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EVALUATION OF THE IMPACT OF DIGESTATE FORMED DURING BIOGAS PRODUCTION ON THE CONTENT OF HEAVY METALS IN SOIL

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ABSTRACT

The aim of the study was to identify and assess the impact of four digestive masses obtained from different organic substrates on the content of heavy metals in soil. The study utilized soil derived from fertilizer and equipment. Timothy grass was used as a test plant. The effect of a fertilizer on the analyzed mass was compared with the objects of reference, which were: a control object (without fertilization), fertilized objects with the use of ammonium nitrate, fresh pig slurry and mineral fertilizer YaraMila. Experiment was conducted in quadruplicate, consisting of the total of 76 objects. Based on the survey, it was found that the use of digestive for fertilizing purposes is justified because of its impact on various soil parameters and is comparable to the impact of traditional fertilizers such as manure, ammonium nitrate and mineral compound fertilizers. The use of the digestive did not cause greater accumulation of heavy metals in the soil, than it is in case of the use of ammonium nitrate fertilizer or fresh manure, which further confirms that these products are safe and can be applied alternatively with traditional fertilizers.

Introduction

In Poland and other countries a growing interest in the construction of agricultural biogas plants has been reported recently. The energy produced from renewable sources becomes more and more popular because of environment protection proposals. However, along with this interest, a problem occurs. It is related to management of digestive, which is a by-product of the biogas production. The best and the cheapest way, is to use it for farming as a fertilizer. Unfortunately, it is difficult to convince farmers to use products from the biogas plant.

Waste from an agricultural biogas plant can be a good fertilizer, taking into account that they are properly managed. Research carried out on the digestive shows that its use for the purpose of fertilization is justified because of its proper effect on various parameters of the soil and is comparable to the effect of conventional fertilizers, such as liquid manure, ammonium nitrate and mineral fertilizers.

In the absence of data in literature concerning properties of the digestive fertilizer the aim of this study was to assess the impact of the use of different types of post fermented material on heavy metals content in soil. The study presents an analysis of their impact on the yield and general crop characteristic.

Properties of the digestive material

The unfermented organic compounds are mainly minerals and methane bacteria that remained after the process of anaerobic digestion. It is also known as residues of fermentation, digestive pulp, effluent or sewage digestive. Composition of the digestive material depends primarily on substrates involved in the process of anaerobic digestion.

After the anaerobic fermentation, a digestive mass is directed to the digester's storage tanks (liquid manure lagoons)._There, digestive material is stored and cooled. The fermentation process also takes place next to digestive storage tanks._This makes it possible additionally to obtain up to 20% of extra biogas. Moreover, covered tanks limit emission of odors to the environment.

Due to low total solids content in digestive material (within the range of 3 to 10%), currently it often happens that the digestive solid fraction is separated from the liquid fraction, which reduces the total volume of the fermented material. The solid fraction, prior to further use, can be stored and composted, while the liquid one may be used as a fertilizer or returned to a digester as a treatment dilute reactant. For separation of the two fractions, a belt filter press or a centrifuge is applied. The solid fraction after passage through a filter press may contain approximately up to approx.. 30% of dry matter content. In this form it can be applied for crop fields or grassland.

Table 1 shows the content of heavy metals in the digestive material obtained by anaerobic digestion from liquid manure divided into fractions. The results of laboratory experiments indicate that mass of the digestive compound compared to liquid manure used as starting material has practically the same quantities of Mn, Fe, Cu and Zn.

Table 1
Chemical properties of digestive material obtained from fermentation liquid manure, taking into account heavy metals content

Specification	Mass of the digestive material		
	The digestive liquid manure before separation into fractions	Liquid fraction	Solid fraction
Total solids (%)	1.6	1.5	32.6
Fe ($g \cdot kg^{-1}$ d.m.)	4.0	4.3	4.1
Cu ($mg \cdot kg^{-1}$ d.m.)	1016	1001	170
Mn ($mg \cdot kg^{-1}$ d.m.)	708	610	1042
Zn ($mg \cdot kg^{-1}$ d.m.)	2628	2563	519

Source: Szymańska, 2011; Marcato et al., 2008

Depending on the type of reactants involved in the process of anaerobic digestion, a chemical composition of digestive material was varied. Most of the agricultural biogas plants as the primary substrate for the production of biogas utilize liquid manure or corn silage. On the basis of analysis of reactions that occur during the anaerobic digestion, physical and chemical properties of the digestive material can be generally defined. It is important to evaluate the value of trace microelements content, including heavy metals. Table 2 presents the results of the zinc and copper content in different masses of the digestive material. The results indicate that the highest content of zinc and copper occurred in the mass of the digestive material marked with PS-AB2 (pig liquid manure and pasteurized slaughterhouse waste – 3.8%), and the lowest in CS-AW1 (cattle liquid manure and orange peel residues – 5%).

