

A MINERAL PROFILE OF GRAIN MAIZE AT PHYSIOLOGICAL MATURITY FERTILIZED WITH BIOGAS DIGESTATE SOLIDS PART II. MICRONUTRIENTS AND HEAVY METALS

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Abstract. Biogas digestate solids (BDS) obtained from agricultural biogas plant and used as organic fertilizer, significantly affect dry matter and trace elements (micronutrients + heavy metals, TE) partitioning among parts of seed crop, increasing, in turn, the yield of grain. This hypothesis was verified through a series of field experiments with maize, conducted between 2014 and 2016 at Brody, Poland. A 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 concentration of trace elements in grain depended on the interactional effect of experimental factors, mainly by the applied BDS rate and the course of weather. Shortage of water (2015) resulted in a significant decrease in Fe, Zn and Cd concentration, concomitant with the simultaneous increase of Mn, Zn and Pb concentration in maize grain. The harvest indices (HIs) of TE increased in the following order: Zn > Cd > Cu > Fe > Mn > Pb. The values of HIs were a result of a given element partitioning between grain and vegetative maize parts, such as stem and leaves (Fe, Cu, Cd); leaves (Mn), stem and husk leaves (Zn, Pb). The stem was revealed as a maize organ significantly limiting HI for Fe, but at the same time controlling Pb reallocation to grain. This study also showed that the total uptake of cadmium significantly depended on its concentration in maize grain, both increased due to the shortage of water or nitrogen and through the supply of biogas digestate solids. Each of these factors resulted in Cd concentration above the standardized norm of 0.1 g·kg⁻¹ DM.

Key words: biogas digestate solids, application method and rate, maize organs, micronutrients, heavy metals, partitioning

INTRODUCTION

The nutritional status of crop plants is the key factor for proper growth and health of consecutive groups in the food chain [Maathuis 2009]. Micronutrients fulfil numerous biochemical and physiological functions in plants, used as food for humans or fodder for animals. The shortage of micronutrients in consumed food is one of the most important reasons, threatening human health all over the world. It leads to human malnutrition, negatively impacting their health and activity [White and Broadley, 2009]. On the other hand, some arable soils are seriously contaminated with heavy metals, leading to dysfunction of plant growth, decreasing, in turn, the consumption quality of agricultural products [Lu et al. 2015, Wieczorek et al. 2005].

The primary reason for micronutrients shortage in food is the low content of their available forms in soils, in turn resulted in poor uptake by the grown plants. This problem has been widely documented for iron and zinc [Graham et al. 2012, Hafez et al. 2013]. At the same time, it is less recognized for copper [Rosado 2003]. The modern agriculture, oriented on cultivation of

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high-yielding cultivars, has created another problem, termed as *genetically induced dilution of nutrients*. It has been lately recognized for both seed crops, for example, cereals and vegetables [Marles 2017]. The core of this genetic dilution syndrome are much lower concentrations of many nutrients, including magnesium and especially micronutrients such as zinc, copper in edible parts of plant crops [Davis 1994, Teklić et al. 2013].

There are many potential or even alternative solutions to ameliorate deficiency of micronutrients in agricultural products or food. The simplest one is to increase their content through artificial biofortification [Bouis and Welch 2010]. However, the most rational way to enrich a crop product with micronutrients is to increase their concentration in the soil. The primary solution is to apply manures, which are naturally rich in micronutrients due to their low retention in the animal body [Wang et al. 2016]. The second one, widely practiced by farmers, is the application of mineral fertilizers, mainly in the form of foliar sprayings [Zeidan et al. 2010]. The biosolids, which are more and more frequently used in agriculture, are not only an alternative source of micronutrients, but also of heavy metals [Koupaie and Eskicioglu 2015].

One of the main objectives of biogas digestate application to arable soils is to increase uptake of micronutrients by the grown crops. On the one hand, biogas digestate, especially in the solid form, is a big source of micronutrients. On the other hand, its incorporation into the soil results in acceleration processes of both soil organic matter mineralization and cation exchange. The multidirectional impact of biogas digestate on soil processes leads finally to increased resources of two groups of elements: i) micronutrients, ii) heavy metals. The enlargement of the first pool is expected by farmers, irrespectively of crops grown on the farm. The increasing size of the second one creates a big problem both for the quantity and quality of harvested plant organs, which are directly consumed or subjected to processing. In each country, including Poland, there are rigid legislative norms describing the maximum amounts of heavy metals incorporated into arable soils [Dz. U 2010]. Concentrations of heavy metals in biogas digestate from agricultural biogas plants are, in general, below permissible norms [Möller and Müller 2012, Nkoa 2014]. However, the effect of applied digestate on bioavailability of heavy metals has not been identified yet. Their uptake is governed by numerous processes, responsible for their movement towards a plant root, uptake, accumulation and finally partitioning among plants organs [Carbonell et al. 2011].

