

Bio-fertilizers and Soil Health—An Approach Based on Balance of Elements in the Vegetable Cropping Sequence

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Abstract It has been assumed that bio-fertilizers based on biomass ash and biogas leads to a depletion of soil macronutrients. This hypothesis was experimentally validated. Vegetables were grown in a cropping sequence of radish-green bean-radish grown on light soil and treated with two bio-fertilizers. They were both based on bio-ash and digestate (BAD) composed in contrasting ratio of 2.2:1 (FE1) and 1:2.2 (FE2) and phosphoric rock (15%). The BAD rates were as follows: 0, 20, 40, 80, 160, 320 g m⁻². The total yield of crops was limited by an uptake of K, Mg, and Cu. The decisive role of these three elements can be explained based on the course of their balance with respect to the type and rate of BAD. The absolute value of a particular element balance increased progressively with BAD rates. As a rule, low BAD rates led to depletion, while high rates resulted in the enrichment of soil resources for most elements, including heavy metals. The only exception was Fe and Mn, which soil resources increased along all of the applied BAD rates. The K balance pattern indicates that its supply within BAD, irrespective of the rate, was too low to prevent the exhaustion of its soil reserves. The strong depletion of soil resources at low BAD rate, but element specific, were recorded not only for Ca and Mg, but also for Zn, Cu, Pb and Cd. It can be concluded that soil amendments based on bio-ash and digestate applied in low rates should be enriched with the nutrients, which are crucial for an intensive and healthy production of vegetables.

Keywords Bio-ash · Digestate · Nutrients · Heavy metals · Balance

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1 Introduction—Problematic Areas of Bio-fertilizers Application

The key pillars of sustainable agriculture are the increase of (i) food production and fiber, and recently fuel, and (ii) effective use of non-renewable resources [1]. The latter objective can be, at least partly, fulfilled by a wise use of non-agricultural residues, like biomass ash (BA) or biogas digestate (D). The key reason is the *climate package*, which obligates the EU member countries to increase the proportion of renewable-energy sources up to 20% of the total energy consumption by 2020. In Poland, this target value was fixed at 15% by 2020. The renewable-energy sources in 2020 are biomass (78.9%), including energy crops (27.9%), biofuels (12.2%), biogas (20.2%), and others (18.6%) [2]. In general, BA is considered both as an excellent liming material, leading to soil pH increase, accelerating, in turn, activity of soil organisms [3]. The biogas digestate, as a product of anaerobic digestion of different organic residues, including manures or maize silage, is a good source of nutrients, however their concentration is low and highly variable [4, 5]. The condensate of raw slurry into solids can be used solely or as a substrate for bio-fertilizer manufacturing [6]. The raw bio-wastes or their processed products may contain, depending on the source, different concentration levels of heavy metals (HMs). Therefore, all bio-fertilizers undergo the legalization procedure in order to minimize their negative impact on both soil and consumable crop quality [7, 8]. The most sensitive to the excess of HMs in arable soils are leafy and root vegetables [9, 10]. The maximum levels of harmful metals acceptable in the edible parts of vegetables are based on strictly defined norms, which should be used to evaluate bio-fertilizers as soil amendments [11]. The bio-ash (BA) and biogas digestate (D) physically unified in a conglomerate can exert a big, yet highly diversified impact on both soil agrochemical properties and activity of soil microorganisms. The basis for this hypothesis is: (i) high liming potential of BA, (ii) narrow C:N ratio in D, (iii) low concentration of nutrient, (iv) potential threat of soil enrichment with HMs. Based on these assumptions few issues arise concerning the effect of this type of conglomerate (termed as BAD) on the health condition of soil and consumable crops. The most problematic one is to evaluate the optimum rate of BAD in accordance with growing crop needs and the protection of its edible parts, as a prerequisite of human health.