Table 2
Heavy metal content in the mass of digestive material

Symbol of the digestive material	Zn ($mg \cdot l^{-1}$)	Cu ($mg \cdot l^{-1}$)
PS-EC1	49.2	8.4
PS-EC2	45.9	7
PS-EC3	62.5	7.8
PS-AB1	84.4	14.3
PS-AB2	140.2	15.1
PS-AB3	34.7	4
Average	55.8	8.1
CS-G1	18.1	10.8
CS-G2	28.3	13
CS-G3	10.6	1.4
CS-AW1	7.7	2.8
CS-AW2	8	3,1
CSAW3	27.7	10.8
Average	14.4	6.9

Source: Szymańska, 2013; Alborquerque et al., 2012

where:
1) Group 1: pig liquid manure + add-energy plants
• PS-EC1 – pig liquid manure + rapeseed residue (9.6%),
• PS-EC2 – pig liquid manure + sunflower residue (4.5%),
• PS-EC3 – pig liquid manure + maize residues (5.4%).
2) Group 2: pig liquid manure + animal waste
• PS-AB1 – pig liquid manure + pasteurized slaughterhouse waste (0.6%),
• PS-AB2 – pig liquid manure + pasteurized slaughterhouse waste (3.8%),
• PS-AB3 – pig liquid manure + sludge from the wastewater treatment plant from slaughterhouses (1%) + the biodiesel wastewater (6.5%).
3) Group 3: cow liquid manure + addition of glycerol
• CS-G1 – cow liquid manure and glycerin (4%),
• CS-G2 and CS-G3 – cow liquid muck + glycerol (6%).
4) Group 4: cow liquid manure + additive residues from the agro-industrial
• CS-AW1 – cow liquid manure + orange peel residue (5%),
• CS-AW2 – cow liquid manure + orange peel residues (10%),
• CS-AW3 – cow liquid manure + cow slurry (4.3%) + oats and corn silage (11.6%).

Some of the substances included in biomass, even in small amounts can contain very harmful bacteria which may stop the process of anaerobic digestion. They are divided into toxic substances, which can get into the fermentation chamber together with a substrate as well as into those which go as intermediates in various stages of anaerobic decomposition. Excessive amount of a substrate can lead to distortion or inhibit the fermentation process through adverse effects on bacteria. Trace elements may also affect bacteria in a toxic way, if they occur in high concentrations. Extremely harmful substances are heavy metals, disinfectants, solvents, herbicides, salts and antibiotics. Heavy metals in a free form are harmful to the process of methane fermentation and later they can stay in the digestive material. Hydrogen sulfide can neutralize heavy metals during the fermentation process; therefore, the amount of harmful elements in a fermentation chamber can be reduced. If the concentration of hydrogen sulfide exceeds 50 $mg \cdot l^{-1}$ it can cause inhibition of the fermentation process. Increased concentration of hydrogen sulfide in biogas also contributes to corrosion of thermal energy systems.

The use of fertilizer from digestive material derived from the fermentation liquid manure, solid manure, biomass and other organic matter of the agricultural industry has a very good effect on physical and chemical properties of the soil, the environment and profitability. The mass of the digestive material can also be enriched by addition of macro- or micronutrients, creating organic and mineral fertilizers, which can be adapted to the requirements of various plants (Szymańska, 2013; Podkówka, 2012; Szymańska, 2011; Baadstrop, 2011; Kowalczyk-Juśko, 2010; Borowski and Domański 2009; Palm, 2008; Montusiewicz, 2008; Głodek et al., 2007; Ledakowicz and Krzystek 2005; Romaniuk, 1999).

Research material

The study was based on the experiment using set of pots, and was conducted in the greenhouse Experimental Station of the Faculty of Agriculture and Biology at the University of Life Sciences in Skierniewice. The study utilized sustainable soil fertilizer experiments and timothy grass was used as test plant. Digestive materials of symbols MP1, MP2, MP3, MP4 were mixed with 7.0 kg of soil before sowing timothy grass in doses consistent with the scheme of experiments (tab. 3). Some vases were sown with timothy (without presowing fertilization) and during the growth 50 ml to each of the tested masses were added to each vase (tab. 3).

