

Research Article

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Biogas digestate – benefits and risks for soil fertility and crop quality – an evaluation of grain maize response

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Abstract: The agricultural usability of biogas digestate solids (BDS) as a soil amendment depends upon its impact on soil fertility and the content of minerals in the edible part of the grown crop. This hypothesis was verified in a series of field experiments with maize conducted between 2014 and 2016 at Brody, Poland. The two-factorial experiment consisted of the BDS application method (broadcast and row) and its rate: 0, 0.8, 1.6, 3.2 t ha⁻¹. The post-harvest analysis of soil fertility showed that BDS can, at least partly, replace mineral fertilizers. The supply of N-NO₃ to maize as a growth driving factor was significantly limited by a shortage of iron, potassium and, to some extent, magnesium. As recorded in 2016, the shortage of available Fe resulted in a low pool of N-NO₃, thus significantly decreasing the yield of grain. The shortage of K supply to grain created a pathway for the accumulation of other elements, including heavy metals. The disadvantage of the N-NO₃ pool increase, due to the BDS application, was concomitant with the enhanced intake of cadmium and lead, which consequently exceeded their permissible concentration limits in grain. These unfavorable results of biogas digestate impact on the quality of maize grain can be ameliorated by incorporating zinc into the biogas type of soil amendment and keeping a sufficiently high level of available potassium and iron. The shortage of K can be partly overcome by a better sodium supply, however, its accumulation in grain results in an enhanced accumulation of cadmium and lead.

Keywords: nutrient availability; grain yield; heavy metals; grain quality.

1 Introduction

The anaerobic fermentation is one of the most promising technological solutions involved in fuel production based on renewable resources. Biogas plants operate based on different types of organic substances, which are transformed into a mixture of methane and carbon dioxide, termed as biogas. The EU strategy concerning energy production from renewable resources assumes that, in the coming future, biogas can cover a quarter of produced bioenergy [1]. In its digestion process, agricultural biogas plant uses byproducts only which originate directly from farm production, like manure, straw or food industry biowastes. In the last year's energy, crops and maize silages have become one of the most important feedstocks for biogas plants [2,3].

The secondary product of the anaerobic digestion is the slurry, termed as biogas digestate, or simply digestate (D). The digestate contains a huge number of organic compounds of both plant and microbial origin and numerous mineral elements. Its key characteristic is a low concentration of dry matter, ranging from a few percent to more than ten percent [4]. The mineral composition of digestate depends, to a great extent, on the composition of substrate and the type of digestion process [5]. The concentration of mineral elements in digestate, in spite of the referenced announcement, is not high, but low [4,6]. According to Möller and Müller [4], concentration of N in slurry ranges from 1.2 to 9 kg Mg⁻¹ FW, and phosphorus from 0.4 to 2.6 kg Mg⁻¹ FW. Consequently, a huge volume of produced digestate leads to high cost of its storage to use as a fertilizer [7]. An alternative solution is a separation of the raw slurry into solid and liquid phases [2]. The solid fraction of digestate has a much higher content of

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nutrients, but, at the same time, its C:N ratio increases. The main reason for this process is a considerable loss of its fine organic, as well as, mineral N fractions [8]. Based on the existing literature, solid digestate with high contribution of mineral N fraction ($\geq 2/3$ of total N content) should be treated as bio-fertilizer, while the one with low contribution ($\leq 1/3$), as a soil amendment [7,9].

The recycled pathway of raw, liquid or solid form of digestate as fertilizers is the best way to close the cycle of nutrients, incorporated primarily into soil as mineral fertilizers [10]. The expected effect of digestate on crop production - yield, is a matter of controversy, because it is a result of numerous processes affecting the soil/crop-plant continuum. The first one, as discussed above, concerns the content of mineral elements. It is highly variable due to the natural composition of the feedstock. According to Gutser [11], the fertilizer value of digestate is comparable to dried poultry excrements. The second criterion of the digestate evaluation is linked to its impact on soil health. This term comprises a broad range of soil functions such as i) carbon transformation, ii) nutrient cycling, iii) soil structure maintenance, and iv) pest and disease control. All these processes determine the current status of soil productivity [12]. The C:N ratio of digestate is a decisive characteristic feature for the subsequent pathway of its transformation, following its incorporation into soil. High content of organic matter (OM) in the substrate and concomitant shorter time of its digestion result in a higher C:N ratio of OM in the digestate and vice versa. The amount of applied bio-fertilizer and the ratio of mineral N fraction to the total N content are key indicators of its impact on N transformation pathways in soil during plant growth [2,8]. The digestate, as a fertilizer, is not only the carrier of N, but many other elements, like nutrients and heavy metals [7,14]. The impact of digestate on a particular element's bioavailability is mainly related to the concentration or amounts of nutrients incorporated into soil [4,7,13]. In spite of extensive studies on elemental composition of biogas digestate, the knowledge of its impact on soil processes, however decisive for fertility status and crop response, is still poor.

Soil health can be disturbed by an uncontrolled decrease of acidity, releasing toxic aluminum or by an exhaustive management of soil nutrients, leading to yield reduction [14,15]. The application of wastes, irrespective of their origin, creates a new field of soil productivity instability. The main reason is an incorporation of heavy metals (Cu, Zn, Cr, Cd, Ni, Pb) [16,17]. There are strict legislative norms regarding the maximum amounts of heavy metals incorporated into arable soils [18]. In the light of published reports, concentrations of heavy metals in digestate from agricultural biogas plants are below

permissible norms [4, 7, 18]. The question of the impact of a long-term or repeated application of digestate on the contents of HMs in soil is still open. This problem should not be limited only to lead or cadmium but should also refer to zinc and copper [7]. The effect of applied digestate on HMs bioavailability has not been identified yet. It could be driven by numerous processes responsible for their movement, uptake and plant accumulation.

The crop health with respect to the nutritional value of its edible parts is considered to be based on two approaches. Both are standardized but differ in the applied criteria. The first ones, Recommended Daily Allowance (RDA) or Adequate Intake (AI), clearly define the quantity of a particular nutrient required by human, based on gender and age [19]. The problem of nutrient density in edible parts of staple food is a matter of controversy. It has been documented, as thorough reports show for wheat as well as fruit and vegetables that the increase of grain yield and harvest index of a crop result in a lower density of key nutrients, which are mainly micronutrients [19,20]. On the other hand, crop plants show great variability in their response to a supply of easily available heavy metals, resulting in their accumulation in edible plant parts. The presence of heavy metals in consumed food may significantly disturb functions of essential elements, thus creating a health hazard to human body. The maximum acceptable levels of harmful metals in food, including edible parts of cereals, are standardized [21]. These norms are a useful tool to evaluate digestate as soil amendment. In light of the opinions presented above, a question appears: to what extent can an application of digestate, containing both micronutrients and heavy metals, affect the nutritional value of edible parts of crop plants?

A reliable evaluation of a particular element's sensitivity, i.e. its density in edible part of a crop plant, to the application of digestate should consider four sets of data such as i) yield, ii) post-harvest contents of nutrients and heavy metals, iii) concentration of nutrients in the crop edible part, iv) concentration of heavy metals in the crop edible part. These criteria were evaluated during the study of maize as a test crop fertilized with digestate solids.

