Journal of Elementology ISSN 1644-2296

Przygocka-Cyna K., Grzebisz W., Łukowiak R. 2018.
Effect of bio-fertilizer amendment on agrochemical properties of soil cropped with vegetables. J. Elem., 23(1): 163-177.
DOI: 10.5601/jelem.2017.22.3.1476

ORIGINAL PAPER

EFFECT OF BIO-FERTILIZER AMENDMENT ON AGROCHEMICAL PROPERTIES OF SOIL CROPPED WITH VEGETABLES*

Katarzyna Przygocka-Cyna, Witold Grzebisz, Remigiusz Łukowiak

Chair of Agricultural Chemistry and Environmental Biogeochemistry
Poznan University of Life Sciences, Poland

Abstract

Reuse of agricultural waste as bio-fertilizer is a key to closing the nutrient cycle and saving mineral fertilizers. To analyze the effect of two bio-fertilizers in an interaction with three crops grown in a consecutive crop rotation, a micro-plot experiment on poor loamy sand was carried out. Three series of a two-factorial experiment included two bio-fertilizers as the first factor with contrasting ratios of biomass ash and solids of BD (BAD): FE1 (2.2:1) and FE2, (1:2.2). The second factor was a dose of the applied BAD: 0.0, 20, 40, 80, 160, and 320 g m^{-2}. Two crops were grown in a fixed cropping sequence: radish → green bean →radish. The applied BAD fertilizers resulted in very rapid changes in the soil pH, the content of plant available nutrients as well as heavy metals. The pre-plant patterns of the content of nutrients and heavy metals were only slightly modified by the grown crops. The key reason of the observed stability in soil agrochemical properties was the variability in the plant available P, which significantly affected the content of the other elements, including heavy metals. The effect of phosphorus depended on the amount of BD introduced into the soil. Its higher doses resulted in a simultaneous increase in both the soil pH and the P and Ca content. An insufficiently low dose of BAD led to nutrient exhaustion, which was most severe with respect to K, Mg and Ca. The content of available heavy metals under the effect of the soil available P can be taken controlled, provided the content of available K and Zn is increased.

Keywords: BD, biomass ash, soil, nutrient availability, availability of heavy metals, cropping sequence.

Katarzyna Przygocka-Cyna PhD, Chair of Agricultural Chemistry and Environmental Biogeochemistry, Poznan University of Life Sciences, Wojska Polskiego 71F street, 60-625 Poznań, Poland, e-mail: kasiac@up.poznan.pl ; wojzu@tlen.pl

* This study is part of the research conducted within the EKO-BIONOM project of the NCBiR titled: *Pro-ecological manufacturing organic-mineral fertilizers based on: by products of burning and bio-gasification of biomass.* Agreement No. GEKON1/05/214543/38/2015.

INTRODUCTION

A standard way to improve soil fertility is to apply lime, originating from local resources of lime rocks, and mineral fertilizers, derived from non-renewable resources. In the Polish agriculture, K and P are production limiting factors (Tujaka, Terelak 2012). An alternative pathway for replenishing these two nutrients, in order to keep the soil fertility high, is to use bio-fertilizers produced from agricultural waste (Nkoa 2014). The latest studies focus mainly on ashes from combustion of different kinds of agriculture biomass or forest debris. The key attribute of bio-ash is its high alkalinity. Hence, it can be used for soil pH amelioration. It is well documented that bio-ash is a good source of P, K, and Ca, but the content of any specific nutrient depends on the incinerated plant species. Therefore, bio-ash is considered a good soil amendment, increasing soil fertility. One of the key disadvantages of bio-ash is the content of heavy metals, mainly lead and cadmium, which is a potential threat to any food cycle (Ciesielczuk et al. 2011, James et al. 2012, Piekarczyk 2013).

The biogas production in the last decade has become one of the most progressing branches in agriculture waste utilization. The EU policy for renewable energy assumes a 25% contribution of biogas in the coming future. The main sources of raw material are farmyard manure and maize silage (Holm-Nielsen et al. 2009, Łagocka et al. 2016). The real challenge for both biogas producers and scientists is to develop an efficient strategy of biogas slurry management. Biogas digestate (BD) contains 2-5% of dry matter, and numerous nutrients, easily available to crop plants (Möller and Müller 2012, Kataki et al. 2017). However, there are some disadvantages of slurry management. First of all, pipes need to be installed for long distance transportation directly into fields. Secondly, the EU law prohibits slurry application to arable soils during winter months (Łagocka et al. 2016). In a whole-year operation of a biorafinery it is necessary to account for the cost of tanks for temporary storage of slurry in investment calculations. The disadvantages of separation of solids from the slurry are energy demand and loss of ammonia (Møller et al. 2000).

The simultaneous utilization of both groups of waste (ash and BD) as soil amendments can be considered as a way to close cycles of numerous nutrients (Arthurson 2009). The solid fraction of BD, due to its high content of easily degradable organic matter and bio-ash as a mineral alkaline component, can be used to formulate a new type of bio-fertilizer (Kolář et al. 2008). It should be assumed that any type of bio-fertilizer based on bio-ash requires a validation study oriented on its effect on both soil fertility and its heavy metal content (Sharma et al. 2017).

The main objective of this study has been to evaluate the effect of two contrary types of bio-fertilizers, based on bio-ash and on the solid fraction of biogas digestate, on soil pH and the content of available nutrients and heavy metals. Another objective was to define optimum doses of each tested fertilizer required to maintain or even increase the soil fertility level in a nutrient exhausting, vegetable cropping sequence.