The objective of this paper is to evaluate the impact of the two bio-fertilizers based on the contrasted ratio of bio-ash and digestate on a balance of nutrients and heavy metals in the radish-green bean-radish cropping sequence. This study should indicate the problematic areas of the bio-fertilizer use on soil and its consequent effects on human health.

2 Materials and Methods

The assumed objectives were validated based on data obtained from the micro-plot experiment with vegetables grown in a cropping sequence: radish-green bean-radish. The test was carried out on a light, slightly acid soil with moderate content of available nutrients [for details: 12]. The 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 (D) + phosphoric rock (PR) + elemental sulfur (S^0). The tested BAD differed in a contribution of the principal two components:
 - a. FE1: BA-55% + BDs-25% + PR-15% + S^0 -5%;
 - b. FE2: BA-25% + BDs-55% + PR-15% + S^0 -5%;
2. The second factor: five rates of BAD: 0; 20; 40; 80; 160; 320 g m⁻².

Mineral nitrogen in the form of ammonia nitrate in the rate of 4 g N m⁻² was applied to all plots. There were fertilized only radish crops.

The operational view of a particular element management in the cropping sequence requires a recognition and a definition of its input (**I**) and output (**O**) components. The **Input** components were calculated based on the BAD rate for its type and a specific element content as presented in Table 1. The **Output** components were directly measured for consecutive plants based on dry main yield (root, pods) and byproducts (tops—radish; leaves, stems—green bean) and concentration of the particular element. The **net balance** (**B_n**) formula was as follows:

$$B_n = I - O \quad (1)$$

The calculated data were subjected to the conventional analysis of variance using computer programs STATISTICA 12[®]. The differences between treatments were evaluated with the Tukey's test. In tables, figures, and equation's *F* test results (***, **, * indicate significance at the *P* < 0.1, 1, and 5%, respectively), are given.

Table 1 Content of elements introduced into soil with BAD soil amendments

Macronutrients	FE1	FE2	Trace elements	FE1	FE2
	g kg ⁻¹ DM			mg kg ⁻¹ DM	
Nitrogen, N	26.5	37.0	Iron, Fe	13,586	6906.7
Phosphorus, P	36.8	36.4	Manganese, Mn	1392.4	682.7
Potassium, K	31.1	19.7	Zinc, Zn	205.1	181.0
Calcium, Ca	57.4	40.4	Copper, Cu	58.3	49.0
Magnesium, Mg	9.1	5.2	Lead, Pb	21.8	14.1
Sulfur, S	48.0	48.0	Cadmium, Cd	3.6	2.1

3 Results and Discussion

3.1 Biomass Production

The quantity of any element incorporated into the soil was in accordance with the experimentally fixed rates. The BAD was the key carrier of most elements, excluding phosphorus (P), and nitrogen (N). The first was added to the BAD conglomerate in the form of phosphoric rock (Pc) (Table 1). The second was applied to both radish crops as ammonium nitrate at the seedling stage.

The total crop biomass (TY) is a measure of a particular element accumulation. The patterns of TY response to the type and rates of BAD, which increased in the geometrical order, was significant (Fig. 1a). The total biomass of crops grown on plots treated with FE1 was below the N control up to its rate of 80 g m^{-2} . The rates of FE1 above 80 g m^{-2} resulted again in biomass yield depression. The pattern of biomass production by plants on plots amended with FE2 was quite different. Its maximum was achieved on the plot with 20 g m^{-2} . The next rates resulted in the significant step by step yield decrease, but without depression. The observed difference can be partly explained by the specific impact of crops grown in this cropping sequence. The patterns presented in Fig. 1a were driven by green bean. The highest yield of bean pods was just harvested from the plot fertilized with 20 g m^{-2} of FE2 ($131 \text{ vs. } 118 \text{ g m}^{-2}$ on) the N-control. Only the 1st radish significantly affected the total biomass (data not shown but available by authors; for details see [13]).