Digestive material samples were taken from the laboratory fermentation chambers. Four digestive materials, differing with substrates used for fermentation, were selected for the tests (tab. 4). The fertilizer effect of the analyzed digestive material was compared with the reference objects, which were:

- Controls object without fertilization,
- SA1, SA2 – objects fertilized with ammonium nitrate,
- G1, G2 – objects fertilized with fresh pig liquid manure,
- YM1, YM2 – objects fertilized with mineral YaraMila.

Experiment was conducted in quadruplicate with 76 vases.

Table 3
Experiment data

Objects	Symbol of the digestive material	Dose	Unit
1	Control	0	-
	Pre-sowing fertilization		
2	$MP1_1$	100	$ml\cdot vase^{-1}$
3	$MP1_2$	150	$ml\cdot vase^{-1}$
4	$MP2_1$	100	$ml\cdot vase^{-1}$
5	$MP2_2$	150	$ml\cdot vase^{-1}$
6	$MP3_1$	100	$ml\cdot vase^{-1}$
7	$MP3_2$	150	$ml\cdot vase^{-1}$
8	$MP4_1$	100	$ml\cdot vase^{-1}$
9	$MP4_2$	150	$ml\cdot vase^{-1}$
10	G1	100	$ml\cdot vase^{-1}$
11	G2	150	$ml\cdot vase^{-1}$
12	SA1	0.75	$g\cdot vase^{-1}$
13	SA2	1.5	$g\cdot vase^{-1}$
14	YM1	2.1	$g\cdot vase^{-1}$
15	YM2	4.2	$g\cdot vase^{-1}$
	Extra fertilization		
16	MP1	50	$ml\cdot vase^{-1}$
17	MP2	50	$ml\cdot vase^{-1}$
18	MP3	50	$ml\cdot vase^{-1}$
19	MP4	50	$ml\cdot vase^{-1}$

where:
Controls – object without fertilization
- MP1 – liquid manure (67%) + leaves the head (22%)
- MP2 – liquid manure (87%) + glycerol (13%)
- MP3 – liquid manure (67%) + mushroom substrate (22%)
- MP4 – 100% liquid manure,
- G1 and G2 – fresh manure,
- SA1 and SA2 – ammonium nitrate,
- YM1 and YM2 – YaraMila fertilizer.

Table 4
Fermentation material used in the pot experiment (material was obtained from the Poznan University of Life Sciences in a joint research project)

Symbol of the digestive material	Utilized material for fermentation of substrates	% participation in the batch
MP1	liquid manure	67
	leaves	22
MP2	liquid manure	87
	glycerol	13
MP3	liquid manure	67
	mushroom substrate	22
MP4	liquid manure	100

Research methodology

After the end of the vegetation period, soil samples were taken from each vase. The soil was sieved through a 2 mm sieve. Then air-dried soil samples heavy metals were determined (Zn, Cu, Fe, Mn) in 1 $mol \cdot dm^{-3}$ HCl by AAS.

The results were statistically analyzed using Statistica 10.0 software. A multi-variant analysis was performed and homogeneous Tukey HSD test groups were separated at the significance level of $\alpha = 0.05$.

Research results

When assessing the suitability of various types of waste and industrial by-products, including digestive material for use as a fertilizer, an important aspect is to check the impact of the use of this "product" on the accumulation of heavy metals in soil. For this reason, the present study was carried out by soil analysis concerning copper, zinc, iron and manganese content. The choice of heavy metals was justified by the fact that digestive material typically contains substantial quantities of those metals. Thus, the soil application may lead to the accumulation of the mentioned heavy metals. The presence of heavy metals in post fermentation residues is mainly due to the addition of the pig liquid manure fermentation process, and therefore the use of digestive material should not increase the content of heavy metals in the soil more than the use of traditional liquid manure. The results confirm this hypothesis. Indeed, there was no statistically significant difference between the content of Cu, Zn, Fe and Mn in soil where the tested digestive materials were applied and soil where typical liquid manure was used. In addition, these results indicate that the content of the mentioned heavy metals on objects fertilized with digestive material does not differ from the content in the soil in the control object (Table 5). It can therefore be concluded that the fertilization digestive material is safe and does not cause the accumulation of heavy metals in soil.

Based on the results shown in table 5 it can be concluded, that in comparison to the control, the highest content of zinc was in soil fertilized with digestive material MP 3 with (liquid manure – 67% and mushroom substrate – 22% in the dose of 150 ml) and soil fertilized with ammonium nitrate in 1.5 g dose.

The lowest copper content was in case of the sample fertilized with post-fermented material MP2, which contained in its composition liquid manure – 87%, glycerol 13% and the fertilizer applied in 150 ml dose. The highest copper content in a digestive material was in case of 100% liquid manure, which was used in the extra fertilization in 50 ml dose.