MATERIAL AND METHODS

The effect of bio-fertilizers based on biomass ash and biogas digestate (BAD) on soil agrochemical characteristics was evaluated in three series of artificially prepared micro-plots with consecutively grown vegetables. Soil used in the study was topsoil characterized by a loamy sand texture, classified as light soil. The agrochemical status of the soil was evaluated based on the Mehlich 3 method (MEHLICH 1984). The soil pH was measured in a 1:2.5 soil 0.01 M $CaCl_2$ suspension. Detailed description of the chemical properties of the soil under study clearly indicates slightly acid pH and very low content of available magnesium (Mg) and calcium (Ca), but not of phosphorus (P) and potassium (K) – Table 1.

A two-factorial experiment was arranged as follows:

1. The first factor: two types of BAD fertilizers composed of biomass ash (BA) + a solid residue of biogas digestate (BD) + phosphoric rock (PR) + elemental sulfur (S^0). The tested BAD were composed based on contrary shares of the first two components:
   a. FE1: BA-55% + BDs-25% + PR-15% + S^0-5%;
   b. FE2: BA-25% + BDs-55% + PR-15% + S^0-5%;

Table 1

Soil geochemical status after two-week pre-plant incubation, mg kg^{-1} soil

Factor	Level of factor	pH	P	K	Mg	Ca	Mn	Fe	Cu	Zn	Pb	Cd	Ni
	T0[#]	5.40	158	144	69	569	50.0	140	1.11	3.10	4.20	0.13	0.50
BAD Fertilizer	FE1	5.90	164^a	166	80	612^a	49.3	145	1.11	3.32	4.22	0.13	0.44
	FE2	5.92	178^b	167	79	738^b	51.5	153	1.17	3.71	4.45	0.15	0.42
F test		0.01	6.3^*	0.0	0.0	7.5^*	2.8	2.1	1.6	3.0	2.8	3.5	0.4
Dose, (D) (g m^{-2})	0	5.35	147^a	160^{ab}	74^{ab}	576^a	55.9^b	163	1.09^{ab}	3.35^{ab}	4.27	0.08^a	0.22^a
	20	5.89	167^{ab}	139^a	67^a	538^a	48.3^a	149	1.11^{ab}	3.26^a	4.36	0.14^b	0.46^b
	40	5.80	162^{ab}	130^a	68^{ab}	543^a	46.6^a	143	1.02^a	3.18^a	4.28	0.14^b	0.48^b
	80	6.03	166^{ab}	147^{ab}	74^{ab}	648^{ab}	50.7^{ab}	146	1.17^{ab}	3.28^a	4.40	0.15^b	0.45^b
	160	6.32	182^{bc}	185^b	86^b	844^{bc}	49.3^{ab}	146	1.13^{ab}	3.50^{ab}	4.28	0.15^b	0.47^b
	320	6.08	204^c	238^c	106^c	900^c	51.7^{ab}	146	1.32^b	4.54^b	4.43	0.17^b	0.49^b
F test		0.8	8.6^{***}	18.0^{***}	13.2^{***}	7.9^{***}	4.2^*	1.1	2.7^*	3.4^*	0.2	13.6^{***}	9.3^{***}
F test for the interaction													
BAD x D		0.21	1.32	1.60	0.34	2.68^*	0.23	0.94	0.11	0.60	0.41	0.70	0.20

[#] Soil agrochemical status before the experiment; [a] numbers marked with the same letter are not significantly different; ***, **, * indicate significant differences at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively.

2. The second factor: control treatment and five doses of BAD: 0; 20; 40; 80; 160; 320 g m^{-2}.

A detailed description of the chemical composition and amounts of particular elements incorporated into the soil is presented in Table 2. Two crops

Table 2

Chemical composition and the amount of elements incorporated into the soil with BAD fertilizers

Fertilizer type	Content of the element	Fertilizer dose (g m^{-2})				
		20	40	80	160	320
FE1						
Element	(g kg^{-1})	amount of the element (g m^{-2})				
P	36.8	0.75	1.50	3.00	6.01	12.0
K	31.1	0.66	1.33	2.66	5.31	10.6
Ca	57.4	1.28	2.56	5.11	10.2	20.5
Mg	9.1	0.19	0.38	0.77	1.53	3.06
S	48.0	0.96	1.92	3.84	7.68	15.4
	(mg kg^{-1})	amount of the element (mg m^{-2})				
Fe	13586	271.7	543.4	1086.7	2173.8	4347.5
Mn	1392.4	27.9	55.7	113.9	222.8	445.6
Zn	205.1	4.10	8.20	16.40	32.8	65.6
Cu	58.3	1.17	2.33	4.67	9.33	18.7
Pb	21.8	0.44	0.87	1.75	3.49	6.98
Cd	3.6	0.07	0.14	0.29	0.58	1.15
Ni	14.9	0.30	0.60	1.19	2.38	4.77
FE2						
	(g kg^{-1})	amount of the element (g m^{-2})				
P	36.4	0.73	1.46	2.91	5.82	11.65
K	19.7	0.39	0.79	1.58	3.15	6.31
Ca	40.4	0.81	1.61	3.23	6.46	12.91
Mg	5.2	0.10	0.21	0.42	0.84	1.68
S	48.0	0.96	1.92	3.84	7.68	15.36
	(mg kg^{-1})	amount of the element (mg m^{-2})				
Fe	6907.6	138.2	276.3	552.6	1105.2	2210.4
Mn	682.7	13.7	27.3	54.6	109.2	218.5
Zn	181.0	3.62	7.24	14.48	28.96	57.91
Cu	49.0	0.98	1.96	3.92	7.83	15.66
Pb	14.1	0.28	0.56	1.13	2.26	4.52
Cd	2.1	0.04	0.08	0.17	0.33	0.67
Ni	16.0	0.32	0.64	1.28	2.56	5.11