2 Materials And Methods

Studies on the impact of biogas digestate solids (BDS) on maize were verified based on a series of field experiments carried out in 2014, 2015, and 2016 at RGD Brody (Poznan University of Life Sciences Experimental Station, 16°28'E and 52°44'N). According to the FAO/WRB, the studied soil has been classified as typical Luvisols. The sum of

Table 1: Chemical composition and amounts of applied elements with a particular rate of biogas digestate solids (BDS).

Rate of applied BDS fertilizer	OS g kg ⁻¹	N _t	N-NH ₄	P	K	Mg	Cu mg kg ⁻¹	Zn	Mn	Fe	Pb	Cd
	711	26.1	0.4	3.4	46.5	5.4	325	210	165	982	2.80	1.64
t ha ⁻¹	kg ha ⁻¹						g ha ⁻¹					
0.8	569	20.8	0.32	2.72	37.2	4.32	260	168	132	786	2.24	1.31
1.6	1138	41.8	0.64	5.44	74.4	8.64	520	336	264	1571	4.48	2.62
3.2	2275	83.5	1.28	10.88	148.8	17.28	1 040	672	528	3142	8.96	5.25

Table 2: The key soil agrochemical properties before maize sowing.

Year	Soil layer, m	pH ¹	P ² mg/kg soil	K ²	Mg ²	N-NO ₃ kg/ha	N-NH ₄	N _{min} ³	N _f ⁴
2014	0.0-0.3	5.6	180 ^H	330 ^H	220 ^G	39	10	49	51
	0.3-0.6	5.8	128 ^G	240 ^G	250 ^G	30	10	40	
2015	0.0-0.3	5.7	170 ^H	280 ^G	180 ^G	35	15	50	46
	0.3-0.6	5.9	150 ^H	230 ^G	230 ^G	32	12	44	
2016	0.0-0.3	6.2	149 ^H	220 ^G	172 ^G	25	21	46	61
	0.3-0.6	6.4	110 ^G	210 ^G	122 ^L	22	11	33	

¹1 M KCl; ²Mehlich3, classes: G – good; H – high; G – good; L – low; ³0.01 M CaCl₂;

⁴total sum of N_{min} + N_f = 140 kg/ha

precipitation during the growing season (April-September) was 410 mm in 2014, 284 in 2015, and 417 in 2016, whereas the long-term average is 317 mm. In 2015, maize vegetation was affected by drought in August with precipitation of 15 mm and concomitant temperature of 22.1°C versus 17.6°C (long-term average).

The two-factorial trial consisted of the following application methods: i) broadcast (Br), ii) row (Ro) and the rate of BDS: 0.0, 0.8, 1.6, 3.2 t ha⁻¹. The characteristics of BDS and the amounts of applied elements are presented in Table 1. The broadcast applied BDS was incorporated into the soil just before maize sowing and mixed at the depth of 7 cm. The row applied BDS was incorporated into soil just after sowing. The application row was prepared by the knife method, in the distance of 7 cm from the seed row and at the depth of 7 cm. Maize (variety *Eurostar*, FAO 240) was used as a test plant. The individual plot size, replicated four times, was 22.4 m². At maturity, crops were harvested from the area of 11.2 m². The grain yield was adjusted to 85% of dry matter weight.

The amount of mineral nitrogen (N_{min}) in spring, including both soil N_{min} resources (0.6 m) and N fertilizer (N_f as ammonium nitrate), was established at 140 kg ha⁻¹. Any other nutrients, except N, were not applied. The basic properties of soil under study are shown in

Table 2. All other agro-technical measurements were carried out in accordance with the best farming practice in maize production.

Composite soil samples (0-30; 30-60 cm) for N_{min} determination were collected at the beginning of the experiment and at maize harvest. For N_{min} determination, 20 grams of soil samples were shaken for 1 h with 100ml of a 0.01-M CaCl₂ solution (soil/solution ratio 5:1; m/v). Composite soil samples (0-30 cm) for a determination of available forms of nutrients (P, K, Mg, Zn, Cu, Mn, Fe) as well as cadmium and lead, were collected at the beginning of the experiment and after the maize harvest. The soil samples were then air-dried and crushed to pass a 2-mm mesh size. The extractable nutrients and heavy metals were determined based on the Mehlich 3 method [22]. The content of available P in the extract was determined calorimetrically, while the content of K, Mg and Ca, Fe, Mn, Zn, Cu, Pb, Cd, and Ni were determined using a FAAS.

The harvested samples of maize grain used for the determination of the element's concentration were first dried at 65°C. Nitrogen concentration was determined using a standard macro-Kjeldahl procedure. The plant materials for elements determination were mineralized at 600°C. The obtained ash was then dissolved in 33% HNO₃. The phosphorus concentration was measured by

the vanadium-molybdenum method using a Specord 2XX/40 at a wavelength of 436 nm. The contents of K, Mg and Ca, Fe, Mn, Zn, Cu, Pb, and Cd were determined using a FAAS.

The experimentally obtained data were subjected to the conventional analysis of variance using the computer program STATISTICA 10®. The differences between the treatments were evaluated with the Tukey's test. In tables and figures, results of the F test (***, **, * indicate significance at the $P < 0.1\%$, 1% , and 5% , respectively) are given. The stepwise regression was applied to define the best set of variables for the yield discriminative crop characteristics.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results and Discussion

3.1 Growth conditions and grain yield

The content of plant available phosphorus (P) before the experiment setup was, in general, at a level suitable for maize (Table 1). This cannot be concluded for potassium (K), the content of which was good, but below the requirement of a high productive crop, especially in the year 2016. The same was noticed for magnesium (Mg) [23]. These fertility gaps were fulfilled, at least partly, by the application of BDS fertilizer (Table 2). The content of heavy metals (Pb, Cd) incorporated with BDS into the soil, was below the norms for organic fertilizers, based on Poland's permissible limits [24]. The only copper content was above norms, treating BDS as compost [24,25]. The total mineral N content in soil at the experiment setup, including soil (N_{min}) and fertilizer (N_f), was 140 kg ha^{-1} . This amount of N is sufficiently high to exploit a yielding potential of maize under Polish soil-climatological conditions [23]. The structure of both N sources was very similar in 2014 and 2015, stressing the dominance of N_{min} . Quite a different structure was observed in 2016, when N_f was the main source of N. The total amount of N incorporated in BDS was very close to the quantity of N in the respective rate of farmyard manure [11]. The C:N ratio in BDS was 11:1, indicating a high potential for mineralization [4,7]. The course of weather in 2015 only, can be considered as unfavorable for maize growth due to a shortage of water in August, covering "the critical window period," which is crucial for the grain yield development [26].

The grain yield of maize showed a significant year-to-year variability (Table 3). On average, yields harvested

in 2014 and 2015 were by 1.8 t ha^{-1} higher compared to 2016. This difference cannot be explained by the course of weather. The yield obtained in dry 2015 was even higher, compared to 2014, with much better distribution of precipitation during the growing season. A positive trend of the row method of BDS application was recorded in the first two years and a negative in the third year of study. The observed response of grain yield to BDS rate application followed the quadrate regression model. Its optimum rate of 2.19 t ha^{-1} resulted in the maximum yield of 11.02 t ha^{-1} . It was by 2.484 t ha^{-1} higher compared to the N control, where P and K were not applied. This result clearly corroborates the opinion of high fertilizer value of digestate, as a replacement for mineral fertilizers applied to various crops [10,13,27].