The lowest content of iron in the soil in comparison to the control sample was in case of those containing ammonium nitrate in 1.5 g dose and samples digestive MP2, which contained liquid manure – 87% and glycerol – 13%, in 50 ml dose of extra fertilization. The highest content of this element was in MP1 sample, which contained liquid manure – 67% and leaves – 22%, in 100 ml dose, and a fresh liquid manure in 150 ml dose.

The smallest manganese content was determined in MP3 samples, which contained liquid manure – 67% and mushroom substrate – 22%, with the dose of 150 ml and SA1 (ammonium nitrate in 0.75 g dose). The highest manganese content was detected in MP1 samples, which contained liquid manure – 67% and leaves – 22% in 50 ml dose and SA2 ammonium nitrate in 1.5 g dose.

Table 5
Content of heavy metals in soils (mg·kg^{-1})

Test objects	mg Zn·kg^{-1}	mg Cu·kg^{-1}	mg Fe·kg^{-1}	mg Mn·kg^{-1}
Soil output	4.52	1.66	2146.89	36.93
Controls	4.95	1.73	2293.35	32.66

Objects fertilized with traditional fertilizers

The term fertilization	Pre-sowing fertilization		Pre-sowing fertilization		Pre-sowing fertilization		Pre-sowing fertilization	
Dose	1 dose	2 doses	1 dose	2 doses	1 dose	2 doses	1 dose	2 doses
Liquid manure	5.07	5.73	1.73	2.01	2468.34	2707.77	38.65	35.38
Ammonium nitrate	5.21	5.88	1.79	1.66	2299.74	2244.49	32.32	43.97
YaraMila	5.05	5.03	1.90	1.84	2351.60	2462.40	35.16	33.35

Objects fertilized of the digestive material

Term fertilization	Pre-sowing fertilization		Extra fertilization	Pre-sowing fertilization		Extra fertilization	Pre-sowing fertilization		Extra fertilization	Pre-sowing fertilization		Extra fertilization
Dose	100 ml	150 ml	50 ml	100 ml	150 ml	50 ml	100 ml	150 ml	50 ml	100 ml	150 ml	50 ml
MP1	5.76	5.22	5.24	1.94	1.74	1.95	2581.38	2438.75	2292.54	39.34	37.24	34.07
MP2	5.60	5.35	5.53	1.60	1.58	1.77	2432.37	2361.32	2247.24	34.64	37.89	34.17
MP3	5.44	5.80	5.25	1.69	1.92	1.97	2381.22	2460.64	2558.01	35.77	32.25	38.00
MP4	5.56	5.59	5.12	1.77	1.76	2.02	2318.53	2272.22	2342.36	34.27	36.34	34.63

Discussion and conclusions

On the basis of experiments it was concluded that the use of the digestive material as a fertilizer does not cause an increased accumulation of heavy metals in soil than it is in case of ammonium nitrate or fresh liquid manure.

In addition, the results of the study showed that the contents of heavy metals (Cu, Zn, and Mn Fn) in soil fertilized with the post fermented material used in the site experience did not differ from the contents of the control objects.

It can be concluded that fertilization using digestive material is safe and does not cause the accumulation of heavy metals in a soil.

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OCENA WPŁYWU MASY POFERMENTACYJNEJ POWSTAJĄCEJ PODCZAS PRODUKCJI BIOGAZU NA ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE

Streszczenie. Celem pracy było określenie i ocena wpływu stosowania czterech materiałów pofermentacyjnych uzyskanych z różnych substratów organicznych na zawartość metali ciężkich w glebie. Do badań wykorzystano glebę pochodzącą z trwałych doświadczeń nawozowych. Rośliną testową była trawa tymotka. Efekt nawozowy analizowanych mas porównywany był z obiektami odniesienia, do których należały: kontrola (obiekt bez nawożenia), obiekty nawożone saletrą amonową, świeżą gnojowicą świńską oraz nawozem mineralnym YaraMila. Doświadczenie prowadzone było w czterech powtórzeniach, łącznie obejmowało 76 obiektów. Stosowane masy pofermentacyjne nie spowodowały większego gromadzenia metali ciężkich w glebie, niż ma to miejsce w przypadku stosowania saletry amonowej czy świeżej gnojowicy, co dodatkowo potwierdza, że są to produkty bezpieczne i mogą być alternatywą dla tradycyjnych nawozów.

Słowa kluczowe: biogaz, fermentacja metanowa, nawozowe wykorzystanie masy pofermentacyjnej, doświadczenie wazonowe