The key objective of this study was to recognize the impact of increasing rates of applied biogas digestate, depending on the application method and the rate of the content of four micronutrients such as iron, manganese, zinc, copper and two heavy metals, such as cadmium and lead maize organs at harvest. The second objective was to assess the partitioning of the studied elements among maize parts, with special emphasis on their accumulation in grain.

MATERIALS AND METHODS

The general information about the experiment was described by Przygocka-Cyna [2017]. The basic properties of soil under study, concerning the content of the available forms of studied trace elements are shown in Table 1. Composite soil samples (0–30 cm) for a determination of available forms of micronutrients (Fe, Mn, Zn, Cu) as well as heavy metals, such cadmium (Cd) and lead (Pb), were collected at the beginning of the experiment. 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 [Mehlich 1984]. The concentration of these elements in the extraction solution was determined using a FAAS. The plant materials for trace elements determination were mineralized at 600°C. The obtained ash was then dissolved in 33% HNO₃. The concentrations of Fe, Mn, Zn, Cu, Pb, and Cd were determined using a FAAS.

Table 1. Soil agrochemical properties before maize sowing¹ (mg·kg⁻¹ soil)

Year	Fe	Mn	Zn	Cu	Cd	Pb
2014	1020	105	71	13.2	1.3	35.1
2015	995	96	32	6.5	1.8	12.8
2016	884	115	43	14.7	1.3	41.8

¹Mehlich 3 method

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.

RESULTS AND DISCUSSION

Iron (Fe). Iron concentration (Fe_c), averaged over treatments and years and with respect to maize organs decreased in the following order (Table 2):

$$LE > HL > ST > GR > CC.$$

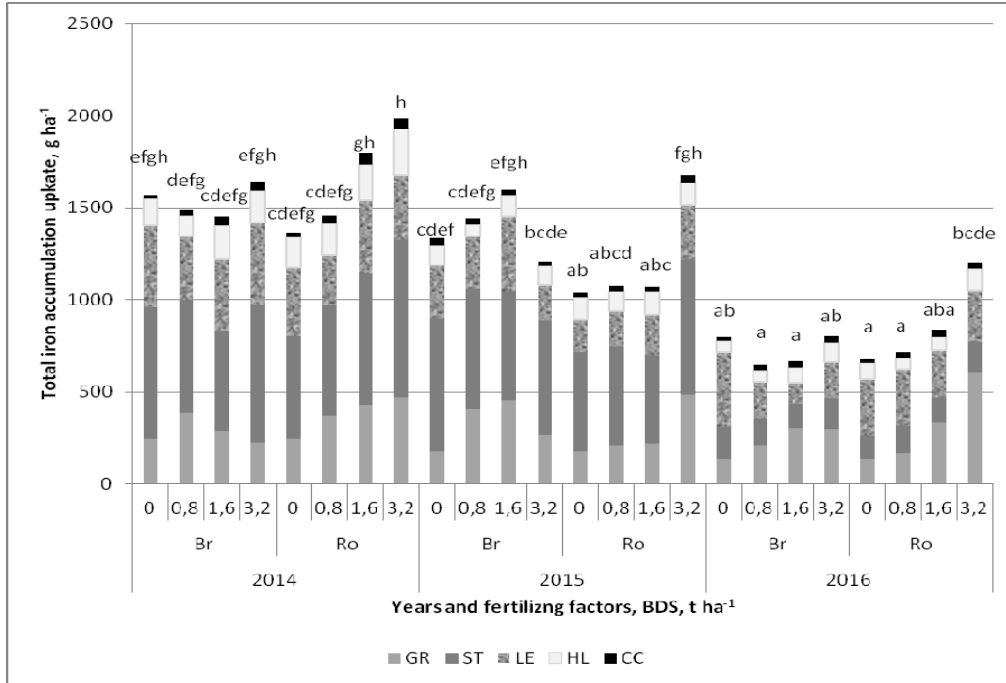
Iron concentration in grain was significantly governed by interaction of all studied factors. The row applied BDS resulted in a strong increase in the Fe_c in grain in response to its applied rate. As a rule, the highest Fe_c was recorded on plots treated with 3.2 t·ha⁻¹ of BDS. On plots with the broadcast applied BDS, the maximum Fe_c values were much lower and were achieved on plots fertilized with 0.8 (2014, 2015) or 1,6 t·ha⁻¹ (2016). The recorded values for Fe_c in grain grown on the N plot ranged from 18 to 29 mg·kg⁻¹, whereas on the BDS treated plots from 19 to 67 mg·kg⁻¹. The first range is close to that published by Sager and Hoesch [2005]. Slightly lower values of Fe_c were recorded in the dry 2015. The observed increase can be explained by a high input of iron with applied BDS into the soil. Fe_c reached the top values, however, under the interaction of two distinct factors. The first one was a very high rate of BDS and the second, stress conditions due to water shortage in 2015 or nitrogen shortage in 2016. This finding corroborates the study by Kandianis et al. [2013] who showed that some varieties of maize increases Fe_c in grain under water shortage.