3.2 The post-harvest content of available elements

The post-harvest content of bioavailable elements should give an answer concerning BDS impact on both grain yield of maize and soil fertility. Its impact on soil fertility requires an evaluation of four groups of elements (Table 3, 4, and 5). The first group refers directly to the mineral N content (N_{min}), which is composed of N-NO_3 and N-NH_4 . The total amount of residual N_{min} in the top layer (0-30 cm), averaged over experimental treatments, was extremely high, but year-to-year variable. The highest N_{min} quantity was recorded in 2015, characterized by a deep drought in August. The advantage of N-NH_4 content over N-NO_3 in this particular year clearly indicates favorable conditions for organic N mineralization. The lowest content of N_{min} was recorded in 2016. The residual content of N_{min} requires special attention due to its potential threat for the environment [28]. The net change of both N mineral forms was, except 2015, negative or close to zero (Table 5). The Figure 1 analysis clearly indicates a wide year-to-year variability in the net content change of both mineral N forms with respect to the N control. The excess of N_{min} thanks to BDS application clearly showed, irrespectively of the method of BDS application, in 2015. The main reasons were high precipitation in June and July (170 mm), concomitant with subsequent increased temperatures in August. The conjunction of these processes led to an accelerated mineralization of organic N. As a result, the net change of the post-harvest content was significantly related to the net change of N-NH_4 content:

$$\Delta \text{N-NO}_3 = 0.5 \Delta \text{N-NH}_4 + 5.89 \text{ for } R^2 = 0.36, \\ n = 54, \text{ and } P \leq 0.01 \quad (1)$$

Table 3: Yield of grain and the content of nutrients and heavy metals in the top-soil as affected by BDS application, mg kg⁻¹ soil.

Factor	Level of factor	N-NO ₃	N-NH ₄	P	K	Mg	Zn	Cu	Mn	Fe	Cd	Pb	pH	GY t ha ⁻¹
Years (Y)	2014	13.0 ^b	3.0 ^a	177.6 ^b	305.6 ^c	263.0 ^c	45.8 ^a	13.0 ^a	123.1 ^{ab}	1021.7 ^b	0.25 ^b	4.60	5.29 ^a	10.55 ^b
	2015	11.9 ^b	13.4 ^b	181.5 ^b	252.0 ^b	191.5 ^b	44.1 ^a	21.9 ^c	117.1 ^a	1004.7 ^b	0.25 ^b	4.52	5.40 ^b	10.63 ^b
	2016	2.8 ^a	1.4 ^a	163.9 ^a	183.6 ^a	146.6 ^a	52.6 ^c	18.0 ^b	127.8 ^b	632.7 ^a	0.14 ^a	4.51	5.56 ^c	8.80 ^a
F		286.1 ^{***}	298.3 ^{***}	6.30 ^{**}	132.6 ^{***}	127.2 ^{***}	20.34 ^{***}	295.3 ^{***}	7.72 ^{**}	374.9 ^{***}	219.4 ^{***}	0.38	22.85 ^{***}	44.1 ^{***}
Application (AP)	Br	9.8 ^b	5.3 ^a	181.2 ^b	246.5	194.4	48.8 ^b	18.2 ^b	124.0	900.4 ^b	0.21	4.62	5.36	9.88
	Ro	8.7 ^a	6.6 ^b	167.4 ^a	247.6	206.3	46.3 ^a	17.0 ^a	121.4	872.4 ^a	0.21	4.46	5.47	10.11
F		8.70 ^{**}	8.59 ^{**}	10.6 ^{**}	0.04	3.90	4.76 [*]	17.1 ^{***}	1.35	4.57 [*]	0.43	3.33	11.6 ^{**}	1.67
Rate (R)	0.0	7.7 ^a	4.8 ^a	168.4 ^{ab}	264.3 ^b	182.1 ^a	49.4	17.1 ^a	116.5 ^a	863.0 ^a	0.20	4.54	5.40	8.54 ^a
	0.8	9.1 ^b	6.3 ^b	155.4 ^a	270.3 ^b	202.2 ^{ab}	46.3	17.1 ^a	122.5 ^{ab}	880.9 ^{ab}	0.21	4.48	5.41	10.12 ^b
	1.6	11.3 ^b	8.6 ^c	176.3 ^b	237.5 ^a	205.5 ^b	46.3	18.2 ^b	125.7 ^b	884.5 ^{ab}	0.22	4.66	5.40	10.78 ^b
	3.2	8.9 ^b	4.1 ^a	197.2 ^c	216.1 ^a	211.7 ^b	48.0	17.9 ^b	125.9 ^b	917.1 ^b	0.21	4.47	5.46	10.52 ^b
F		15.27 ^{***}	20.89 ^{***}	17.07 ^{***}	16.73 ^{***}	4.52 ^{**}	1.65	3.54 [*]	3.79 [*]	2.96 [*]	1.12	0.95	0.87	31.51 ^{***}
F for the interaction														
Y x AP		2.54	9.47 ^{***}	1.68	3.11	3.55 [*]	2.22	2.98	2.62	3.97 [*]	1.41	0.01	0.02	3.41 [*]
Y x R		16.72 ^{***}	30.02 ^{***}	4.51 ^{**}	9.19 ^{***}	2.84 [*]	1.48	4.53 ^{**}	0.74	0.38	2.62 [*]	1.61	1.28	1.84
AP x R		18.22 ^{***}	2.84 [*]	1.95	0.41	4.30 ^{**}	2.84 [*]	5.49 ^{**}	0.61	0.70	1.14	3.44 [*]	5.63 ^{**}	0.54
Y x A x R		15.06 ^{***}	3.07 [*]	1.61	1.01	0.95	0.95	2.02	0.45	3.66 ^{**}	0.28	3.03 [*]	3.77 ^{**}	1.47

^anumbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05, respectively.

¹1.0 M KCl; ²average for the respective treatments.

Table 4: Matrix of correlations between extractable soil elements, soil pH, and grain yield, n = 72.