Only five from 12 studied elements significantly responded to the BAD, clearly stressing the advantage of FE2 over FE1 (data not shown, but available by Authors, [12]). The effect of FE2 was observed for nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), and copper (Cu). The observed response indicates that digestate incorporated into the soil affects a series of processes, thus increasing the pool of plant available nutrients [14]. The stepwise regression procedure showed that the TY was governed by three nutrients:

$$TY = 47.6 + 0.02K + 0.07Mg + 0.05Cu \text{ for } R^2 = 0.94, n = 72, \text{ and } P \leq 0.001 \quad (2)$$

The supply of these three nutrients to plants was too low, limiting the dry matter production by crops grown in the sequence: radish \rightarrow green bean \rightarrow radish.

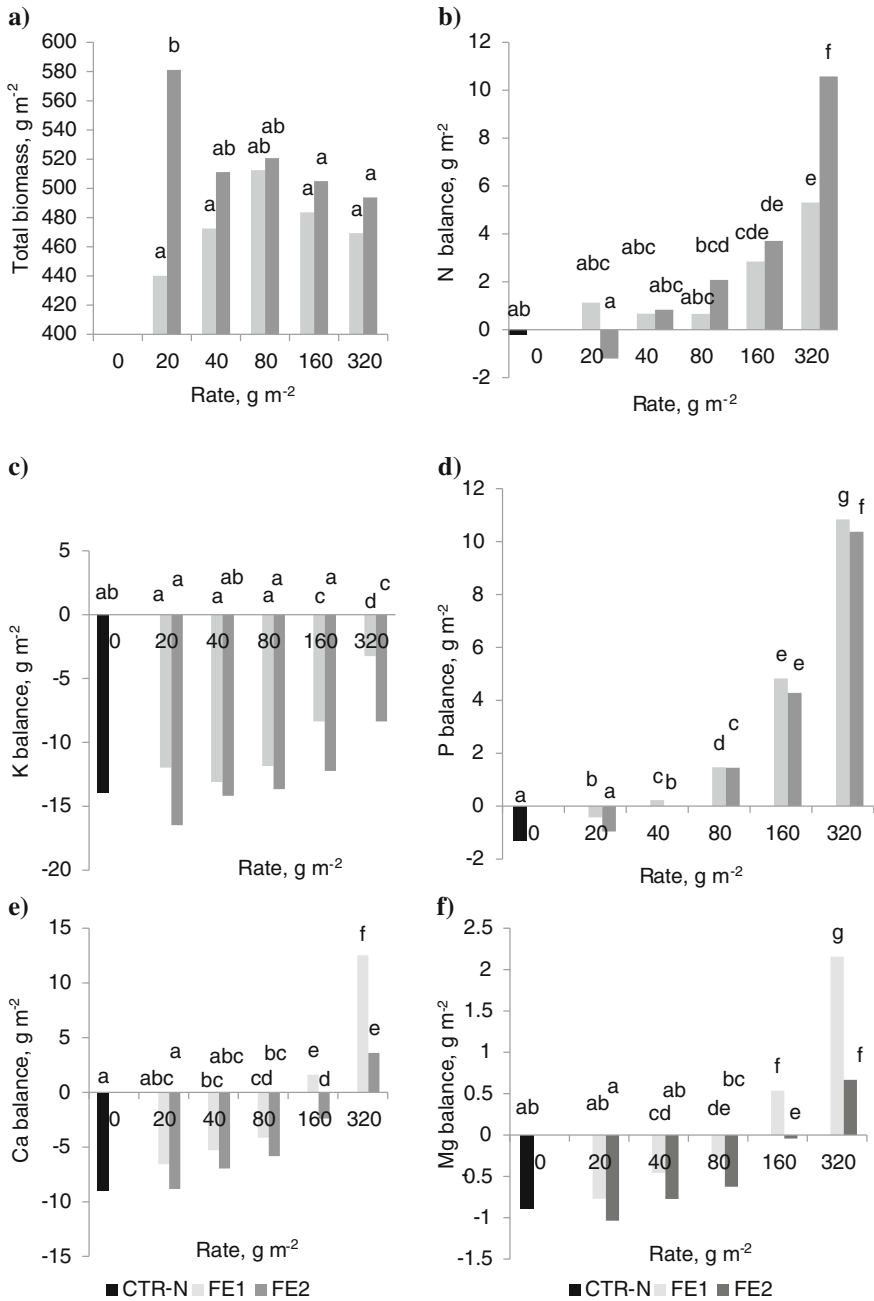


Fig. 1 Dry yield of total biomass of vegetables grown in radish-green bean-radish rotation and balance of macronutrients

3.2 Balance of Elements

The observed controversies with respect to the type and rate of BAD can be explained by the balance analysis of nutrients and heavy metals (Table 2). The total biomass of grown crops, as results from the stepwise regression model was governed by the net balance of five elements:

$$TY = 33.7 + 40P_b - 28K_b - 61.9Mg_b + 0.14Fe_b - 32.2Cu_b \text{ for } R^2 = 0.91, \text{ and } n = 72 \quad (3)$$

This equation follows, to a considerable degree, the model presented by the Eq. (2). The negative signs for K, Mg, and Cu indicate the depletion of their soil resources. It means that supply of these three nutrients was too low with respect to requirements of the grown crops. The detailed balance trends are explained in the following three groups (i) macronutrients, (ii) micronutrients, (iii) heavy metals.

