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HEAVY METAL CONTENT IN SUBSTRATES IN AGRICULTURAL BIOGAS PLANTS

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ABSTRACT

The content of heavy metals in soil should be continuously monitored, especially in organic crops. Exceeding the permissible concentrations of these elements may lead not only to inhibition of plant growth but also to ingestion into the organisms of animals that feed on these plants.

Keywords:
biogas plant,
heavy metals,
digestate,
impurities,
substrate

Heavy metals usually enter the soil via precipitation or manure. There is a noticeable increase in interest in digestate for fields fertilization. Therefore, the authors decided to test the heavy metal content in substrates (slurry and solid input) and digestate. The 15x3 samples tested showed that only trace amounts of heavy metals were present. The study shows that the content of these elements in the digestate is not the sum of the elements supplied to the digester with the substrates. In most of the samples tested, lead concentrations did not exceed 5 $mg \cdot kg^{-1}$. The lowest amounts of cadmium (an average of 0.28 $mg \cdot kg^{-1}$) were observed in the slurry, and the highest (an average of 0.34 $mg \cdot kg^{-1}$) in the solid substrate fed to the digester. Slurry had the lowest mercury and cadmium contents (average 0.012 $mg \cdot kg^{-1}$and 5.8 $mg \cdot kg^{-1}$). The highest concentration of chromium was registered in the digestate (average 3 $mg \cdot kg^{-1}$) and this was on average 0.3 $mg \cdot kg^{-1}$ higher than the feedstock and 0.5 $mg \cdot kg^{-1}$ than the slurry

Introduction

Agricultural biogas plants belong to the group of renewable energy sources (RES), which has led to increased interest in them in recent years (Skibko et al., 2021; Czekała et. al., 2023). Agricultural biogas plants, compared to other renewable energy sources, produce energy that is approximately constant over time, thus has a good impact on the stability of rural electricity grids (Suproniuk et al., 2019; Hołdyński et al., 2022; Kuboń et al., 2023). It is assumed that building biogas power plants will reduce the greenhouse effect, increase regional energy security and the wealth of farmers' wallets (Sikora et al., 2020; Tymińska et al., 2023). Integrating animal production with an agricultural biogas plant could benefit small and medium-sized farms. It would enable the use of animal waste which is often an additional economic (Horobets, 2020) and environmental (Trypolska et al., 2023) burden for a farm. It would increase the economic viability of agricultural production and allow the farm to achieve its energy security (Kuboń and Krasnodębski, 2010; Borek et al., 2021; Czekała et al., 2023).

An increasing amount of municipal organic waste associated with everyday human activities is generated worldwide. Approximately 2 billion tonnes of waste is generated annually (0.11-4.54 kg/person/day), and a significant proportion of it, about one-third, is not adequately managed from an environmental perspective (Van et al., 2019). Highly developed countries generate about 680 million Mg of municipal waste annually (about 34% of waste generated worldwide), with food and green waste accounting for 32% of all waste (mainly plastics, cardboard, paper, glass, and metal). Waste collected from middle- and low-income countries collectively contains as much as 53-56% of organic waste (Hoornweg and Bhada-Tata, 2012; Niemiec et al., 2017). Although it is not yet possible to estimate the percentage of food waste globally, in the retail and consumption phases, the percentage of food lost after harvest in a farm and in transport, storage, and processing phases is approximately 13.8%.

The most common substrates used in biogas plants are sewage sludge (accounting for about 62% of substrates), followed by manure (e.g., animal manure and slaughterhouse waste) (16%), food and agro-industrial waste (15%) (Frigon et al., 2012; Tyagi et al., 2018, Kukharets, et al. 2021, Larina et al. 2021). The most common waste substrate for agricultural biogas plants is slurry, the generated amount of which depends primarily on animal husbandry technology. However, due to its low organic matter content, it is most often supplemented with other substrates, e.g., biomass from targeted crops, of which maize silage is the most efficient (Michalski, 2009). Livestock accounts for almost 40% of the total agricultural production in high-income countries and 20% in developing countries. As much as 34% of the protein supply in the human diet comes from livestock (Campuzano and González-Martínez, 2016; FAO, 2018). According to the FAO (Food and Agriculture Organisation of the United Nations), Europe's livestock population 2019 consisted of 143 million pigs, 77 million cattle, and 74 million sheep and goats (Iglesias et al., 2021). The amount of livestock manure depends on many aspects which include the feeding regime or the stage of the rearing process (Ogbuewu et al., 2011). When manure is not properly processed, livestock farming activities negatively impact the environment (Velthof et al., 2014). On the other hand, manure (from animals) is an attractive natural resource for production of renewable energy and significantly improves soil fertility (Tallou et al., 2020). The low C/N ratio found in manure, the high nitrogen content, the low volatile solids (VS) content, and, in some cases, the high proportion of lignocellulosic biomass are significant limitations to the use of manure in fermentation (Tsapekos et al., 2016; Issah et al., 2020). Manure processing (mainly manure and slurry) has more benefits when carried out under anaerobic conditions in biogas plants compared to the direct application of untreated manure on agricultural fields (Bhunia et al., 2021; Urra et al., 2019).

A substrate commonly used in biogas plants is also plant matter. Raw plant biomass that can be converted to methane with high fermentation yields should have high concentrations of lactic and acetic acid and low concentrations of butyric acid and ammonia (Amon et al., 2007; McEniry et al., 2014; Szparaga et al., 2019; Sobol et. al., 2020; Romaniuk et al. 2021). When growing crops for biogas production, attention should be paid to dry matter yield per unit area, content of readily fermentable components, and ease of storage after fresh matter harvest. Compared to other crops, maize has a high dry matter yield per hectare under cultivation. The amount of biogas possible from the crop depends mainly on the harvest timing and the dry matter yield. Dry matter (30%) is harvested from early maize varieties. Later varieties are characterised by a predominance of vegetative to generative parts.