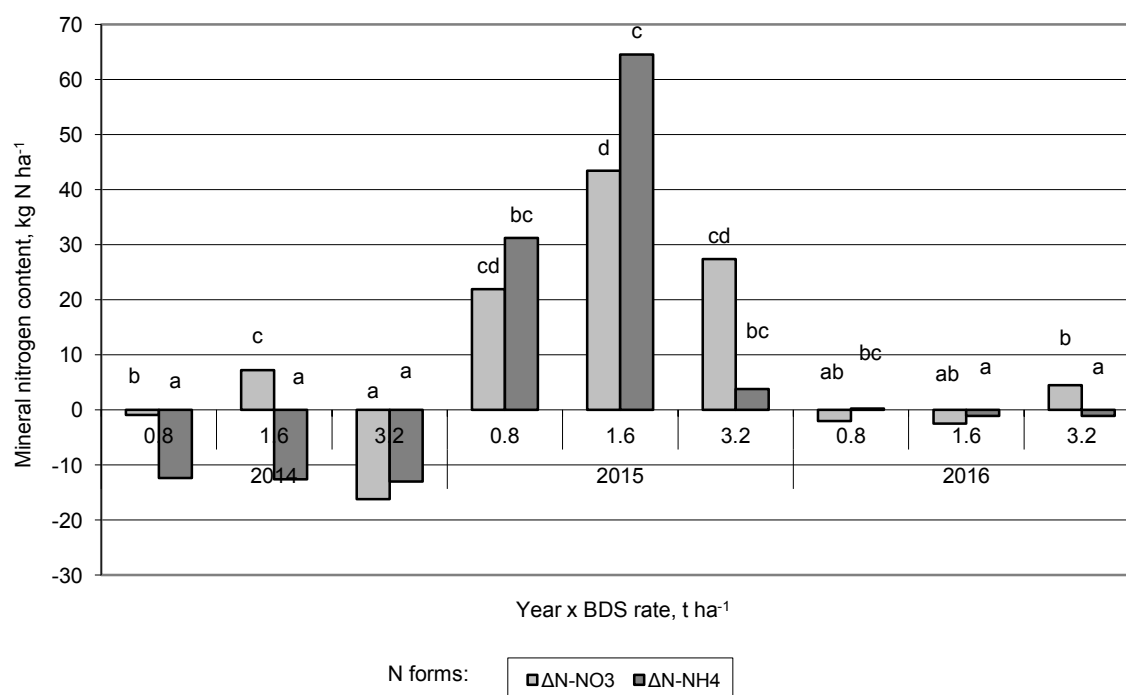
Characters	N-NH ₄	P	K	Mg	Zn	Cu	Mn	Fe	Cd	Pb	pH	GY
N-NO ₃	0.47 ^{***}	0.28 [*]	0.62 ^{***}	0.49 ^{***}	-0.43 ^{***}	-0.06	-0.23	0.80 ^{***}	0.73 ^{***}	0.14	-0.39 ^{**}	0.45 ^{***}
N-NH ₄	1.00	0.07	0.12	0.01	-0.27 [*]	0.55 ^{***}	-0.33 ^{**}	0.42 ^{***}	0.44 ^{***}	-0.01	-0.10	0.34 ^{**}
P		1.00	-0.04	0.20	-0.05	0.08	0.02	0.28 [*]	0.24 [*]	0.06	-0.24	0.23
K			1.00	0.53 ^{***}	-0.33 ^{**}	-0.40 ^{***}	-0.30 [*]	0.68 ^{***}	0.62 ^{***}	0.07	-0.43 ^{***}	0.23
Mg				1.00	-0.41 ^{***}	-0.48 ^{***}	0.07	0.62 ^{***}	0.64 ^{***}	0.07	-0.45 ^{***}	0.57 ^{***}
Zn					1.00	0.07	0.12	-0.48 ^{***}	-0.55 ^{***}	0.32 ^{**}	0.21 [*]	-0.40 ^{***}
Cu						1.00	-0.07	-0.06	-0.05	0.08	0.17	0.06
Mn							1.00	-0.30 [*]	-0.26 [*]	-0.02	0.11	0.12
Fe								1.00	0.83 ^{***}	0.05	-0.53 ^{***}	0.58 ^{***}
Cd									1.00	0.16	-0.49 ^{***}	0.61 ^{***}
Pb										1.00	-0.19	0.05
pH											1.00	-0.29 [*]

***, **, * significance at 0.001; 0.01; 0.05, respectively.

Table 5: The post-harvest evaluation of the impact of BDS on the net change (Δ) of the soil element content and grain yield with the respect to the N control.

Factor	Level of factor	N-NO ₃ mg kg ⁻¹ soil	N-NH ₄	P	K	Mg	Zn	Cu	Mn	Fe	Cd	Pb	Δ GY t ha ⁻¹
Year (Y)	2014	-3.30 ^a	-12.67 ^a	-3.96 ^a	-30.33 ^a	61.32 ^c	-5.67 ^a	2.10 ^c	14.29 ^b	45.10	0.04 ^b	0.38 ^c	2.87 ^b
	2015	30.93 ^c	33.21 ^c	31.56 ^b	-37.19 ^a	14.65 ^b	0.53 ^b	0.42 ^b	4.88 ^a	31.01	0.00 ^a	0.01 ^b	1.39 ^a
	2016	0.01 ^b	-0.63 ^b	-3.98 ^a	1.90 ^b	-2.96 ^a	-2.43 ^a	-0.56 ^a	5.35 ^a	17.48	-0.01 ^a	-0.40 ^a	1.55 ^a
F		88.1 ^{***}	99.6 ^{***}	13.4 ^{***}	8.09 ^{**}	23.1 ^{***}	6.74 ^{**}	24.4 ^{***}	3.63 [*]	0.89	29.3 ^{***}	17.7 ^{***}	14.1 ^{***}
App (AP)	Br	12.58 ^b	2.80 ^a	17.06 ^b	-22.29	16.43	-0.84 ^b	1.48 ^b	9.91	49.88 ^b	0.01	0.11 ^b	1.78
	Ro	5.84 ^a	10.47 ^b	-1.32 ^a	-21.46	32.25	-4.20 ^a	-0.18 ^a	6.43	12.52 ^a	0.01	-0.11 ^a	2.09
F		8.43 ^{**}	7.75 ^{**}	8.06 ^{**}	0.01 ^a	3.94	5.93 [*]	25.6 ^{***}	1.17	4.87 [*]	0.67	4.15 [*]	1.51
Rate (R) t ha ⁻¹	0.8	6.34 ^a	6.38 ^b	-13.03 ^a	7.15 ^b	20.11	-3.08	0.02 ^a	5.99	17.95	0.01	-0.06	1.58
	1.6	16.06 ^b	17.0 ^c	7.84 ^b	-25.71 ^a	23.35	-3.07	1.12 ^b	9.19	21.51	0.01	0.12	2.24
	3.2	5.24 ^a	-3.43 ^a	28.81 ^c	-47.07 ^a	29.55	-1.42	0.82 ^{ab}	9.35	54.14	0.01	-0.07	1.98
F		8.77 ^{***}	18.3 ^{***}	13.9 ^{***}	13.9 ^{***}	0.48	0.64	4.29 [*]	0.46	1.85	0.53	1.34	2.33
F for the interaction													
Y x AP		2.46	8.54 ^{***}	1.28	2.87	3.59 [*]	2.76	4.81 [*]	2.28	4.23 [*]	2.20	0.01	3.10
Y x R		7.21 ^{***}	18.01 ^{***}	2.20	8.79 ^{***}	0.33	1.23	5.18 ^{**}	0.27	0.35	0.93	0.05	0.12
AP x R		18.80 ^{***}	1.92	0.67	0.43	4.40 [*]	3.24	6.53 ^{**}	0.45	0.24	1.92	4.31 [*]	0.37
Y x A x R		16.10 ^{***}	2.05	1.22	0.70	0.61	0.98	3.07 [*]	0.15	3.88 [*]	0.22	4.25 ^{**}	1.12

^anumbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05, respectively.