The highest Fe_c recorded for true leaves was mainly year-dependent. The highest was recorded in the dry 2015 and the lowest in 2016, poor in available nitrogen [Przygocka-Cyna, 2017]. This corroborates the study by Rastija et al. [2012], who showed that some maize cultivars are sensitive to the type of weather, increasing Fe_c in leaves under unfavorable growth conditions, i.e. water shortage. A more distinctive impact of years on Fe_c was observed for stem. It was 3 times lower in 2016 when compared to 2014. For this plant organ, the impact of the BDS rate was quite different for the broadcast compared to the row method of fertilizer application. It decreased in response to increasing BDS rates for the first method, but the opposite trend was recorded for the second one. Husk leaves showed a strong increase in Fe_c in response to the row applied fertilizer. The higher rates of BDS resulted in a progressive, and at the same time, significant Fe_c increase. The pattern of Fe_c in the corncob was, in general, very similar to that observed for grain. The grain yield (GY) weakly depended on Fe_c in maize organs, showing, as

Table 2. Iron profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Fe concentration (g·kg ⁻¹ DW)				Plant parts – Fe accumulation (g·ha ⁻¹)					TOT-Fe	FeHI (%)	
		GRc	STc	LEc	HLc	CCc	GR	ST	LE	HL			CC
Years (Y)	2014	31.5 b	84.3 b	199 b	167	23.6 b	332 b	669 b	377 a	176 c	41.8 b	1595 c	20.8 a
	2015	27.9 a	78.0 b	216 b	165	18.9 a	299 ab	608 b	260 b	107 b	31.1 a	1305 b	22.2 a
	2016	30.4 ab	27.2 c	156 a	169	20.5 b	273 a	149 a	259 b	83 a	30.6 a	794 a	32.8 b
F test value		3.1*	145.8***	8.5***	0.0	6.9**	6.4**	157.6***	37.3***	80.7***	16.6***	191***	53.0***
Application method (AM)	Br	28.2 a	65.2	199	150 a	20.7	282 a	484	311	110 a	33.4	1221	24.7
	Ro	31.6 b	61.2	182	184 b	21.2	320 b	466	286	134 b	35.5	1242	25.9
F test value		7.5**	1.8	1.9	15.5***	0.2	7.8**	0.5	3.9	15.1***	1.4	0.4	1.3
BDS rate (R) (t·ha ⁻¹)	0.0	21.8 a	64.6	197	157 ab	17.2 a	185 a	471 ab	334 b	115 ab	24.4 a	1129 a	16.8 a
	0.8	28.5 b	62.3	182	137 a	20.0 ab	291 b	450 a	266 a	99 a	32.3 ab	1138 a	25.8 b
	1.6	31.4 b	57.0	197	176 bc	23.5 b	336 bc	433 a	299 a	128 ab	41.2 b	1238 a	29.3 b
	3.2	38.0 b	68.8	185	198 c	23.3 b	391 c	548 b	294 a	146 b	39.9 b	1420 b	29.3 b
F test value		31.0***	2.7	0.4	9.6***	8.4***	41.5***	3.8*	4.7**	10.3***	18.6***	15.8***	32.1***
F test value for selected interactions													
AM x R		40.9***	3.1*	3.9*	2.0	2.9*	31.9***	2.5	4.4**	1.5	3.1*	15.8***	11.8***
Y x AM x R		3.8**	0.4	1.1	0.3	1.3	3.7**	0.9	5.0***	0.7	1.1	3.8**	1.2