The use of natural fertilisers in agriculture improves the yield obtained in terms of both quantity and quality. They introduce macro-elements (nitrogen, phosphorus, potassium) and micro-elements into the soil. The use of organic fertilisers also reduces the occurrence of nitrates and nitrites in plants. Organic fertilisation increases the plants' carbohydrates, easily digestible proteins, and B vitamins. In carrots, potatoes, savoy cabbage, spinach, leeks, and lettuce fertilised with organic fertilisers, increased content of iron, magnesium, phosphorus, and potassium was also observed (Crinnion, 2010; Balanda et al., 2022).

Organic fertilisers tend to have low contents of arsenic, mercury lead, and other heavy metals, unlike some mineral fertilisers (Singh and Pandey, 2012; Arvaniti et al., 2006). Table 1 shows the maximum levels of heavy metals allowed in Poland for organic fertilisers. If exceeded, such fertilisers are disposed of, as they can endanger crops and the environment.

In recent years, organic agricultural products have become increasingly popular. Such products are provided by organic farms, where the use of crop protection chemicals and mineral fertilisers has been reduced as much as possible. One way to reduce the use of mineral fertilisers is to replace them with digestate from biogas plants (Żelezik, 2009). The digestate, which contains organic matter and essential mineral compounds, is an alternative to mineral fertilisers and can compete with natural fertilisers.

Table 1.
Maximum concentrations of heavy metals allowed in natural fertilisers (Łagocka et al., 2016)

Metal	Permissible content (mg·kg $^{-1}$)
Cadmium (Cd)	5
Chrome (Cr)	100
Nickel (Ni)	60
Lead (Pb)	140
Mercury (Hg)	2

A positive aspect of anaerobic digestion in the formation of digestate is that it reduces pathogens, kills viruses, fungi, Listeria, Salmonella, and Escherichia coli bacteria, and inactivates plant seeds (Sassi et al., 2018; Zhou et al., 2020). The digestate can be used as a fertiliser in both liquid and solid form. The solid phase is usually formed by mechanical or thermal separation of the liquid part of the digestate. The macronutrient and micronutrient content of solid digestate depends on the composition of the input raw materials to the fermentation process and the retention time of the raw materials in the fermenter (Abubaker et al., 2012). Due to its chemical composition and physical properties, applied solid digestate can positively influence biomass yield and soil structure (Dubský et al., 2019). Liquid digest can be considered as a diluted substrate solution containing a wide range of nutrients in a form acceptable to plants (Kolář et al., 2010). Digest in liquid form appears to be a suitable raw material for application to arable land during the growing season, both in terms of fertilisation and irrigation (Makádi et al., 2012). The dry matter in liquid digestate is in the range of 0.8-4.0%. Nitrogen is mainly present in mineral form, with a concentration of 0.15-0.30%, comparable to the potassium content. As NPK proportions are variable in each digestate, it is necessary to analyse the individual components before applying such fertiliser to the field (Coelho et al., 2018). The digest has a similar nitrogen content in fresh matter as manure (0.2-1.0%) but a higher pH value in the range 7-8 (Kratzeisen et al., 2010). Digestate on agricultural land as an organic fertiliser is already considered for standard use (Lijó et al., 2015). The studies show that using digestate from agricultural biogas plants reduces the environmental risks of using mineral fertilisers while achieving comparable crop yield parameters. At the same time, it should be emphasised that the availability of nutrients is very dependent on the substrates used in the biogas plant, and it cannot be stated unequivocally that the use of anaerobic digestion by-products will achieve better yields of field crops (Tsachidou et al., 2019; Sogn et al., 2018; Barwnicki et al, 2022).

Heavy metals, harmful to organisms (including plants), that may be present in substrates used in agricultural biogas plants include:

1. Lead (Pb) - Strongly toxic to plants and organisms, can lead to severe tissue damage and metabolic disorders. It accumulates mainly in roots and aboveground plant parts such as

leaves. It can damage cell membranes, leading to impaired cell permeability and function. Excess lead in soil can interfere with the ability of plants to take up water and nutrients, as well as cause oxidative stress in plant cells and a variety of metabolic processes in plants, such as the metabolism of carbohydrates, fats, or proteins, further affecting their development and function.

2. Cadmium (Cd) - Strongly toxic to plants and can interfere with nutrient uptake. Excess cadmium can damage plants' roots, leaves, and other parts, inhibiting their growth and development. It can damage chloroplasts, leading to a reduction in the ability of plants to carry out photosynthesis.
3. Mercury (Hg) - Occurs in various forms, some highly toxic. It can disrupt metabolic processes and lead to damage to plant tissue. It can also interfere with photosynthesis, which is crucial for converting solar energy into chemical energy and can reduce the ability of plants to take up and assimilate nutrients.
4. Chromium (Cr) - Although chromium is a trace element and is essential for plants in tiny amounts, excess amounts can harm plants. Excess toxic chromium can damage plant roots and interfere with metabolic and physiological processes, reducing growth and development.
5. Nickel (Ni) - A trace element that plants require in small quantities. It is part of enzymes and proteins that are essential to metabolic processes. However, excess nickel in the soil can have harmful effects. The toxic effects of nickel can damage plant cells and tissues and interfere with plants' ability to take up and assimilate nutrients. Excess nickel can affect plant morphology, leading to the deformation of leaves, shoots, and roots.

Excessive heavy metals in soil can lead to soil and water contamination, posing a risk to human, animal, and environmental health. They can accumulate in plant tissues, especially in the roots and aboveground parts, threatening the organisms that feed on these plants. Therefore, controlling and limiting emissions of these elements and avoiding their accumulation in soil is extremely important. There is a lack of research results in the literature showing the content of heavy metals in the substrates of agricultural biogas plants. Therefore, the authors decided to fill this research gap by conducting a two-year study on the content of heavy metals in the slurry, input, and digestate substrate of an agricultural biogas plant. The study was designed to check the number of heavy metals delivered to the agricultural biogas plant with the substrate and delivered to the ground with the digestate.

