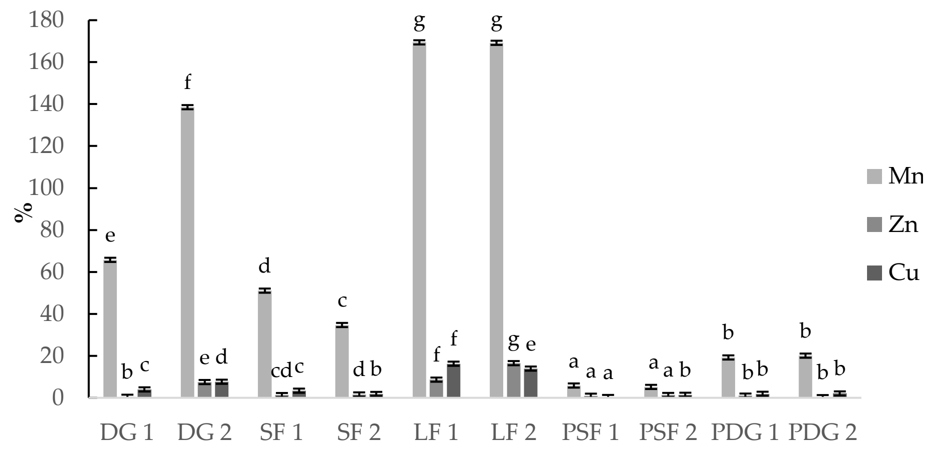


**Figure 4.** Apparent heavy metals recovery (A*HMs*R) from different forms of digestate. The standard deviation within each treatment ($n = 3$) is indicated by the line extending the column. Values followed by the same letters in the column (separately for HMs) are not statistically different ($p < 0.05$).

## 4. Conclusions

Biogas production has become more popular and regionally concentrated in recent decades, creating areas with high digestate surpluses compared with crop lands and pastures. The situation creates a need for the development of digestate processing technologies that allow the acquisition of valuable digestate-based products. Different processing technologies can be employed to produce nutrient-rich products. Mechanical separation of DGs leads to the separation of fresh matter and nutrients into the liquid and solid fraction. More than 80% of nitrogen and 87% of potassium flows from DGs to the LFs, whereas more than 60% of phosphorus and 70% of magnesium flows to SFs. All tested DGBPs were relatively valuable by-products that should be used as fertilizers due to their richness in plant-available nutrients. The non-treated digestate (DG) and liquid fraction (LF) may have the advantage to deliver nutrients to plants more rapidly that the pelletized form (PDGs and PSFs). The nutrients used in the form of DGs and LFs were fully consumed by the maize (apparent nutrients recovery exceeded 100%). This means that fertilization with these products does not lead to losses of soil nutrients. Pelletized forms of digestate can be applied as a slow-release organic fertilizer. This type of fertilizer has recently been promoted due to its lower negative impact on the natural environment. However, the conducted study showed that its production could lead to significant nitrogen losses (more than 95%) by ammonia volatilization.

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