3.2.1 Macronutrients

For the first group, the positive balance was recorded for N and P. On average, N_b for FE2 was higher by 51% compared to FE1 (Fig. 1b). A detailed analysis, as presented in Fig. 1b, clearly shows a slight N mining on the N-control plot. It means that the 80 g m^{-2} of N fertilizer applied to the studied crops was entirely exploited. The negative N_b was also recorded for the plot with 20 g m^{-2} of FE2, where the highest yield of green bean pods was harvested [13]. The lack of this type of response for the respective FE1 plot indicates another reason for yield depression than N supply. For all other treatments, N_b was positive, increasing exponentially with the amount of N fertilizer. This trend indicates a surplus of nitrogen in the soil-plant system, being in part responsible for yield drop on plots treated with the highest rates of BAD.

The K_b was negative along with BAD rates, reaching on average, much lower values for plots fertilized with FE2 (Fig. 1c). The obtained results clearly indicate that K was a critical nutrient for crops growing in sequence: radish-green bean-radish. The K negative balance was a result of high needs of radish plants for K [15]. The deepest K mining was not an attribute of the N-control, but it was an attribute of the plot with 20 g FE2 m^{-2} . The K exhaustion gap decreased in accordance with the increasing BAD rate. This pattern coincides with the pattern of the total biomass production of the studied crops (Fig. 1a). The K_b alone explains 84% of the TY variability:

$$TY = 32.19K_b + 31 \text{ for } R^2 = 0.84, n = 72, \text{ and } P \leq 0.001 \quad (4)$$

Table 2 Effect of BAD bio-fertilizers on nutrients and heavy metals budgeting in intensive cropping sequence with radish-green bean-radish