Materials and Methods

Investigations of the chemical composition of the substrates present in the agricultural biogas plant were carried out over two years by taking monthly samples for testing (8 samples were taken in the first year of the study and 7 in the second). Three samples were taken each time: one from the slurry tank, one from the mixer of substrates fed into the biogas plant, and one from the digestate tank. All these samples were submitted to a certified laboratory to determine their chemical composition.

The primary production medium in the biogas plant under study was electricity generated from 0.6 MW gas turbine in which the produced biogas was combusted. The thermal energy generated at the biogas plant was a by-product and was only used to heat the biogas plant buildings (during the winter season) and to maintain a constant temperature value in the digester. The biogas produced was used in its entirety, after purification, in the electricity generation process. The number of substrates consumed on average per year by the biogas plant under study is summarised in Table 2.

Table 2.
Summary of substrates used at the biogas plant under study (annual average over the two-year study period)

Substrate	Use in a biogas plant	
	Gross	Net
Maize silage	10 050 Mg·year^{-1}	25.61 Mg·year^{-1}
Bovine slurry	6 800 m^3·year^{-1}	18.63 m^3·year^{-1}
Cattle manure	5 000 Mg·year^{-1}	13.70 Mg·year^{-1}
Water	300 m^3·year^{-1}	

The concentration of nitrogen present in the input substrates was not high and did not cause technological problems. From a technological point of view, the sulphur contained in the slurry did not cause problems, as it was "dissolved" in the maize silage. Therefore, the biological desulphurisation used in the biogas plant analysed was sufficient. The raw materials (maize, silage, cattle, manure) were fed directly into the fermenter via a solids dosing unit. Cattle slurry was pumped into the fermenter from an underground tank (filled from the slurry tank vehicles), and water (which was an additive to dilute the fermentation mass) was pumped through the water supply lines entering the reactor. A pump was connected the fermenter to the digestate tank. When the fermentation substrate was fed into the fermenter, the pump pumped the same amount into the digestate storage tank.

Results and Discussion

The first element tested in the agricultural biogas plant analysed was lead (Pb) - Figure 1. According to the data presented in Table 1, the lead content should not exceed 140 mg·kg^{-1}.

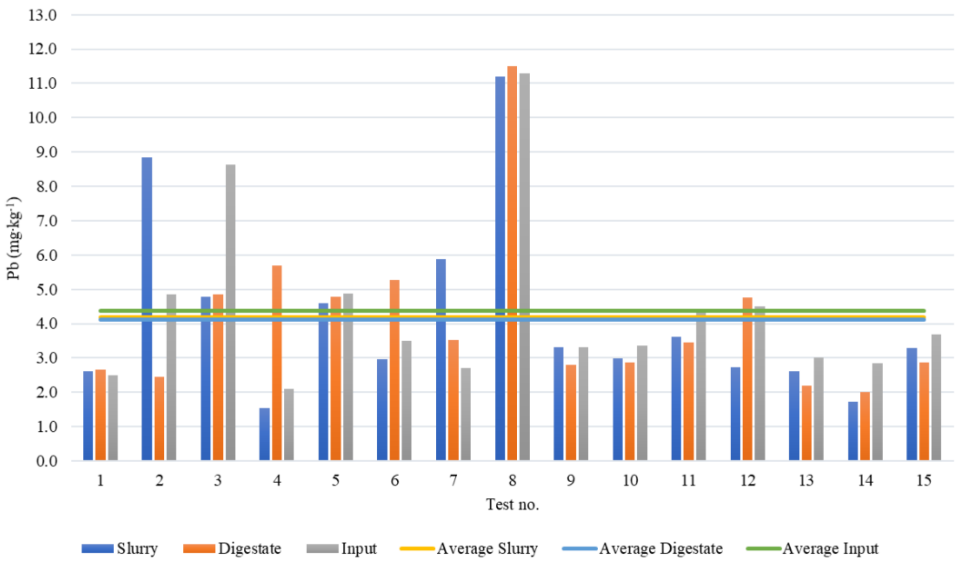

Figure 1. Comparison of the amount of lead present in the digestate, feedstock, and slurry

The test results had considerably lower values, not exceeding 12 mg·kg^{-1} of fresh weight in any samples, which is in line with the guidelines reported by Łagocka (Łagocka et al., 2016). Such high values occurred in the last sample of the first year of the study. In other cases, the values were lower and fluctuated around 5 mg·kg^{-1}. It is noteworthy that lead is present in both slurry and residual input, but no summation of this element was observed in the digestate.

Also, no exceedance of the permissible concentration was observed for cadmium, and the approximately 0.35 mg·kg^{-1} fresh weight recorded in the study was significantly less than the required 5 mg·kg^{-1}. In this case, the highest values were found in sample No. 5 (however, they did not exceed 0.85 mg·kg^{-1}) - Figure 2.

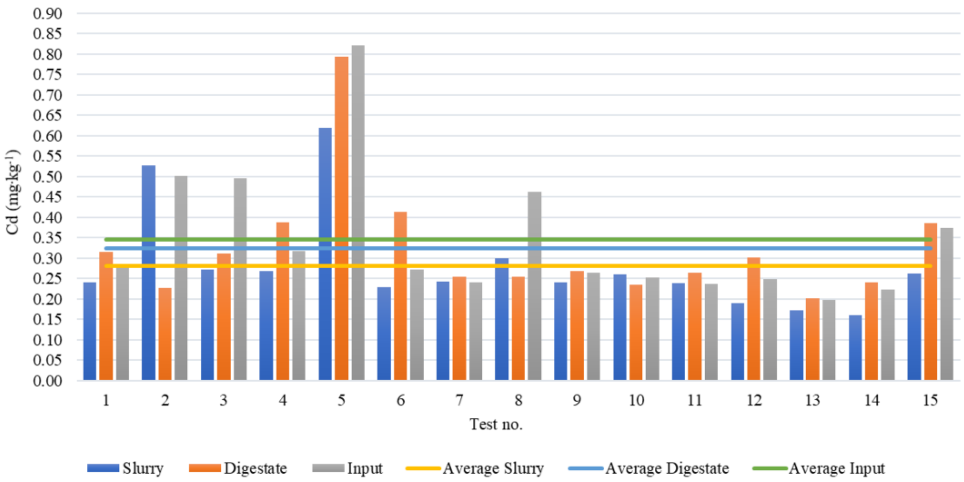

Figure 2. Comparison of the amount of cadmium found in the digestate, input, and slurry