grown consecutively in a cropping sequence of radish → snap bean → radish were tested. The BAD fertilizers were applied in one dose at the beginning of the experiment and mixed into the soil layer of 7 cm. Mineral nitrogen at 4 g N m^{-2} was applied to all plots with radish, including the BAD control. P and K fertilizers were not applied there. The content and quantities of nutrients and heavy metals added in the soil with the BAD fertilizers are presented in Table 2. They are expressed in kg and g per ha in order to demonstrate the applied quantities. The water moisture regime during the whole experiment, which was 5.5 months, was kept at the field capacity. The incubation period, preceding crop cultivation, lasted 14 days. Composite soil samples (0-7 cm) were collected four times: at the beginning and at the end of each plant's growing season (where the termination of one plant's growing process was the onset of the growth of the next one). The soil samples were then air-dried and crushed to pass a 2-mm mesh size sieve. The extractable nutrients and heavy metals were determined based on the Mehlich 3 method (Mehlich 1984). The content of available P in the extract was determined colorimetrically, while the content of K, Mg and Ca, Fe, Mn, Zn, Cu, Pb, Cd, and Ni was determined using FAAS.

The experimental data were subjected to a conventional analysis of variance using the computer program Statistica 12®. Differences between treatments were evaluated with the Tukey's test. In tables and figures, equations of the *F* test results (***, **, * indicate significance at the $P < 0.1\%$, 1%, and 5%, respectively) are given.

RESULTS AND DISCUSSION

The pre-plant evaluation of soil agrochemical properties

Application of BAD resulted in a soil pH change, showing a constant tendency, i.e. pH increasing progressively with the increasing fertilizer doses (Table 1). The initial content of soil available phosphorus (P) was high. The FE2 showed a significantly higher impact on the P content compared to FE1. However, the amounts of P incorporated into the soil with both BAD fertilizers were the same. Therefore, the observed increase in the content of plant available P can only be explained by the amount of degradable organic substances introduced into soil via BAD fertilizer. The FE2 was 2.2-fold richer in organic substances than FE1. The C:N ratio in the solid fraction of BD tends to be very narrow, ranging from 3.0 to 8.5 (Møller, Müller 2012). Hence, the FE2 composition could create much more favourable conditions for efficient hydrolysis of phosphoric rock (PR), which was the primary form of BAD fertilizers. This hypothesis is supported by the study of Loria and Sawyer (2005), who recorded a higher content of available P in response to an application of BD. This effect was probably enforced by the intensive release of protons from decomposing digestate (De La Fuente et al. 2013).

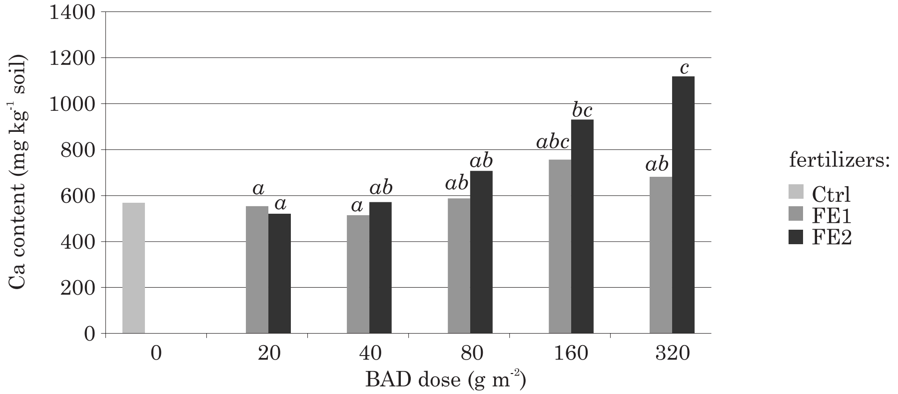

Fig. 1. The effect of BAD fertilizers on the available calcium content following the pre-plant incubation. [a] Numbers marked with the same letter are not significantly different

In the second group of nutrients, composed of potassium (K), magnesium (Mg) and calcium (Ca), only the latter element responded significantly to the type of BAD fertilizer. As shown in Figure 1, the net increase in the content of available Ca was influenced by the type of BAD fertilizer. For FE1, it started from the dose of 1.6 t ha^{-1}, whereas for FE2 the effect was seen since the dose of 0.8 t ha^{-1}. In addition, the latter one raised the Ca content in the soil treated with 3.2 t ha^{-1} to over 1000 mg kg^{-1}, i.e. improving the fertility class of the treated soil. This result cannot be explained by the amount of calcium applied to the soil with this dose of BAD. It was much higher in FE1. The observed phenomenon was probably due to the activity of microorganisms, which received a higher amount of organic matter from digestate (De La Fuente et al. 2013). The presented data clearly indicate that the low doses of BAD were not high enough to increase the content of available cations. The observed trend was even more conspicuous for K and Mg, as there was a noticeable correlation between their content. The relationship between K and Mg is presented below:

$$Mg = 0.321K + 25.8 \quad \text{for } R^2 = 0.76, \text{ and } n = 36.$$

The third group of nutrients was represented by micronutrients. In general, they did not respond to the BAD type of fertilizer. Based on the micronutrient rank order proposed by Zbíral (2016), the content of manganese (Mn), iron (Fe), and zinc (Zn), which was averaged over the experimental treatments, can be classified as falling within the medium class, whereas copper (Cu) content belonged to the low class. The impact of a BAD dose was nutrient specific. The content of available Mn and Fe decreased significantly in response to the increasing doses of BAD. Iron requires much more attention. As shown in Figure 2, the content of available Fe decreased, following the pH value of 5.2. The content of Cu and Zn showed a progressing, yet unstable response to the increasing doses of BAD.