**Figure 1:** The post-harvest status of mineral N with respect to the N control.

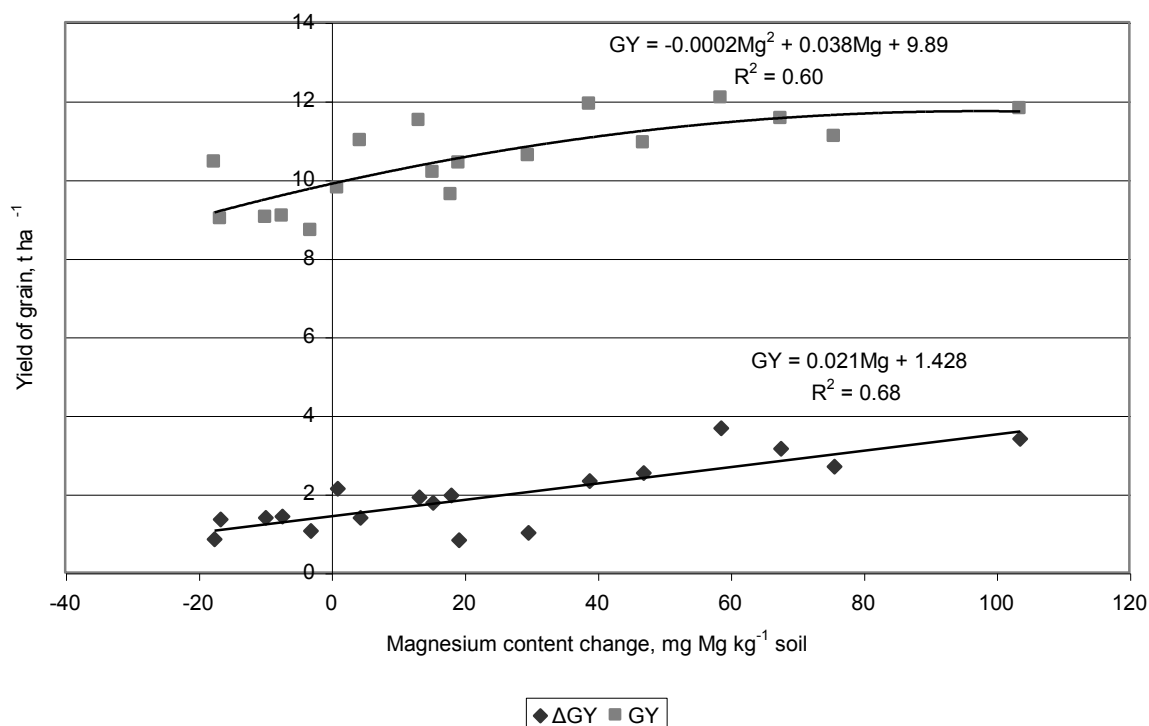


Figure 2: The effect of magnesium post-harvest change with respect to the N control on the net yield increase and final grain yield.
Legend: ΔGY – grain yield net increase; GY – grain yield.

This equation clearly indicates that each kilogram of $N-NH_4$ produced 0.5 kg $N-NO_3$. These results stress the strong mineralization power of biogas digestate under favorable external conditions [2,10].

The second group, consisting of P, K, and Mg, should be considered with special care, because BDS was a single carrier of these nutrients. The post-harvest content of P, irrespective of the year, was at the same level as recorded before the experiment setup (Table 2). However, the net change was only positive in 2015. The P content increase, compared to the BDS control, appeared first on the plot with 1.6 t ha⁻¹. It means that the supply of P was not the growth limiting factor, provided that its amount applied in BDS was high enough to replace its soil resources. The post-harvest content of K showed an elevated year-to-year variability, with a considerable decreasing trend during the growing season. It is necessary to stress strong relationships of K content with available pools of Fe, Cd, $N-NO_3$, and Mg, but not with the grain yield (Table 4). The positive relationships between K and $N-NO_3$ suggest its strong dependence on N transformation processes. It is well documented that NH_4^+ ions are involved in K^+ release from soil cation exchange complex [29]. During the season, K content decrease was enforced in 2014 and 2015, resulting in a strong negative net change compared to the

N control. This change was imposed on plots fertilized with high rates of BDS (Table 5).

The analysis of the post-harvest Mg content indicates its crucial role as the yield factor. The post-harvest Mg content increased in the first two years of the study compared to its pre-sowing content (Table 1, and 3). The net change of available Mg (ΔMg) was extremely high in 2014, followed by much lower, but a positive increase in 2015. The critical role of available Mg pool is summarized in Figure 2. The net yield increase due to the net change of Mg content was linear. It univocally stresses a strong impact of BDS on the size of Mg pool for maize. The net release of available Mg due to BDS application reached its optimum for ΔMg of 95 mg kg⁻¹ soil, resulting in the maximum yield of maize of 11.7 t ha⁻¹. It is necessary to stress that the content of available Mg was not only positively correlated with $N-NO_3$, but also with Cd contents.

The third group taken into consideration/in focus consists of micronutrients such as zinc (Zn), copper (Cu), manganese (Mn), and iron (Fe). The post-harvest Zn content was significantly higher in 2016 compared to both previous years. At the same time, as a result of ΔZn analysis, it was, except for 2015, much lower in soil fertilized with BDS. The status of soil Zn suggests that the amount of zinc incorporated into soil with BDS was too low to cover

the requirements of maize, resulting in the depletion of its available soil pool [30]. The second important piece of information is that both the content of available Zn and its net change (ΔZn) negatively impacted respective Cd characteristics, as presented for the available Cd content:

$$\text{Cd} = -0.008\text{Zn} + 0.58 \text{ for } R^2 = 0.52, n = 24, \text{ and } P \leq 0.001 \quad (2)$$

This equation clearly stresses that any increase in the content of available Zn resulted in the drop of plant ready for use Cd. This conclusion is important for crop protection against harmful element such as Cd, which uptake by crop plants can be reduced by both soil and foliar application of zinc fertilizers [31]. It has been concluded that soil amendments based on biogas digestate should be enriched with zinc as an agent, ameliorating Cd activity in the soil. The content of available Cu showed a significant year-to-year variability. Its net change was (except for 2016) positive, indicating a sufficiently good supply from BDS to maize in years with high yields. It is necessary to stress its significant net increase with respect to the N control as recorded in treatments with higher BDS rates.

Manganese (Mn) and iron (Fe) require special attention. The post-harvest analysis showed a net change of their soil contents in response to BDS application (Table 5). The content of Mn was only driven by the year-to-year variability, being significantly higher in 2014. In contrast, the content of Fe responded to both experimental factors in each growing season. It is necessary to indicate a very strong relationship between Fe and N-NO_3 contents:

$$\text{N-NO}_3 = 0.295e^{0.0036\text{Fe}} \text{ for } R^2 = 0.80, n = 72 \quad (3)$$

This equation clearly shows that the N-NO_3 content variability significantly depended on the pool of soil available Fe. It can be concluded, that in 2016 its available pool was too low to increase the content of N-NO_3 as a decisive yield forming factor, and therefore the drive of grain yield of maize.

The pattern of cadmium (Cd) and lead (Pb) content response to the application of BDS was quite different. The content of Cd showed only a year-to-year variability, being significantly lower in 2016 as compared to 2014 and 2015 (Table 3). The effect of BDS resulted in a net change of the content of Cd available pool in those two years (Table 5). It is necessary to stress strong relationships of Cd content with Fe, following by N-NO_3 , K, Mg, N-NH_4 , however negative with Zn at the same time (Table 4). Among these relationships, a special attention is devoted to N-NO_3 and Cd pair:

$$\text{Cd} = -0.0007\text{N-NO}_3^2 + 0.021\text{N-NO}_3 + 0.095 \text{ for } R^2 = 0.71, n = 72 \quad (4)$$

This equation clearly shows that the content of available Cd increased along with the level of N-NO_3 content of 15 mg kg^{-1} , resulting in the maximum Cd content of 0.25 mg kg^{-1} . This strong relationship suggests that any increase in the net content of soil nitrate N resulted in the concomitant increase of both the content of ready for use cadmium and grain yield. As a result, the content of available Cd presented itself as the best predictor of the yield:

$$\text{GY} = -393.8\text{Cd}^2 + 36.44\text{Cd} + 10.48 \text{ for } R^2 = 0.32, n = 72 \quad (5)$$

This equation informs that the optimum content of $0.05 \text{ Cd mg kg}^{-1}\text{soil}$ resulted in the maximum yield of 11.33 t ha^{-1} . It also indicates that BDS impact on the $\text{N}_{\min}$ pool led to the intensification of Cd bio-availability. Therefore, any intensification of the processes responsible for N transformation creates, in turn, a potential threat for the increase of the harmful element content, such as cadmium.