The lowest amounts of cadmium (average 0.28 mg·kg^{-1}) were observed in the slurry, and the highest (average 0.34 mg·kg^{-1}) in the solid feedstock fed to the digester. Interestingly, the average amount of cadmium found in the digestate was between the amounts observed in the slurry and the feedstock. According to Śmiechowska and Florek, the largest contributors to dietary cadmium intake are cereals, grain products, vegetables, and potatoes (Bosiacki et al., 2022). According to the study by Ociepa and Mrowiec, fertilizing the soil with natural fertilizers increases the amount of cadmium in the soil by about 0.02 mg·kg^{-1} (Ociepa et al., 2014). This value is about 15 times lower than the amount of cadmium found in the samples studied by the authors. At the same time, it should be remembered that the bioaccumulation of cadmium depends mainly on the soil's pH and calcium content (He et al., 2022).

For mercury, the permissible concentration was 2 mg·kg^{-1} fresh weight (Łagocka et al., 2016). The values recorded by the authors were more than 100 times lower - Figure 3. According to Kopeć and Gondek, the mercury content e of phosphate fertilizers ranges from 0.01 to 1.20 mg·kg^{-1} (Kopeć and Gondek, 2009), which far exceeds the values recorded in the samples studied by the authors.

The scatter of measured values in individual samples was much smaller in the case of mercury than for the previous elements (no samples with significantly higher Hg content than the others were observed). However, a different pattern can be observed - the slurry had the lowest mercury content (0.012 mg·kg^{-1} on average), while the content of this element in the input and digest reached 0.016 mg·kg^{-1} on average. This element will most likely enter the digester with the maize silage.

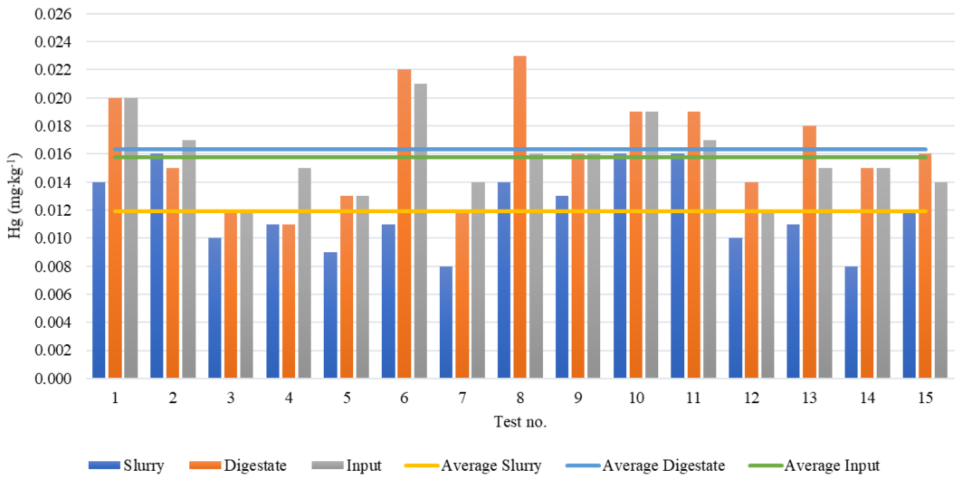

Figure 3. Comparison of the amount of mercury present in the digestate, feedstock, and slurry

Another heavy metal tested was nickel. In this case, too, the recorded amount of this element was significantly (mostly more than six times) below the required 60 mg·kg^{-1} fresh weight – Figure 4.

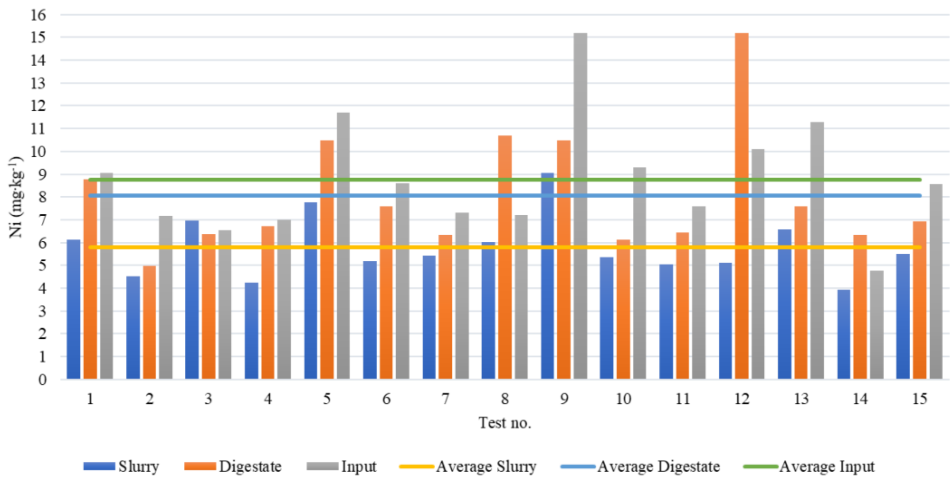

Figure 4. Comparison of nickel amounts in digestate, feedstock, and slurry

In the case of nickel, like mercury, the lowest amounts of this element are found in slurry (average 5.8 mg·kg^{-1}). However, more significant differences were observed between Ni concentrations in the digest (average 8.1 mg·kg^{-1}) and in the feedstock (average 8.9 mg·kg^{-1}). The feedstock was characterised by the highest Ni content, suggesting that some Ni entered the biogas during fermentation. As shown in a study by other authors (Dong et al., 2023), nickel is the only one of the elements studied that shows geo-accumulation.