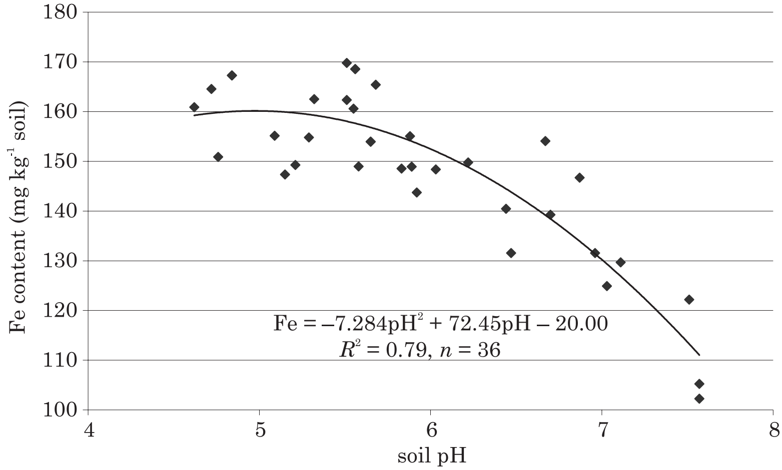

Fig. 2. The content of plant available iron following the pre-plant incubation as a function of soil pH variability

The fourth group of elements comprises heavy metals, represented by lead (Pb), cadmium (Cd) and nickel (Ni). It ws only the content of Pb that did not respond to either of the experimental factors. It is interesting to notice that the Pb content in the soil showed a positive correlation with the P content and a negative correlation with the Mg content. In general, the stepwise regression corroborates the above conclusion:

$$Pb = 1.43 + 0.008P^{***} - 0.011Mg^{***} + 0.674Cu^{**} + 0.011Fe^{***}$$
$$\text{for } R^2 = 0.84 \text{ and } n = 36.$$

The post-harvest evaluation of soil agrochemical properties

The post-harvest evaluation of soil agrochemical characteristics was conducted on soil samples taken up directly after the harvest of each of the particular crop cultivated in the cropping sequence composed of radish-green bean-radish (Table 3).

Soil pH

The key soil property, i.e. soil pH, is in general, considered as the main cause of soil agrochemical variability (Ohno and Erich 1990). The general pattern of soil pH response to increasing doses of both fertilizers was established during the growth of the first crop, i.e. radish. Its cultivation resulted in a significant drop in soil pH in the plot fertilized with 0.2 t ha^{-1} of BAD as compared to the N control. The further pH trend was significantly affected by an interaction of the fertilizer type, its doses and the crop (Figure 3). The application of FE2 resulted in an exponential increase in soil pH, exceeding 6.5 in response to the BAD dose higher than 0.8 t ha^{-1}. The effect of FE1 was much weaker, reaching only 5.5 in the plot with 0.8 t ha^{-1}. The initial

Table 3

Soil geochemical status after final harvest (mg kg^{-1} soil)

Factor	Level of factor	pH	P	K	Mg	Ca	Mn	Fe	Cu	Zn	Pb	Cd	Ni
Crop (C)	Re$^{\#}$	5.66^{a}	142^{a}	179^{c}	86^{c}	634^{c}	55^{b}	161^{b}	1.14	3.60	4.08^{a}	0.08^{a}	0.16^{a}
	Be	5.55^{a}	178^{b}	122^{a}	75^{a}	496^{a}	52^{a}	153^{a}	1.15	3.76	4.66^{b}	0.19^{b}	0.57^{c}
	Re^	6.22^{b}	142^{a}	138^{b}	82^{b}	563^{b}	53^{a}	169^{c}	1.11	3.68	4.10^{a}	$0{,}09^{a}$	0.27^{b}
F test		35.6^{***}	195.7^{***}	45.1^{***}	33.2^{***}	15.0^{***}	8.5^{***}	30.3^{***}	1.9	1.0	88.3^{***}	486.7^{***}	281.7^{***}
BAD fertilizer	FE1	5.55^{a}	149^{a}	140^{a}	79^{a}	492^{a}	53	163^{b}	1.12	3.53	4.30	0.11^{a}	0.34
	FE2	6.08^{b}	158^{b}	153^{b}	83^{b}	637^{b}	53	159^{a}	1.15	3.83	4.26	0.12^{b}	0,33
F		58.8^{***}	27.8^{***}	5.7^{*}	12.4^{***}	49.9^{***}	0.1	7.1^{**}	2.5	10.2^{**}	0.9	7.7^{**}	0.1
Dose (D) (g m^{-2})	0	5.81^{c}	146^{a}	141^{ab}	77^{a}	667^{c}	54^{ab}	157	1.10^{a}	3.42	4.26	0.12^{ab}	0.31
	20	5.44^{a}	152^{ab}	132^{a}	77^{a}	451^{ab}	53^{a}	165	1.12^{ab}	3.56	4.30	0.11^{a}	0.34
	40	5.47^{ab}	147^{a}	135^{ab}	79^{a}	422^{a}	52^{a}	163	1.10^{a}	3.63	4.25	0.12^{a}	0.33
	80	5.86^{cd}	148^{ab}	139^{ab}	82^{ab}	537^{b}	52^{a}	159	1.10^{a}	3.48	4.25	0.11^{a}	0.34
	160	6.13^{cd}	157^{b}	158^{b}	82^{ab}	644^{c}	54^{ab}	160	1.19^{b}	3.63	4.29	0.12^{ab}	0.35
	320	6.18^{d}	173^{c}	174^{c}	87^{c}	665^{c}	56^{b}	161	1.19^{b}	4.36	4.33	0.14^{b}	0.34
F test		13.6^{***}	24.1^{***}	6.9^{***}	7.4^{***}	19.1^{***}	3.1^{*}	1.8	5.3^{***}	2.6^{*}	0.4	4.6^{***}	0.7
F test for the interaction													
C x BAD		5.88^{**}	1.49	1.88	3.22^{*}	2.10	0.32	0.74	0.89	0.66	1.39	2.29	1.15
C x D		2.14^{*}	0.89	1.09	1.54	1.64	0.45	0.32	1.35	0.86	0.82	1.05	1.48
BAD x D		7.29^{***}	1.58	3.35^{**}	3.78^{**}	6.61^{***}	2.21	1.84	1.28	2.64^{*}	0.60	0.39	0.22
C x BAD x D		0.37	0.61	0.41	0.30	0.89	0.54	0.70	0.47	0.67	0.89	0.49	0.61