Factors	Level of factors	Macronutrients (g m ⁻²)										Micronutrients (mg m ⁻²)									
		N	P	K	Ca	Mg	Fe	Mn	Zn	Cu	Pb	Cd	Fe	Mn	Zn	Cu	Pb	Cd			
BAD	FE1	1.73 ^a	2.61 ^b	-10.4 ^b	-1.82 ^b	0.05 ^b	1319 ^b	131.9	8.82	4.01 ^b	1.08 ^b	0.29 ^b									
	FE2	2.62 ^b	2.31 ^a	-13.2 ^a	-4.90 ^a	-0.45 ^a	626 ^a	56.1	4.54	2.86 ^a	0.25 ^a	0.13 ^a									
<i>F</i> test		8.91 ^{**}	38.7 ^{***}	67.7 ^{***}	100.3 ^{***}	217 ^{***}	499 ^{***}	1324 ^{***}	10.0 ^{**}	179 ^{***}	500 ^{***}	405 ^{***}									
Rate (R) (g m ⁻²)	0	-0.25 ^a	-1.30 ^a	-14.0 ^a	-9.00	-0.88	-84	-13.6	-13.0	-2.19	-1.16	-0.09									
	20	-0.04 ^{ab}	-0.69 ^b	-14.2 ^a	-7.70	-0.90	113	5.53	-10.1	-1.19	-0.86	-0.03									
	40	0.75 ^{ab}	0.12 ^c	-13.6 ^a	-6.13	-0.62	326	27.5	-6.99	0.12	-0.47	0.03									
	80	1.37 ^b	1.46 ^d	-12.8 ^a	-4.99	-0.45	728	69.6	1.19	2.03	0.17	0.14									
	160	3.28 ^c	4.55 ^e	-10.3 ^b	-0.40	0.25	1553	152.0	17.3	6.58	1.72	0.37									
<i>F</i> test	320	7.94 ^d	10.60 ^f	-5.8 ^c	8.07	1.41	3203	319.8	51.7	15.3	4.59	0.83									
		72.0 ^{***}	573 ^{***}	64.0 ^{***}	281 ^{***}	465 ^{***}	1058 ^{***}	2489 ^{***}	22.0 ^{***}	391 ^{***}	229 ^{***}	127 ^{***}									
F for the interaction																					
BAD × Rate		11.8 ^{***}	4.36 ^{**}	6.28 ^{***}	17.2 ^{***}	39.3 ^{***}	1100 ^{***}	277 ^{***}	14.0 ^{**}	25.6 ^{***}	91.5 ^{***}	85.5 ^{***}									

^{a-f}Numbers marked with the same letter are not significantly different; ***, **, * significance at *P* < 0.001; 0.01; 0.05, respectively

The P balance (P_b) was positive, but the impact of the BAD type was low, showing a slightly higher P balance in soil fertilized with FE1 (Fig. 1d). It was negative on the control N plot and fertilized with 20 g BAD m^{-2} .

The calcium balance (Ca_b) was on average much more negative in soil fertilized with FE2 (Fig. 1e). The negative Ca_b was recorded for most plots receiving less than 80 g m^{-2} of FE1 and 160 g m^{-2} of FE2 BAD. As in the case of K, the supply of Ca in the applied BAD was too small to cover the requirements of the tested crops. It is well recognized that green bean exerts high requirements for Ca [16]. This opinion was corroborated in this study, because the fresh yield of green pods (PY_{FW}) responded significantly to Ca_b , but only in the FE1 treatment:

$$PY_{FW} = 3.9Ca_b^2 + 15.9Ca_b + 1541 \text{ for } R^2 = 0.46, \text{ and } n = 36 \quad (5)$$

The critical Ca_b for the maximum yield of pods, equal to 1557 g m^{-2} , was -2.03 g m^{-2} . The obtained regression model clearly informs that plots fertilized with FE1 revealed both a significant shortage, as well as an excess of Ca over K, which could be the reason for the disturbance of green bean growth and yield [16].

The magnesium balance (Mg_b), averaged over BAD rates, was positive for FE1 at its rate of 160 g m^{-2} , whereas it was only positive for FE2, when its rate doubled (Fig. 1f). Only the yield of bean grown on the FE1 plot showed a significant response to Mg_b :

$$PF_{FW} = 207.5Mg_b^2 + 263.3Mg_b + 1511 \text{ for } R^2 = 0.51, \text{ and } n = 36 \quad (6)$$

The critical Mg_b for the maximum yield of pods, equal to 1594 g m^{-2} , was -0.63 g m^{-2} . The presented results for Ca, and Mg with respect to the total biomass produced by crops in the sequence: radish-green bean-radish, implicitly indicate the shortage of both nutrients applied in rates below 160 g m^{-2} for FE1, and 320 g m^{-2} for FE2. A strong relationship between both indices ($R^2 = 0.99$) points at bio-ash as the key source of their supply to plants.