The last element analysed was chromium. The average Cr content in the analysed samples did not exceed 3 mg·kg^{-1}fresh weight, which was many times lower than the required 100 mg·kg^{-1} – Figure 5.

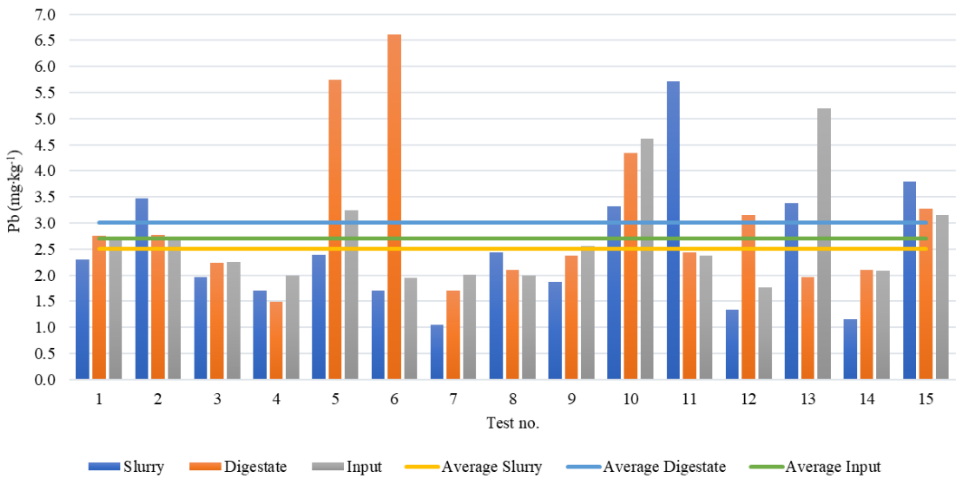

Figure 5. Comparison of the amount of chromium in the digestate, the input, and the slurry

The highest concentration of chromium, in contrast to the other elements analysed, was recorded in the digestate (average 3 mg·kg^{-1}), and this was, on average, 0.3 mg·kg^{-1} higher than the feedstock and 0.5 mg·kg^{-1} higher than the slurry. Also noteworthy is that for two samples (Nos. 5 and 6), the Cr value measured in the digestate was more than twice as high as in the other samples taken on these days.

Conclusions

The content of heavy metals in the soil should be constantly monitored, mainly as they can transfer from plants to the animals that feed on them. Therefore, it is also worth checking that the fertilisation process does not deliver these elements to the soil in significant quantities. As the use of digestate as a natural fertiliser has now increased (due to its high nutritional and environmental value), it was necessary to check whether heavy metals are supplied to the soil with the digestate. The study conducted by the authors shows that the amounts of elements such as lead, mercury, cobalt, nickel, or chromium delivered to the soil with the digestate are many times lower than the values required for natural fertilisers. The lead concentrations in the tested slurry, feedstock, and digest samples are similar. The remaining elements are least present in the untreated slurry, while no summation of their amounts was observed, delivered to the digester with slurry or solid input (maize silage and manure). The study also shows that only for mercury and chromium the average content of these elements in the digestate is higher than the concentration found in slurry and feedstock. In the remaining cases, the anaerobic digestion process in the fermenter influences the reductions in analysed the heavy metals. Even though only trace amounts of heavy metals present in the digestate were obtained in the study, according to the authors, mandatory measurement of the content of these elements should be introduced (e.g., quarterly) to reduce the possibility of contamination of soils with these elements.

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References

Abubaker, J., Risberg, K. & Pell, M. (2012). Biogas residues as fertilisers–Effects on wheat growth and soil microbial activities. *Applied Energy*. *99*, 126-134. https://doi.org/10.1016/j.apenergy.2012.04.050.

Amon, T., Amon B., Kryworuchko, W., Zollitsch, W., Mayer K., Gruber, L. (2007) Biogas production from maize and dairy cattle manure-Influence of biomass composition on the methane yield. *Agriculture, Ecosystems & Environment*. *118*, 173-182. https://doi.org/10.1016/j.agee.2006.05.007.

Arvaniti, F., Magkos, F. & Zampelas A. (2006). Organic food: buying more safety or just peace of mind? A critical review of the literature. *Critical Reviews in Food Science and Nutrition*. 46, 23-56. DOI: 10.1080/10408690490911846.

Balanda, O., Serafinowska, D., Marchenko, O. & Svystunova, I. (2022). Innovative Technology of Accelerated Composting of Chicken Manure to Obtain an Organic Fertilizer with a High Content of Humic Acids. *Agricultural Engineering*. *26*(1), 133-144. https://doi.org/10.2478/agriceng-2022-0011.

Barwicki, J., Borusiewicz, A., Holden, L., Kulcsar, L., Skibko, Z., Żuchowski, I., & Romaniuk, W. (2022). Leaching of elements from soil in grassland field crops treated with raw and acidified slurry. Agricultural Engineering, *26*(1), 145-156.

Bhunia, S., Bhowmik, A. & Mukherjee, J. (2021). Agronomic Efficiency of Animal-Derived Organic Fertilizers and Their Effects on Biology and Fertility of Soil: a Review. *Agronomy*. *11*, 823. https://doi.org/10.3390/agronomy11050823.

Borek, K., Romaniuk, W., Roman, K., Roman, M. & Kuboń, M. (2021). The analysis of a prototype installation for biogas production from chosen agricultural substrates. *Energies*. *14*(8), 2132. https://doi.org/10.3390/en14082132.

Bosiacki, M., Bednorz, L. & Spiżewski T. (2022). Concentration of heavy metals in urban allotment soils and their uptake by selected vegetable crop species – a case study from Gorzów Wielkopolski, Poland. *Journal of Elementology*. *27*(2), 405-421. DOI: 10.5601/jelem.2022.27.1.2275.