^{a} Numbers marked with the same letter are not significantly different; $^{\#}$ Re – radish; ^Be – green bean; ***, **, * indicate significant differences at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively.

pattern of the pH response to BAD was enforced during green bean cultivation. Its main feature was a significant drop in soil pH, irrespective of the fertilizer type. Radish, following green bean, caused a reverse effect of BAD on soil pH, although maintaining the primary pattern. The sudden drop in soil pH in response to the low doses of BAD is the most intriguing aspect of its impact on soil agrochemical characteristics. It indicates a low soil buffer capacity of soil in the study in response to the introduction of easily decomposable organic matter. This phenomenon is frequently observed in soil amended with organic matter with a narrow C:N ratio (ARTHURSON 2009). BAD fertilizers represent the same case.

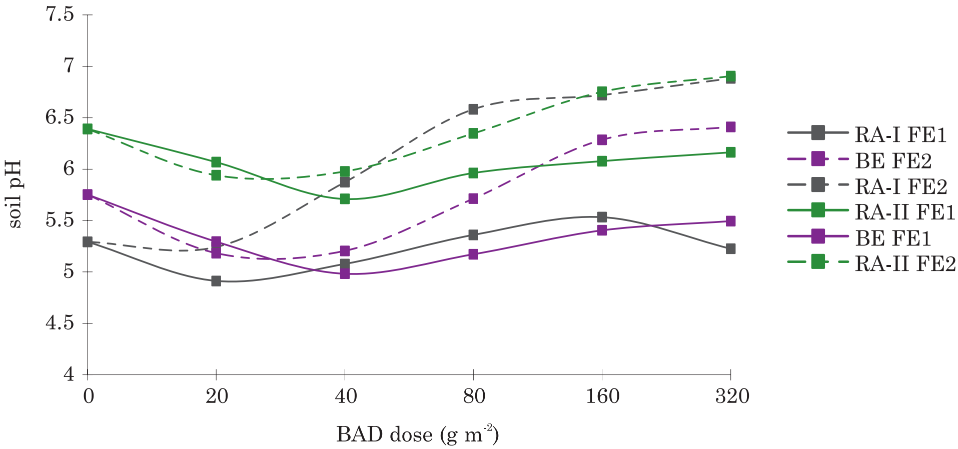

Fig. 3. The response of soil pH to impact of the type and dose of BAD fertilizers in consecutive cropping sequences

Macronutrients

The second group of soil properties studied is represented by the content of available macronutrients (Table 3). All of them showed a significant response to the cropping sequence. The content of available P was significantly lower following radish as compared to green bean. At the same time, it was much higher in the soil treated with FE2. The effect of BAD doses was highly specific. A significant increase as compared to the N control was first recorded in the treatment of 1.6 t ha^{-1} of the applied fertilizer. The lack of interaction between the experimental factors indicates a constant effect of FE2 on P availability. The highest post-harvest P content in the soil cropped with green bean can be explained by the strong acidifying potential of this crop. As a result, this process leads to the increasing dissolution of P unavailable resources in both soil and applied fertilizers (Arcand, Schneider 2006).

The other three macronutrients, such as K, Mg and Ca, show an opposite response to crops grown in the studied sequence. A significantly lower content of all the three nutrients was recorded in the soil cropped with green bean. The strongest difference was found for potassium. The key reason was a high requirement of green bean for this nutrient (Przygocka-Cyna et al. 2018). The advantage of FE2 over FE1 was mostly revealed in treatments with low doses of BAD and the P content never dropped below that in the N control (Figure 4). The K content showed a very similar pattern to the soil pH variability in response to BAD doses. The K content remained at the N control level, provided 1.6 t ha^{-1} of BAD was applied. This pattern was even more pronounced for Mg and Ca (Figures 5 and 6). The stabilizing effect of FE2 on the content of available Mg appeared first at a BAD dose of 0.4 t ha^{-1}, and at a dose of whereas 3.2 t ha^{-1} of FE1. These two figures clearly point to digestate as the key factor affecting K nd Mg release from the soil exchange complex (Chung and Zasoski 1994). The observed phenomenon can be expla-

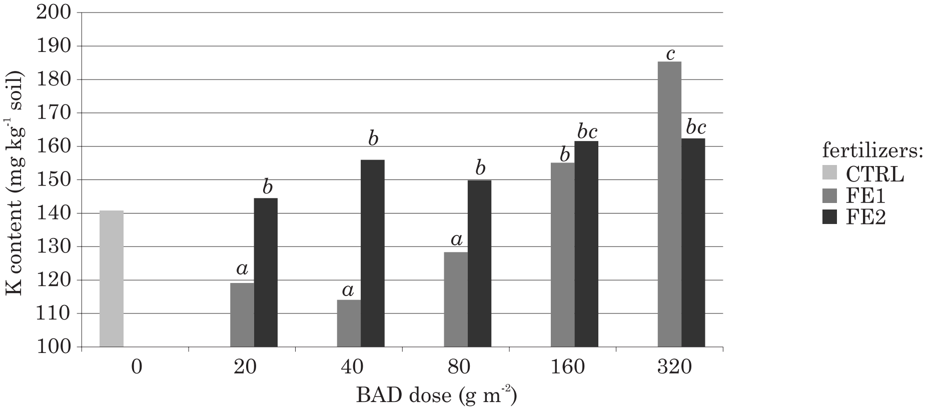

Fig. 4. The effect of BAD fertilizers on the post-harvest content of plant available potassium. [a] numbers marked with the same letter are not significantly different