3.2.2 Micronutrients

The second group comprises of four micronutrients which can be divided into two sub-groups. In general, Fe and Mn showed a net positive balance over the entire set of tested BAD rates (Fig. 2a, b). The relationship between both indices was ideal ($R^2 = 1.0$). Both elements showed high relationship with Ca_b ($R^2 = 0.98$), indicating bio-ash as their key source. The patterns of the Zn, and Cu responses to BAD rates were quite different (Fig. 2c, d). The Zn_b followed the same patterns as observed for Ca_b and Mg_b (Fig. 2c, d). For Zn its soil accumulation started from the rate of 80 g m^{-2} for FE1 and 160 g m^{-2} for FE2. For Cu_b this trend was revealed earlier. Both indices correlated with each other ($R^2 = 0.99$) and with P_b , indirectly indicating the phosphoric rock as an important source for plants ($Zn_b = 0.97$; $Cu_b = 0.99$).

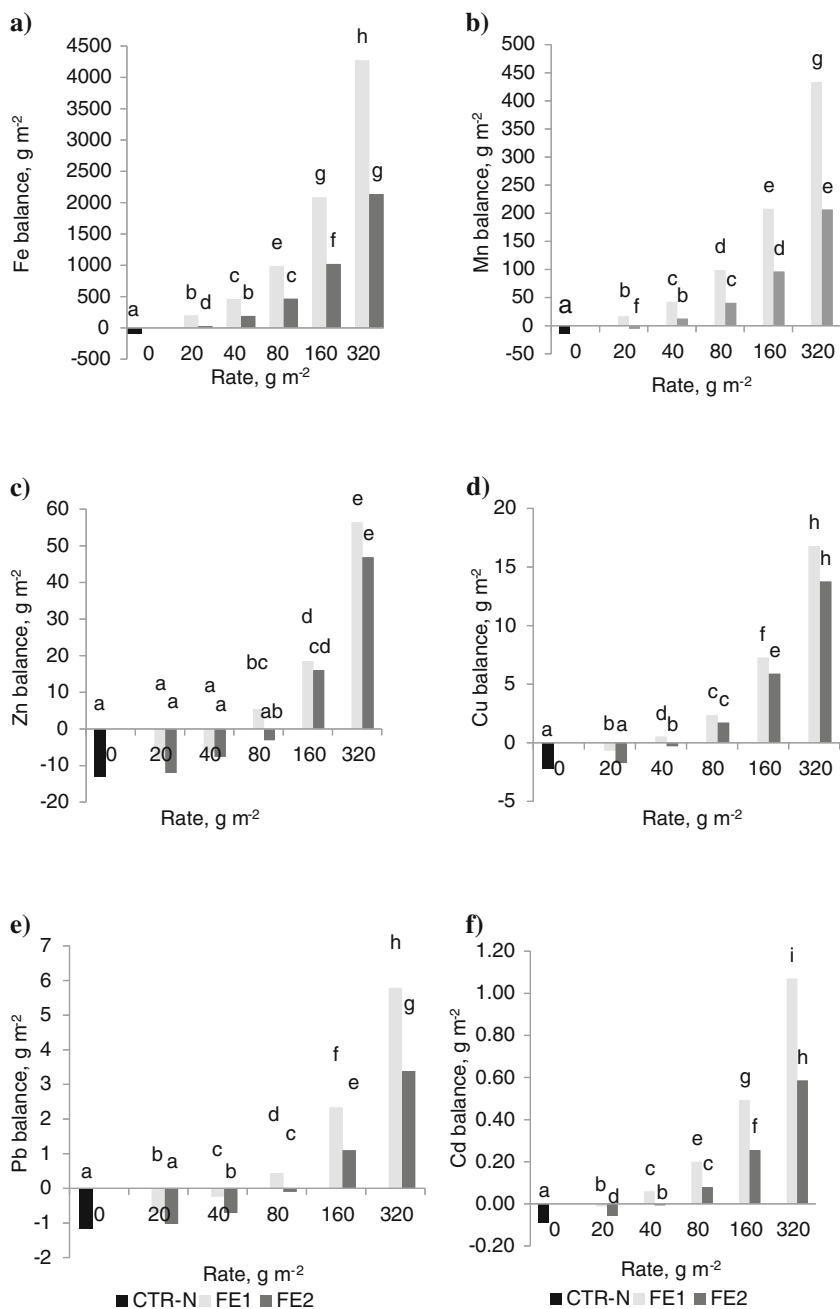


Fig. 2 Balance of micronutrients and heavy metals in cropping sequence of radish-green bean-radish

3.2.3 Heavy Metals

The content of heavy metals in bio-fertilizers is considered with special care [6, 8, 11]. The Pb balance (Pb_b) in response to BAD rates showed the same pattern as noticed for Zn_b (Fig. 2e). Its value was driven by balances of other elements:

$$Pb_b = -0.29 + 0.18P_b + 0.63Mg_b + 0.001Fe \text{ for } R^2 = 0.99, n = 72 \quad (7)$$

This model indicates two different sources of lead, i.e. bio-ash as the main one (Mg, Fe) and phosphoric rock as the secondary one. The pattern of cadmium balance (Cd_b) as shown in Fig. 2f is very similar to the one recorded for Zn (Fig. 2c). Its indices were governed by the following set of elements:

$$Cd_b = -0.007 - 0.003N_b + 0.0002Fe_b + 0.01Cu_b + 0.039Pb_b \text{ for } R^2 = 0.99, n = 72 \quad (8)$$