Campuzano, R. & González-Martínez, S. (2016). Characteristics of the organic fraction of municipal solid waste and methane production: A review. *Waste Management*. 54, 3-12. https://doi.org/10.1016/j.wasman.2016.05.016.

Coelho, J.J., Prieto, M.L., Dowling, S., Hennessy, A., Casey, I., Woodcock, T. & Kennedy, N. (2018). Physical-chemical traits, phytotoxicity and pathogen detection in liquid anaerobic digestates. *Waste Management*. *78*, 8-15. https://doi.org/10.1016/j.wasman.2018.05.017.

Crinnion, W. (2010). Organic foods contain higher levels of certain nutrients, lower levels of pesticides and may provide health benefits for the consumer. *Environmental Medicine*. *15*, 4-12., PMID: 20359265.

Czekała, W., Pulka, J., Jasiński, T., Szewczyk, P., Bojarski, W. & Jasiński J. (2023). Waste as substrates for agricultural biogas plants: A case study from Poland. *Journal of Water and Land Development*. *56*, 45-50. DOI: 10.24425/jwld.2023.143743.

Czekała, W., Nowak, M., & Bojarski, W. (2023). Anaerobic digestion and composting as methods of bio-waste management. Agricultural Engineering, *27*(1), 173-186.

Dong, H., Gao, Z., Liu, J. & Jiang, B. (2023). Study on the Accumulation of Heavy Metals in Different Soil-Crop Systems and Ecological Risk Assessment: A Case Study of Jiao River Basin. *Agronomy*. *13*(9), 2238. https://doi.org/10.3390/agronomy13092238.

Dubský, M., Chaloupková, Š., Kaplan, L., Vondráčková, S. & Tlustoš, P. (2019). Use of solid phase of digestate for production of growing horticultural substrates. *Horticultural Science*. *46*, 34–42. DOI: 10.17221/221/2016-HORTSCI.

FAO. (2018). World Livestock: Transforming the Livestock Sector through the Sustainable Development Goals. Food and Agriculture Organization of the United Nations. Rome, Italy.

Frigon, J.C., Mehta, P. & Guiot, S.R. (2012). Impact of mechanical, chemical and enzymatic pre-treatments on the methane yield from the anaerobic digestion of switchgrass. *Biomass Bioenergy*. *36*, 1-11. https://doi.org/10.1016/j.biombioe.2011.02.013

He, P., Liang, B., Chen, B., Xu, Z. & Jiang, H. (2022). Effectiveness of Cadmium Bioavailability in Paddy Soil and Effective Factors of Cadmium Accumulation in Rice in the High Geological Background of Northeast Chengdu Plain. *J. Southwest Univ. Sci. Technol.*, 37, 38-43, 97. (In Chinese), DOI:10.20036/j.cnki.1671-8755.2022.03.006.

Hołdyński, G., Skibko, Z. & Borusiewicz, A. (2022). Impact of Wind Power Plant Operation on Voltage Quality Parameters-Example from Poland. *Energies*, *15*, 5573. https://doi.org/10.3390/en15155573.

Hoornweg, D. & Bhada-Tata, P. (2012). What a Waste: A Global Review of Solid Waste Management. *World Bank: Washington, DC, USA*; Retrieved August 6, 2023, from the World Wide Web: http://hdl.handle.net/10986/17388.

Horobets, O.V. (2020) Classification of agricultural waste and selection of their utilization technology. *Waste Management*, *4*, 225-229. DOI https://doi.org/10.32846/2306-9716/2020.eco.4-31.35.

Iglesias, R., Muñoz, R., Polanco, M., Díaz, I., Susmozas, A., Moreno, A.D. & Guirado, M. (2021). Carreras, N.; Ballesteros, M. Biogas from Anaerobic Digestion as an Energy Vector: Current Upgrading Development. *Energies*. *14*, 2742. https://doi.org/10.3390/en14102742.

Issah, A.A., Kabera, T. & Kemausuor, F. (2020). Biogas optimisation processes and effluent quality: A review. *Biomass Bioenergy*. *133*, 105449. https://doi.org/10.1016/j.biombioe.2019.105449.

Jędrejek, A. & Jarosz, Z. (2016). Regional Opportunities to Produce Agricultural of Bio-Gas. Institute of Soil Science and Plant Cultivation – PIB in Puławy, *Scientific Yearbooks of the Association of Agricultural and Agribusiness Economists*. Puławy, *18*, 61-66.

Kolář, L., Kužel, S., Peterka, J. & Borová-Batt, J. (2010). Agrochemical value of the liquid phase of wastes from fermentem during biogas production. *Plant Soil Environment*. 56, 23-27, DOI: 10.17221/180/2009-PSE.

Kopeć, M. & Gondek, K. (2009). The content of mercury in plans of the mountain grassland (Czarny Potok) after 40 years of veried mineral fertilization. *Ecological engineering*. No *21*, 7-14. Retrieved August 3, 2023, from the World Wide Web: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwi0koGN9dyBAxVfhv0HHVpcD-sQFnoECA4QAQ&url=https%3A%2F%2Fyadda.icm.edu.pl%2Fbaztech%2Felement%2Fbw-meta1.element.baztech-article-BPG8-0064-0030%2Fc%2FKopec.pdf&usg=AOvVaw1YsQr32-xDjVAI5hBrcha_&opi=89978449

Kratzeisen, M., Starcevic, N., Martinov, M., Maurer, C. & Müller, J. (2010). Applicability of biogas digestate as solid fuel. *Fuel*. *89*, 2544-2548. https://doi.org/10.1016/j.fuel.2010.02.008.

Kuboń, M. & Krasnodębski, A. (2010). Logistic costs in competitive strategies of enterprises. *Agricultural Economics*. 56(8), 397-402. https://doi.org/10.17221/67/2010-AGRICECON.