The content of available Pb was driven by an interactional effect of both experimental factors in each year of the study (Table 3, 4, 5). Its net change, as shown in Figure 3, was recorded in 2014 and 2015 on plots with broadcast application of BDS. Its depletion was recorded in all other treatments, especially in 2016. Its net increase showed a strong relationship with the content of copper and lead.

3.3 Elements concentration in maize grain

The concentration of elements in the edible part of a particular crop is an important indicator of its food nutritional value [20]. The *genetic dilution effect* is a result of two crop characteristics, i.e. its dry matter yield and the concomitant increase of the harvest index [19,20]. The effect of soil amendment, as biogas digestate requires, therefore, a deep evaluation of maize grain nutritional value, taking into account the yield and contents of both nutrients and heavy metals.

The content of N was significantly lower in 2016, showing at the same time a considerable dependence on the content of the K content in kernels (Table 6, 7). The obtained yields, even for the N control, indicate a good supply of N [32]. It means that the supply of nitrogen from the BDS was sufficiently high to exploit the yield potential of maize. The pattern of N concentration response to the

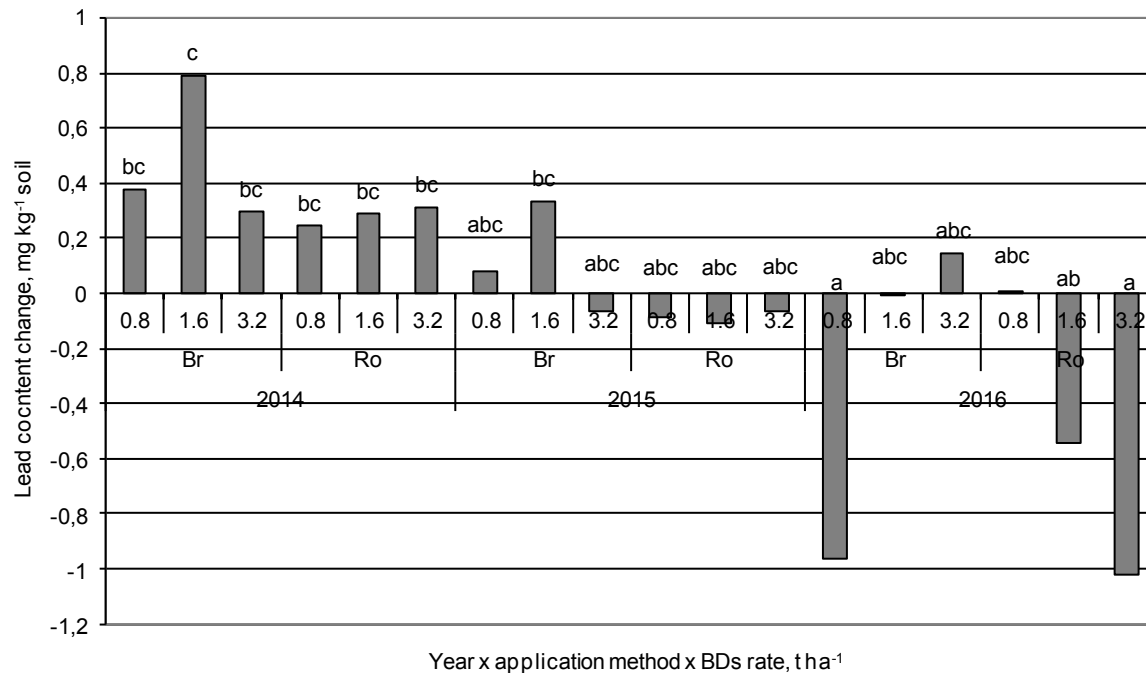


Figure 3: The post-harvest change in the content of plant available lead with the respect to the N control.

Table 6: Grain yield and concentration of elements in maize kernels as affected by BDS application.

Factor	Level of factor	N	P	K	Mg	Ca	Na	Zn	Cu	Mn	Fe	Cd	Pb
		g kg ⁻¹				mg kg ⁻¹							
Year (Y)	2014	15.5 ^b	2.15 ^a	4.02 ^c	1.37 ^a	0.246 ^a	0.134 ^a	17.0 ^b	1.74 ^a	3.95 ^b	31.5	0.09 ^a	0.14 ^a
	2015	15.1 ^b	2.02 ^a	2.66 ^b	1.31 ^a	0.333 ^c	0.240 ^b	11.2 ^a	2.32 ^b	4.70 ^c	27.9	0.16 ^c	0.22 ^c
	2016	14.4 ^a	2.36 ^b	1.96 ^a	1.77 ^b	0.276 ^b	0.120 ^a	16.1 ^b	1.82 ^a	2.61 ^a	30.4	0.12 ^b	0.16 ^b
F		13.91***	8.30***	246.4***	30.45***	50.13***	127.2***	48.75***	19.30***	73.89***	3.10	21.65***	75.90***
App (AP)	Br	15.1	2.20	2.83	1.52	0.278	0.149 ^b	15.0	1.93	3.77	28.2	0.11 ^a	0.17
	Ro	14.9	2.16	2.93	1.45	0.292	0.146 ^a	14.6	1.99	3.73	31.6	0.14 ^b	0.17
F		2.09	0.30	1.83	1.93	0.380	6.62*	0.59	0.60	0.08	7.54**	21.64***	0.12
Rate (R)	0.0	14.6 ^a	1.96 ^a	2.63 ^a	1.31 ^a	0.267 ^a	0.136 ^a	13.5 ^a	1.86 ^a	3.86 ^b	21.8 ^a	0.07 ^a	0.18 ^{ab}
	0.8	15.0 ^{ab}	2.53 ^b	3.05 ^{bc}	1.54 ^b	0.298 ^b	0.167 ^b	15.8 ^b	1.85 ^a	3.95 ^b	28.5 ^b	0.14 ^b	0.16 ^a
	1.6	15.4 ^b	2.12 ^a	3.07 ^c	1.57 ^b	0.280 ^{ab}	0.183 ^b	16.3 ^b	1.89 ^a	3.24 ^a	31.4 ^b	0.15 ^b	0.17 ^a
	3.2	14.8 ^{ab}	2.10 ^a	2.77 ^{ab}	1.52 ^b	0.295 ^b	0.173 ^b	13.6 ^a	2.24 ^b	3.97 ^b	38.0 ^c	0.14 ^b	0.19 ^b
F		4.21*	13.38***	7.88***	4.86**	4.11*	9.23***	8.07	5.30**	5.94**	30.95***	19.44***	5.15**
F for the interaction													
Y x AP		0.39	0.62	1.52	3.76*	4.79*	11.6***	4.90*	0.54	18.94***	16.29***	4.57*	3.27*
Y x R		0.85	4.22**	1.84	3.67**	1.57	5.02***	3.76**	10.59	4.28**	13.32***	1.81	5.47***
AP x R		3.91*	0.46	3.50*	0.66	0.64	1.85	0.13	1.16	0.57	40.86***	3.80*	2.78
Y x A x R		0.35	2.18	6.65***	2.78*	0.68	2.34*	5.18***	1.73	5.89	3.75**	2.47*	7.13***

^anumbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05. respectively.