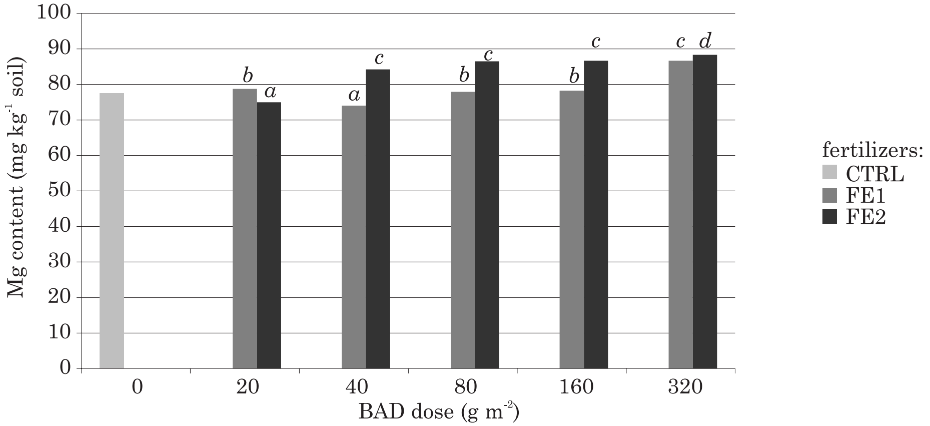

Fig. 5. The effect of BAD fertilizers on the post-harvest content of plant available magnesium. [a] numbers marked with the same letter are not significantly different

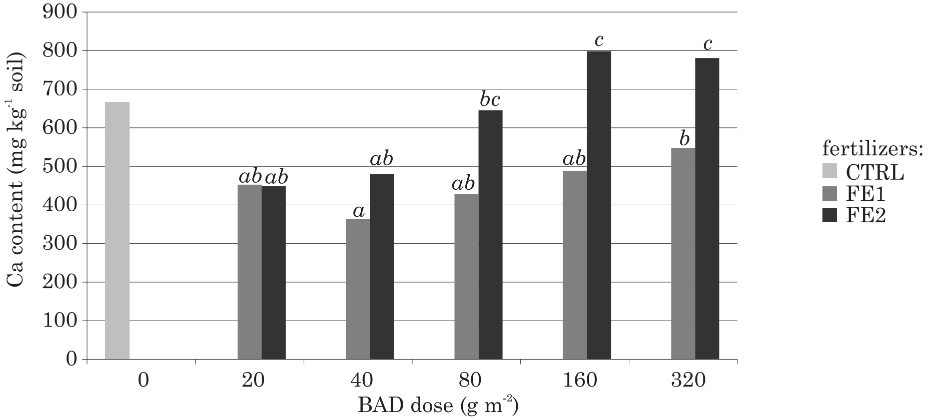

Fig. 6. The effect of BAD fertilizers on the post-harvest content of plant available calcium. [a] numbers marked with the same letter are not significantly different

ined by both a higher amount of the two nutrients introduced into the soil with FE2 and its higher impact on the K release from soil resources due to cation exchange processes. The same pattern of the response of both nutrients to the type and applied dose of BAD is corroborated by their strong relationship (Table 4). The content of available Mg can be simply explained based on the K content:

$$Mg = 0.192K + 52.8 \quad \text{for } R^2 = 0.69 \text{ and } n = 36.$$

This linear function clearly indicates that any increase in the content of available K leads to a simultaneous increase in soil Mg.

Micronutrients

The third group of characteristics studied is composed of four micronutrients such as Mn, Fe, Cu, and Zn. The first two elements showed a significant response to the cropping sequence. The observed trends were almost the same as recorded for macrocations. The content of Mn was only slightly lower compared to its pre-plant value. However, it did not depend on the fertilizer type. Its positive response to BAD doses was weak and revealed first in the plot with 3.2 t ha^{-1}. The content of Mn showed a significant relationship with other nutrients, but especially with potassium (Table 4). The content of Fe, in spite of high variability induced by the cropping sequence, was almost constant. FE2 caused a significant drop in The Fe content compared to FE1. A negative relationship between the content of P and Fe was observed in the soil fertilized with FE2. This phenomenon can be expla-

Table 4

Correlation matrix of the content of nutrients and selected trace elements in soil averaged over the three-course rotation (n = 36)

Specification	P	K	Mg	Ca	Mn	Fe	Cu	Zn	Pb	Cd	Ni
pH	-0.01	0.23	0.48**	0.70***	0.15	0.06	0.22	0.31	-0.33*	-0.19	-0.20
P	1.00	-0.19	-0.23	-0.04	-0.08	-0.57***	0.48**	0.59***	**0.83*** **	**0.90*** **	**0.80*** **
K		1.00	**0.83*** **	0.56***	0.76***	0.10	0.39*	0.26	-0.48**	-0.47***	-0.63***
Mg			1.00	0.62***	0.62***	0.17	0.34*	0.29	-0.56***	-0.47**	-0.59***
Ca				1.00	0.38*	-0.30	0.36*	0.14	-0.38*	-0.22	-0.36*
Mn					1.00	0.30	0.52**	0.34*	-0.22	-0.32	-0.42*
Fe						1.00	-0.16	-0.03	-0.50**	-0.62***	-0.48**
Cu							1.00	0.55**	0.25	0.28	0.19
Zn								1.00	0.23	0.30	0.15
Pb									1.00	**0.94*** **	**0.91*** **
Cd										1.00	**0.95*** **

***, **, * indicate significant differences at p < 0.001, p < 0.01, and p <0.05, respectively; n.s. – not significant ined only by a negative relationship between the content of available P and Fe (Figure 2). The content of Cu was low, but responded positively to the highest doses of BAD. It showed a weak, but positive relationship with the P content.