Kuboń, M., Skibko, Z., Tabor, S., Malaga-Toboła, U., Borusiewicz, A., Romaniuk, W., Zarajczyk, J. & Neuberger, P. (2023). Analysis of Voltage Distortions in the Power Grid Arising from Agricultural Biogas Plant Operation. *Energies*. *16*, 6189. https://doi.org/10.3390/en16176189.

Kukharets, S., Hutsol, T., Glowacki, S., Sukmaniuk, O., Rozkosz, A. & Tkach, O. (2021). Concept of Biohydrogen Production by Agricultural Enterprises. *Agricultural Engineering*, *25*(1), 63-72. https://doi.org/10.2478/agriceng-2021-0005.

Łagocka, A., Kamiński, M. & Cholewiński, M. (2016). Biogas fermentation by-products – the utilization as a full-value fertilizer and its impact on the rural areas. *II International Conference of the Society for Human Ecology*. January 2016. University Publishing House of the West Pomeranian University of Technology in Szczecin, 124-125. Retrieved August 3, 2023, from the World Wide Web: https://www.researchgate.net/publication/314371943_Korzysci_ekologiczne_ze_ stosowania_pofermentu_z_biogazowni_rolniczych_jako_nawozu_organicznego.

Larina, Y., Galchynska, J., Kucheruk, P., Zghurska, O., Ortina, G., Al-Nadzhar, F., Marusei, T., Kuboń, M. & Dzieniszewski, G. (2021). Estimation of the Domestic Agricultural Sector Potential for the Growth of Energy Cultures for Bioenergy Fuel Production. *Agricultural Engineering*. *25*(1) 73-82. https://doi.org/10.2478/agriceng-2021-0006

Lijó, L., González-García, S., Bacenetti, J., Negri, M., Fiala, M., Feijoo, G. & Moreira, M.T. (2015). Environmental assessment of farm-scaled anaerobic co-digestion for bioenergy production. *Waste Management*. *41*, 50-59. https://doi.org/10.1016/j.wasman.2015.03.043.

Makádi, M., Tomócsik, A. & Orosz, V. (2012). Digestate: A new nutrient source–review. *Biogas*. 14, 295–312. DOI: 10.5772/31355.

McEniry, J., Allen, E., Murphy, J. & O'Kiely, P. (2014). Grass for biogas production: The impact of silage fermentation characteristics on methane yield in two contrasting biomethane potential test systems. *Renewable Energy*, *63*, 524-530. https://doi.org/10.1016/j.renene.2013.09.052.

Michalski, T. (2009). Biogas plant in every municipality - is there enough raw material. *Wieś Jutra*. *3*, Poznań. 12-14.

Niemiec, M., Sikora, J., Szelag-Sikora, A., Kubon, M., Olech, E., & Marczuk, A. (2017). Applicability of food industry organic waste for methane fermentation. *Przemysł chemiczny*. *96*(3), 685-688. https://doi.org/10.15199/62.2017.3.38.

Ociepa, E., Deska, I. & Mrowiec, M. (2014). Effect of compound fertilizers on the concentration of heavy metals in soil and biomass of virginia mallow. *Engineering and Environmental Protection*, t. 17, nr 4, s. 647-660.

Ogbuewu, I.P., Odoemenam, V.U., Obikaonu, H.O., Opara, M.N., Emenalom, O.O., Uchegbu, M.C., Okoli, I.C., Esonu, B.O. & Iloeje, M.U. (2011). The growing importance of neem (Azadirachta indica A. Juss) in agriculture, industry, medicine and environment: A review. *Research Journal of Medicinal Plants*. *5*, 230–245. https://scialert.net/abstract/?doi=rjmp.2011.230.245

Romaniuk, W., Mazur, K., Borek, K., Borusiewicz, A., Wardal, W. J., Tabor, S., & Kuboń, M. (2021). Biomass energy technologies from innovative dairy farming systems. *Processes*. 9(2), 335. https://doi.org/10.3390/pr9020335

Sassi, H.P., Ikner, L.A., Abd-Elmaksoud, S., Gerba, C.P. & Pepper, I.L. (2018). Comparative survival of viruses during thermophilic and mesophilic anaerobic digestion. *Science of the Total Environment*. *615*, 15-19. DOI: 10.1016/j.scitotenv.2017.09.205

Sikora, J., Niemiec, M., Szeląg-Sikora, A., Gródek-Szostak, Z., Kuboń, M. & Komorowska, M. (2020). The Effect of the Addition of a Fat Emulsifier on the Amount and Quality of the Obtained Biogas. *Energies*. *13*(7), 1825. https://doi.org/10.3390/en13071825.

Singh, A. & Pandey, J. (2012). Metal contamination and health risk from consumption of organically grown vegetables influenced by atmospheric deposition in a seasonally dry tropical region of India. *Bulletin of Environmental Contamination and Toxicology*. *89*, 384-389. https://doi.org/10.1007/s00128-012-0690-z

Skibko, Z., Romaniuk, W., Borusiewicz, A. & Porwisiak, H. (2021). Use of pellets from agricultural biogas plants in fertilisation of oxytrees in Podlasie, Poland. *Journal of Water and Land Development*. *51*(4), 124-128. https://doi.org/10.24425/jwld.2021.139022.

Sobol, Z., Jakubowski, T., & Wrona, P. (2020). Impact of UV-C stimulation of tubers, immersion of potato sticks in water and frying fat type on the content of fat in dry mass of French fries. Agricultural Engineering, *24*(1), 47-55.

Sogn, T.A., Dragicevic, I., Linjordet, R., Krogstad, T., Eijsink, V.G. & Eich-Greatorex, S. (2018). Recycling of biogas digestates in plant production: NPK fertilizer value and risk of leaching. *International Journal of Recycling of Organic Waste in Agriculture*. 7, 49-58. https://doi.org/10.1007/s40093-017-0188-0.