This set of elements clearly informs about the complex processes responsible for Cd_b in the bio-fertilizer \rightarrow soil \rightarrow plant system. The Pb_b relationships with Pb and Fe clearly point at bio-ash as the key lead source. This conclusion was fully corroborated by Cyna and Grzebisz [13], who showed an elevated concentration of Pb in radish root on plots fertilized with BAD rate of 80 g m⁻². The higher BAD rates resulted in exponential increase of Pb concentration in this radish part. In general, it coincides with Pb net balance.

4 Conclusions

The type of BAD bio-fertilizer significantly affected the pattern of biomass response to its rates. In general, the supply of K, Mg, and Cu to plants grown in the sequence: radish \rightarrow green bean \rightarrow radish was too low, limiting the dry matter production. On plots fertilized with the highest BAD rates, the Ca/K antagonism was probably one of the main reasons for yield depression. In addition, they resulted in high accumulation of heavy metals in soil, creating a real threat to the health of grown vegetables. Six groups of element balances were distinguished. The first, represented by N and P was, in general, positive following a particular fertilizer composition for FE2 or yield for FE1. The second one represented by K was negative, clearly indicating the exhaustion of its soil resources. This process resulted in yield depression on plots with BAD rates below 80 g m⁻². The third one, comprising of Ca and Mg, followed the experimental design, indicating soil resource depletion on plots with low BAD rates and accumulation on plots with high BAD rates. It showed much stronger imbalance on plots treated with BAD rich in digestate, indicating its impact on the available pool of soil resources of both nutrients. The

fourth one composed of Zn and Cu followed the general pattern of response to the type and rate of BAD, but both elements showed significant relationships with P_b , indicating an influence of phosphoric rock on their balance. Patterns of Pb and Cd balance were significantly correlated with each other and with Fe_b and Mn_b , pointing at bio-ash as their main source.

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