Heavy metals

Content of three heavy metals such as lead (Pb), cadmium (Cd) and nickel (Ni) was examined during the study. All of these elements showed an elevated increase in soil cropped with green bean. Available content of Pb and Ni was not influenced by the BAD type and dose. For Pb, a significant impact of both factors on its content was recorded in the soil under the first

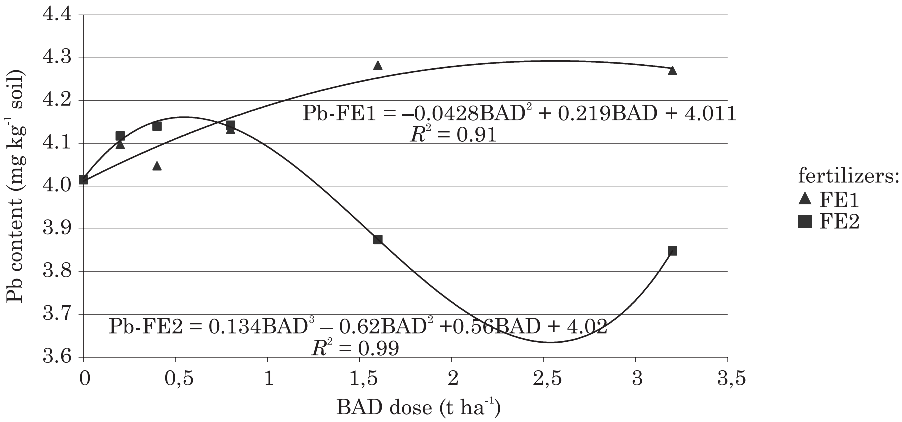

Fig. 7. The response of the available post-harvest lead content to the type and dose of BAD fertilizers

crop, i.e. radish. The effect of a BAD dose was fertilizer specific (Figure 7). In the soil fertilized with FE1, changes in the available Pb content can be described by a quadrative regression model with the optimum BAD dose being 2.56 t ha^{-1}. It resulted in the Pb maximum of 4.29 mg kg^{-1} soil. A much more complicated course of Pb was recorded for FE2. Its content increased exponentially up to the BAD dose of 0.8 t ha^{-1}, and then declined sharply in plots with its higher doses. It is necessary to stress a strong relationship between the content of Pb and the other two heavy metals. As shown in Figure 8, any increase in the Pb content resulted in the progressive response of the available content of Ni and Cd. It was only the content of Cd that showed a significant response to both experimental factors. Its content was higher in the soil treated with FE2. However, this effect was only due to a much higher content of Cd in the soils cropped with green bean. Even more important is the fact that the content of available Cd was significantly related to the content of three other elements, i.e. nutrients:

$$Cd = –0.122 + 0.0025P – 0.0004K – 0.027Zn \quad \text{for } R^2 = 0.94 \quad \text{and } n = 36.$$

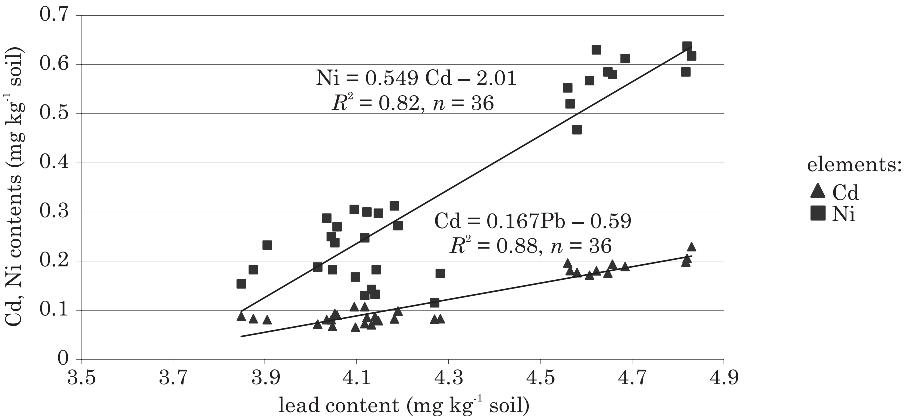

Fig. 8. The effect of the available lead content on the content of other heavy metals

The impact of these three elements was contradictory. A positive effect was exerted by only P, while both K and Zn produced a negative impact. The content of available Ni showed strong sensitivity to the cropping sequence. Its content was the highest in the soil cropped with green bean. This crop exerted a significant impact on its content during the radish growth, as recorded at harvest. The Ni content was significantly governed by the same set of nutrients as recorded for Cd:

$$\mathrm{Ni} = -0.148 + 0.008\mathrm{P} - 0.002\mathrm{K} - 0.109\mathrm{Zn} \quad \text{for } R^2 = 0.91 \quad \text{and } n = 36.$$