Table 7: Matrix of correlation between concentrations of elements in maize kernels and grain yield.

Elements	P	K	Mg	Ca	Na	Zn	Cu	Mn	Fe	Cd	Pb	GY
N	-0.07	0.47***	-0.18	-0.00	0.18	0.02	-0.11	0.09	-0.15	0.04	-0.14	0.40**
P	1.00	0.03	0.54***	-0.19	-0.15	0.30*	-0.01	-0.16	0.08	0.09	-0.16	-0.07
K		1.00	-0.27*	-0.30**	-0.07	0.24*	-0.11	0.18	0.01	-0.15	-0.25*	0.45***
Mg			1.00	-0.20*	-0.14	0.45***	0.11	-0.18	0.09	0.05	-0.12	-0.22
Ca				1.00	0.59***	-0.46***	0.29*	0.20	0.06	0.38**	0.47***	0.15
Na					1.00	-0.41***	0.39**	0.58***	0.14	0.36**	0.43***	0.36**
Zn						1.00	-0.41**	-0.25*	0.09	-0.22	-0.38**	-0.13
Cu							1.00	0.50***	0.04	0.18	0.47***	0.29*
Mn								1.00	0.10	0.06	0.33**	0.31**
Fe									1.00	0.18	-0.28*	0.13
Cd										1.00	0.14	0.36**
Pb											1.00	0.14

***, **, * significance at 0.001; 0.01; 0.05, respectively.

increasing BDS rates depended on the method of the fertilizer application:

1. Br: $N = -0.105BDS^2 + 0.57BDS + 14.66$; $R^2 = 0.97$ (6)
2. Ro: $N = -0.396BDS^2 + 1.189BDS + 14.52$; $R^2 = 0.87$ (7)

The optimum BDS rate for the broadcast method of BDS application was 2.66 t ha^{-1} and 1.5 t ha^{-1} for the row method. Irrespective of the BDS application method, the maximum N concentration was constant, reaching 15.4 g kg^{-1} DW. As presented in Table 7, the N concentration in the grain was significantly correlated with the content of available Fe. This nutrient, as shown in equation No 3, considerably limited the N-NO_3 pool.

The concentration of P, in contrast to N, was the highest in 2016. It was at the lowest level of frequently published ranges [33]. It is necessary to stress its significant relationship with the concentration of Mg. The concentration of K showed a strong year-to-year variability. Its concentration in 2014 was at the level of 4 g kg^{-1} , but in 2014 reached only 2 g kg^{-1} . Therefore, K can be treated as the key limiting nutrient for both the grain yield and N concentration. The yield response to K density in grain followed the quadrate regression model:

$$GY = -0.657K^2 + 4.944K + 2.016 \text{ for } R^2 = 0.57 \text{ and } n = 24 \quad (8)$$

This model simply shows that the yield of grain increased up to the K level concentration of 3.76 g kg^{-1} DW for the maximum yield of 11.3 t ha^{-1} . The required K density was only reached in 2014. Therefore, the K concentration in

maize grain synergistically responded to the supply of K and Mg from their soil available pools as results from the stepwise regression model:

$$K = -0.54 + 0.05K + 0.01Mg \text{ for } R^2 = 0.72 \text{ and } n = 72 \quad (9)$$

It means that plant available pools of K and Mg were limiting factors for the grain yield increase. The concentration of Mg in maize grain followed the model observed for P, being also positively correlated with Zn, as well as with Na and Cu (Table 6, 7). The recorded concentration of Mg was within the top level of the frequently published ranges [26,34]. The application of BDS resulted in a significant increase of its concentration but modified by the course of weather in a particular year of study.

The concentration of calcium (Ca) and sodium (Na) requires special attention, because the highest values of both elements were recorded in dry 2015 (Table 6). The most important message is that Ca concentration in maize kernels showed an antagonistic relationship with the concentration of K, a nutrient limiting the yield of grain (equation No 8). At the same time, it showed synergistic relationships with the concentration of Na, Pb and with Cd in particular. None of those relationships, however, showed any negative influence on the grain yield. In contrast, the concentration of Na was positively correlated with the grain yield. Its advantageous effect on the yield can be explained by the shortage of K. The increase of Ca and Na in maize grain in 2015 can be explained by their higher concentration in the growth medium as imposed by drought and shortage of K [35]. It has been well documented

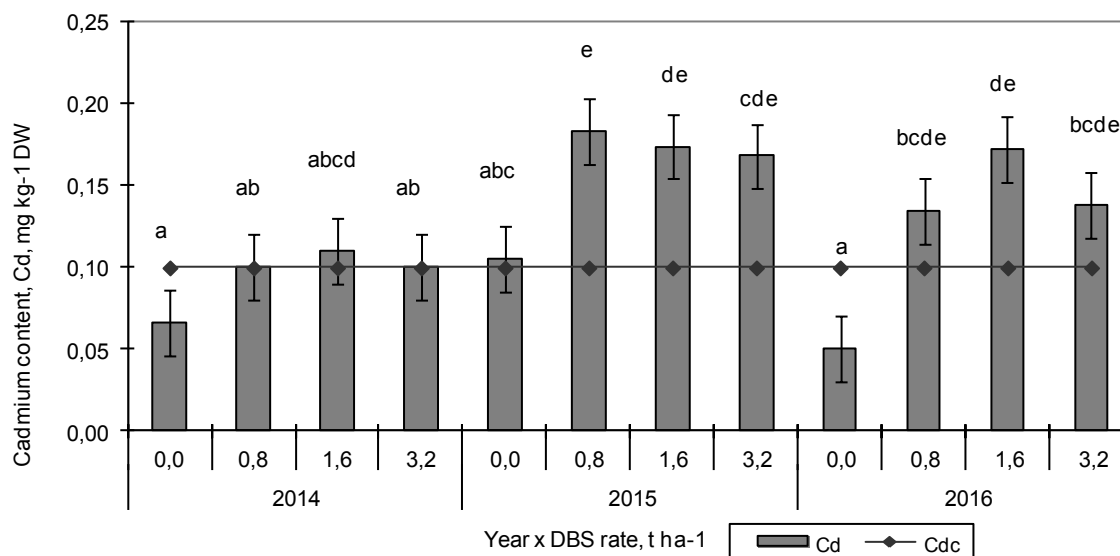


Figure 4: Cadmium concentration in maize grain as affected by the BDS rate in consecutive Years.
 Legend: Cd – real concentration; Cdc – permissible limits – 0.01 mg kg⁻¹ DW.

that low K soil content creates good/favorable conditions for enhanced uptake of sodium [36].

Patterns of microelements concentrated in maize kernels were nutrient specific. Zinc showed the opposite pattern to those recorded for Ca, Na, and Mn. As a result, its concentration was significantly correlated with Mg, but negatively with Cd, Ca, Na, Cu and Pb. Patterns of Cu and Mn concentrations in maize grain followed that reported for Ca and Na. Both nutrients were significantly correlated with each other and with Pb. The recorded Cu and Mn concentrations, and also Zn, except for 2015, were within the ranges reported by Komljenovic et al. [36]. The concentration of iron (Fe) in maize grain increased linearly with the BDS rate, showing a significant response to interactional effects of both experimental factors in each year of study. The progressive response to BDS rates was recorded in 2016 and in 2014, provided that it was a row method application. The recorded iron density was within ranges for 25 genotypes as reported by Kandianis et al. [38].