Suproniuk, M., Skibko, Z. & Stachno, A. (2019). Diagnostics of some parameters of electricity generated in wind farms. *Przegląd Elektrotechniczny*. *11,* 105-108, DOI 10.15199/48.2019.11.28.

Szparaga, A., Tabor, S., Kocira, S., Czerwińska, E., Kuboń, M., Płóciennik, B. & Findura, P. (2019). Survivability of probiotic bacteria in model systems of non-fermented and fermented coconut and hemp milks. *Sustainability*. *11*(21), 6093. https://doi.org/10.3390/su11216093.

Tallou, A., Haouas, A., Jamali, M.Y., Atif, K., Amir, S. & Aziz, F. (2020). Review on cow manure as renewable energy. Smart Village Technology: Polyvalent team in Research and Development; *Springer International Publishing*. Cham, Switzerland, 341–352. https://doi.org/10.1007/978-3-030-37794-6_17.

Trypolska, G., Kyryziuk, S., Krupin, V., Wąs, A. & Podolets, R. (2022). Economic Feasibility of Agricultural Biogas Production by Farms in Ukraine. *Energies*. *15*, 87. https://doi.org/10.3390/en15010087.

Tsachidou, B., Scheuren, M., Gennen, J., Debbaut, V., Toussaint, B., Hissler, C., George, I. & Delfosse, P. (2019). Biogas residues in substitution for chemical fertilizers: A comparative study on a grassland in the Walloon Region. *Science of the Total Environment*. 666, 212-225. https://doi.org/10.1016/j.scitotenv.2019.02.238.

Tsapekos, P., Kougias, P.G., Frison, A., Raga, R. & Angelidaki, I. (2016). Improving methane production from digested manure biofibers by mechanical and thermal alkaline pretreatment. *Bioresource Technology*. *216*, 545-552. https://doi.org/10.1016/j.biortech.2016.05.117.

Tyagi, V.K., Fdez-Güelfo, L.A., Zhou, Y., Álvarez-Gallego, C.J., Garcia, L.I.R. & Ng W.J. (2018). Anaerobic co-digestion of organic fraction of municipal solid waste (OFMSW): Progress and challenges. *Renewable and Sustainable Energy Reviews*. *93*, 380-399. https://doi.org/10.1016/j.rser.2018.05.051.

Tymińska, M., Skibko, Z. & Borusiewicz, A. (2023). The Effect of Agricultural Biogas Plants on the Quality of Farm Energy Supply. *Energies*. *16*, 4600. https://doi.org/10.3390/en16124600.

Urra, J., Alkorta, I. & Garbisu, C. (2019). Potential Benefits and Risks for Soil Health Derived From the Use of Organic Amendments in Agriculture. *Agronomy*. *9*, 542. https://doi.org/10.3390/agronomy9090542.

Van, D.P., Fujiwara, T., Leu Tho, B., Song Toan, P.P. & Hoang Minh, G. (2019). A review of anaerobic digestion systems for biodegradable waste: Configurations, operating parameters, and current trends. *Environmental Engineering Research*. *25*, 1-17. DOI: https://doi.org/10.4491/eer.2018.334.

Velthof, G.L., Lesschen, J.P., Webb, J., Pietrzak, S., Miatkowski, Z., Pinto, M., Kros, J. & Oenema, O. (2014). The impact of the Nitrates Directive on nitrogen emissions from agriculture in the EU-27 during 2000–2008. *Science of the Total Environment*. 468-469. https://doi.org/10.1016/j.scitotenv.2013.04.058.

Żelezik, M. (2009). Why organic farming. Rocznik Świętokrzyski. Ser. B, *Nauki Przyr. Kielce 30*, 155-166.

Zhou, L., Hülsemann, B., Merkle, W., Guo J., Dong, R., Piepho, H.P., Gerhards, R., Müller, J. & Oechsner, H. (2020) Influence of Anaerobic Digestion Processes on the Germination of Weed Seeds. *Gesunde Pflanzen. 72*, 181-194 (2020). https://doi.org/10.1007/s10343-020-00500-y.

ZAWARTOŚĆ METALI CIĘŻKICH W SUBSTRATACH W BIOGAZOWNICH ROLNICZYCH

Streszczenie. Zawartość metali ciężkich w glebie powinna być stale monitorowana, szczególnie w przypadku upraw ekologicznych. Przekroczenie dozwolonych stężeń tych pierwiastków może doprowadzić nie tylko do zahamowania wzrostu roślin, ale także do wchłonięcia przez organizmy zwierzęce, które się nimi żywią. Metale ciężkie trafiają do gleby zazwyczaj drogą opadów lub nawozu. Widoczny jest wyraźny wzrost zainteresowania pofermentem do nawożenia pól. Zatem, autorzy zdecydowali o zbadaniu zawartość metali ciężkich w substratach (w gnojowicy i odpadach stałych) oraz w pofermencie. Zbadane próbki wykazały wyłącznie śladowe ilości metali ciężkich. Badanie pokazuje, że zawartość tych elementów w pofermencie nie jest sumą pierwiastków dostarczonych do fermentora z substratami. W większości zbadanych próbek, zawartość ołowiu nie przekraczała 5 mg·kg^{-1}. Najmniejszą ilość kadmu (średnio 0,28 mg·kg^{-1}) zaobserwowano w gnojowicy a najwyższe (średnio 0,34 mg·kg^{-1}) w stałym substracie zasilającym fermentor. Gnojowica miała najniższe stężenie rtęci i kadmu (średnio 0,012 mg·kg^{-1} oraz 5,8 mg·kg^{-1}). Najwyższe stężenie chromu zostało zanotowanie w fermentorze (średnio 3 mg·kg^{-1}) czyli średnio 0,3 mg·kg^{-1} wyższe niż surowiec oraz 0,5 mg·kg^{-1} niż gnojowica.

Słowa kluczowe: biogazownia, metale ciężkie, poferment, zanieczyszczenia, substrat