Special attention should be paid to zinc, whose content is crucial for the key crop species grown in Poland, especially for oilseed rape, sugar beets and winter wheat (Diatta 2013). Its content was governed by the content of P, K, and Fe:

$$\mathrm{Zn} = -3.947 + 0.02\mathrm{P} + 0.005\mathrm{K} + 0.024\mathrm{Fe} \quad \text{for } R^2 = 0.60 \quad \text{and } n = 36.$$

It can be concluded that the two elements, i.e. K and Zn, can be considered as soil activity controllers of both heavy metals. It is probably the reason of low availability of cadmium to plants in the presence of both nutrients (Nazar et al. 2012). Biomass ash and phosphoric rock introduced into the soil with BAD fertilizers were revealed to be the main source of trace elements, including Zn, but also Pb, Cd, and Ni. This fact should not be surprising because both BAD fertilizers were enriched with phosphoric rock, which contains a certain amount of trace elements, including cadmium (Dissanayake, Chandrajith 2009). On the other hand, ash from biomass is also a significant carrier of cadmium (Ciesielczuk et al. 2011). The above equations clearly summarize the effect of BAD on heavy metals, whose availability can be reduced by enriching this type of fertilizers with K and Zn. It can be concluded that phosphorus introduced into the soil with BAD fertilizers was the decisive factor affecting the availability of the other nutrients. An amount of the applied digestate can be considered as a factor modifying the rate of P release from phosphoric rock, thus affecting the availability of the other nutrients.

CONCLUSIONS

1. The pH changes were progressing in response to the fertilizer doses, but were also modified by the growing crop; a significant drop was exerted by green bean and an increase was induced by radish.

2. Acid soil fertilized with fertilizers based on biomass ash and BD (BAD) resulted in a very rapid, and parallel to a fertilizer dose, increase in the content of plant available phosphorus.

3. Low doses of BAD fertilizers, especially FE1, resulted in the exhaustion of the plant available Ca, Mg, K content.

4. The post-harvest content of plants available micronutrients in the soil to some extend followed the pattern recorded for macronutrients.

5. The post-harvest content of plant available heavy metals significantly and positively correlated with the content of P but negatively with Mg.

REFERENCES

Arcand M.M., Schneider K.D. 2006. *Plant- and soil microbial-based mechanisms to improve the agronomic effectiveness of phosphate rock: a review.* An. Acad. Bras. Ciênc., 78(4): 791-807.

Arthurson V. 2009. *Closing the global energy and nutrient cycles through application of biogas residue to agricultural land – potential benefits and drawbacks.* Energies, 2: 226-242. DOI: 10.3390/en20200226

Ciesielczuk T., Kusza G., Nemś A. 2011. *Fertilization with biomass ashes as a source of trace elements for soils.* Ochr. Środ. Zasob. Natur., 49: 219-227. (in Polish)

Chung J.B., Zasoski R.J. 1994. *Ammonium-potassium and ammonium-calcium exchange equilibria in bulk and rhizosphere soil.* Soil Sci. Soc. Amer. J., 58: 1368-375.

De La Fuente C., Alburqueque J.A., Clemente R., Bernal M.P. 2013. *Soil C and N mineralization and agricultural value of the products of an anaerobic digestion system.* Biol. Fertil. Soil, 49: 313-322. DOI: 10.1007/s00374-012-0719

Dissanayake C.B., Chandrajith R. 2009. *Phosphate mineral fertilizers, trace elements and human health.* J. Nat. Sci. Foundation Sri Lanka, 37(3): 153-165.

Holm-Nielsen J.B., Al Seadi T., Oleskowicz-Popiel P. 2009. *The future of anaerobic digestion and biogas utilization.* Biores. Technol., 100: 5478-5484.

Kolář L., Kužel S., Peterka J., Štindl P., Plát V., 2008. Agrochemical value of organic matter of fermented wastes in biogas production, Plant Soil Environ, 54: 321-328.

Loria E.R., Sawyer J.E. 2005. *Extractable soil phosphorus and inorganic nitrogen following application of raw and anaerobically digested swine manure.* Agron. J., 97: 879-885.

Lindsay W.L., E.C. Moreno. 1960. *Phosphate phase equilibria in soils.* Soil Sci. Soc. Amer. Proc. 24, 177-182.

Łagocka A., Kamiński M., Cholweiński M., Pospolita W. 2016. *Health and environmental bene-*

fits of utilization of post-fermentation pulp from agricultural biogas plants as a natural fertilizer. Kosmos, 65(4), 601-607.

MEHLICH A. 1984. *Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant*. Commun. Soil. Sci. Plant Anal., 15:1409-1416.

MØLLER H., LUND I., SOMMER S. 2000. *Solid-liquid separation of livestock slurry: efficiency and cost*. Biores. Technol., 74(3): 223-229.

NAZAR R., IQBAL N., MASOOD A., KHAN M.I., SYEED S., KHAN N.A. 2012. *Cadmium toxicity in plants and role of mineral nutrients and its alleviation*. Am. J. Plant Sci., 3: 1476-1489.

NKOA R. 2014. *Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: a review*. Agron. Sustain. Devel., 34: 473-492.

OHNO T., ERICH M.S. 1990. *Effect of wood ash application on soil pH and soil test nutrient levels*. Agric. Ecosyst. Environ. 32: 223-239.

PIEKARCZYK M. 2013. *Effect of winter wheat straw ash on the some macro- and micro-elements available forms content in light soil*. Frag. Agron., 30(1): 92-98. (in Polish)

SHARMA B., SARKAR A., SINGH P., SINGH R.P. 2017. *Agricultural utilization of biosolids: a review on potential effects on soil and plant growth*. Waste Manage., 117-132.

TUJAKA A., TERELAK H. 2012. *The balance of phosphorus in the agriculture of Poland*. Pol. J. Agron., 9: 29-33. http://www.ejpau.media.pl/volume13/issue2/art-01.html