The pattern of heavy metal concentrations in grain is important due to their harmful impact on human health [6,17,39]. Their permissible limits are regulated by the EU norms at the level of 0.2 (0.3) and 0.1 mg kg⁻¹ DW for Pb and Cd, respectively [21,40]. Both HMs showed a strong variability exerted by experimental factors and years. On average, the lowest density of both elements was recorded in 2014 (Table 6). The effect of experimental factors was variable in all years of the study (Figure 4). In 2014, the threshold value of 0.1 mg Cd kg⁻¹ DW was only exceeded in the row application treatment of BDS. In 2015, this standard was exceeded on all plots, but the highest increase was

again observed in treatments with row applied BDS. In 2016, the threshold value was exceeded on all plots fertilized with BDS. According to the FAO/WHO report recently published [42] the dietary Cd exposure (daily intake - DI) was estimated to be 0.8 µg kg⁻¹ body weight (BW) day⁻¹. The analysis, based on potential consumption of maize grain at the level of five kg per person per annum [42] showed that DI of Cd was several times lower than the threshold value, ranging from 0.01-0.04 µg kg⁻¹ BW day⁻¹ (data not shown but available by authors).

The Cd concentration showed a significant relationship with Ca and Na (Table 7). The observed increase in Cd concentration in maize grain was, in general, related to the course of weather (2015) concomitant with the low concentration of soil K (2015, 2016). Another fact is that Cd, as well as N concentrations in maize grain showed a positive relationship with the grain yield. These two relationships corroborate a close relationship between Cd and N-NO₃ soil pools and their simultaneous impact on maize yield. These findings suggest that the presence of nitrates in the soil solutions, results in an enhanced uptake of Cd by plants.

The concentration of lead (Pb), as in the case of Cd, was significantly higher in 2015 and 2016 compared to 2014 (Table 6). The effect of experimental factors can be investigated in the background of years (Figure 5). The concentration of Pb in maize kernels in 2014 showed a significant response to BDS, it was however below the threshold value of 0.2 mg Pb kg⁻¹ DW. In 2015, the general pattern of Pb concentration response to BDS was very similar, and the threshold level of 0.2 was, but of 0.3 mg

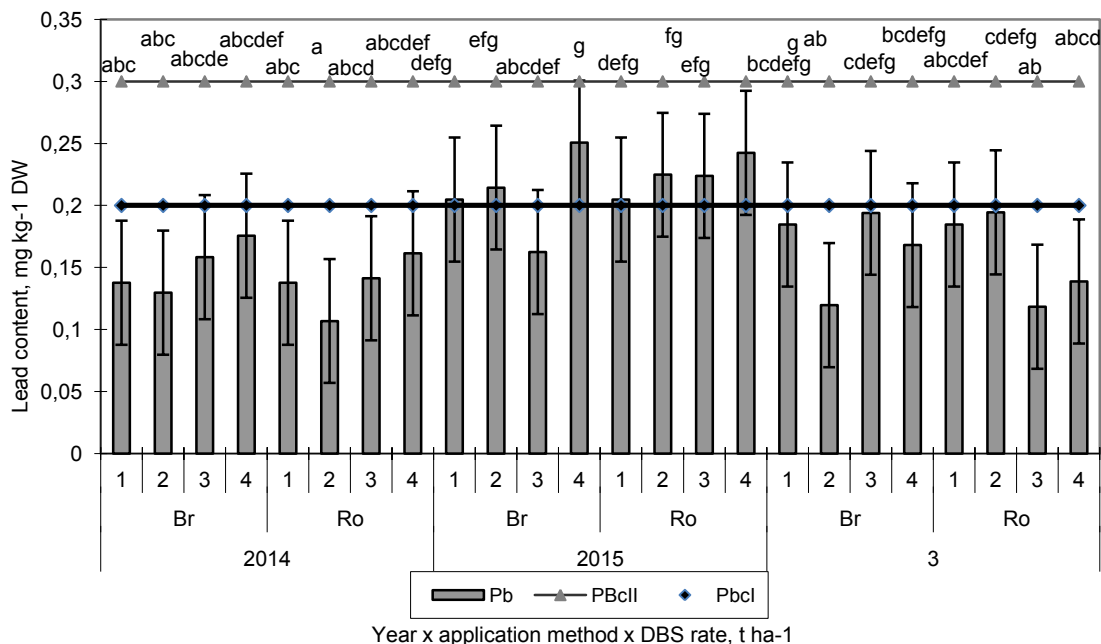


Figure 5: Lead concentration in maize grain as affected by the BDS application method and rate in consecutive years.

Legend: Pb – real concentration; Pbcl – permissible limits of 0.2; Pbcll of 0.3 mg kg⁻¹ DW.

kg⁻¹ DW was not exceeded. In the third year of the study, the concentration values were highly variable, beneath the 1st standard. The dietary exposure of human beings depends on age [41]. For children (1-4 years), it is estimated to be from 0.03 to 9 µg kg⁻¹ BW day⁻¹. Its values below 0.3 kg⁻¹ BW day⁻¹ are considered as save for intelligence quotient (IQ) in children. The analysis of Pb-DI for children was below this value (0.07-0.17 kg⁻¹ BW day⁻¹). For adults, the calculated Pb-DI was in the range of 0.02-0.05 kg⁻¹ BW day⁻¹, i.e. below the norm of 1.2 kg⁻¹ BW day⁻¹.

A positive, synergetic relationship between Pb and Ca, Pb and Cu, and Pb and Mn was observed, but these interactions were significant only in the dry year of 2015. In contrast, the negative relationships were recorded for two pairs, such as Pb and Zn, Pb and Fe (Table 7). The enhanced accumulation of Pb in maize grain concomitant with the increase of calcium accumulation probably took place because both elements enter the same transportation channel [43].

4 Conclusions

The applied solids of biogas digestate (BDS) emerged as a good carrier of nutrients for grain maize, having big potential to replace some of the mineral fertilizers. However, BDS is not able to cover shortages of nutrients,

which are deficient in intensively cultivated soil. In the studied case, the nutrient insufficiency referred to potassium, magnesium, iron and zinc. The BDS turned out to be an excellent agent, significantly enlarging the available Mg pool, which, together with the K pool, affected the grain yield and K concentration in maize grain. The increased supply of N-NO₃ to maize was the yield forming factor, thereby affecting the yield and N content in grain. In the conducted study, the content of available iron was a factor determining the size of the N-NO₃ pool. Its low content in 2016 resulted in a shortage in nitrogen supply to maize, resulting in a significant yield decrease concomitant with the drop of N concentration in grain. The disadvantage of the N-NO₃ pool increase was a rise in the pool of available cadmium. That, successively, resulted in its higher concentration in maize grain, which exceeded the permissible limit. This unfavorable result can be ameliorated by two different actions. The first one should focus on the increase of Zn concentration in digestate. The second one should be directed at the increase of soil fertility level with respect to the content of nutrients, which are exhausted by the grown crop. In the studied case, it referred to the content of available K. The shortage of both nutrients was the reason for the elevated concentration of Cd and Pb in maize grain.

Conflict of interest: Authors state no conflict of interest.

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