Legend: Gr – grain; ST – stems; LE – leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; FeHI – iron harvest index
Numbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05, respectively



Legend: * – BDS rate, t·ha⁻¹; ** – method of BDS application: Br – broadcast, Ro – row
 Numbers marked with the same letter are not significantly different

Fig. 1. The partitioning of iron between maize organs at harvest

indicated by the stepwise regression, a significant relationship with its concentration in stem ($r = 0.45^{***}$).

The total uptake of Fe by maize at harvest (Fe_{tot}) was significantly driven by experimental factors and years, ranging from 676 to 1985 g·ha⁻¹ (Fig. 1). As a rule, Fe_{tot} decreased in consecutive years of study in the following order: 2014 > 2015 > 2016. The relative contribution of grain accumulated Fe (Fe_a) in the Fe_{tot} , termed as the Iron Harvest Index (FeHI) ranged from 14% in 2014 to 50% in 2016. The observed increase in its relative accumulation in grain and simultaneous decrease in stem Fe indicates the latter organ as a main source of Fe for developing maize kernels. The strength of Fe reallocation from vegetative maize parts to grain, increased in the years with stress, like water shortage in 2015, and N shortage in 2016. As a result of interaction of experimental factors and years, the relative post-harvest contribution of stem in the Fe_{tot} was more than 50% lower in 2016 compared to both previous years. A highly specific Fe_a pattern was observed for true leaves, which showed much lower year-to-year variability, but as a rule, the application of BDS resulted in a decrease in its value. The strongest decrease was observed in the dry 2015. The amount of Fe in husk leaves contributed to 10% of Fe_{tot} , ranging from 4 to 14%. The contribution of the corncob was 3% on average, varying from 1 to 6%. The FeHI was significantly driven by Fe accumulation in three maize parts. Its amount in vegetative maize parts showed a negative and in grains a positive impact on FeHI:

$$\text{FeHI} = 22.8 + 0.63\text{GR} - 0.16\text{ST} - 0.03\text{LE} \text{ for } R^2 = 0.81 \text{ and } n = 72 \quad [1]$$

Any increase of the Fe amount in stem and in true leaves at harvest indicates its reduced accumulation in grain. The effect of BDS on Fe_a was, as a rule, positive for grain and the corncob, but negative or neutral, excluding the rate of $3.2 \text{ t}\cdot\text{ha}^{-1}$, to vegetative maize parts.

The grain yield of maize was best predicted by Fe accumulation in stem, true leaves and the corncob:

$$\text{GY} = 8.1 + 0.0025\text{ST} - 0.0042\text{LE} + 0.057\text{CC} \text{ for } R^2 = 0.50 \text{ and } n = 72 \quad [2]$$

The obtained equation clearly indicates iron resources in stems and the corncob as critical for the increase of maize grain yield.

Manganese (Mn). The concentration of manganese in maize parts at harvest (Mn_c), averaged over experimental treatments and years, decreased in the following order (Table 3):

$$\text{LE} > \text{HL} > \text{ST} > \text{CC} > \text{GR}.$$

The true leaves of maize showed 20 times higher Mn_c compared to grain. Its concentration in grain was governed by an interaction of all factors. Its highest values, averaged over all factors, were recorded in the dry 2015. The Mn_c response to BDS was inconsistent and was revealed only in the first years of study. In 2016, the application of BDS resulted in Mn_c decrease. The Mn_c for the N plot ranged from 3.3 to $4.0 \text{ mg}\cdot\text{kg}^{-1}$, whereas for BDS treated plots from around 2 to $7 \text{ mg}\cdot\text{kg}^{-1}$. The first range agrees well with results reported frequently in many studies by Teklić et al [2013]. The second range indicates a strong impact of BDS on Mn_c , depending on growth conditions.

The Mn_c in true leaves was significantly driven by the interaction of all factors (data not shown but available by authors). Its highest values were recorded in 2014, showing a positive response to the BDS rate, especially when row applied. The shortage of water during the grain filling period in 2015 resulted in the significant Mn_c drop, compared to 2014. The observed trend is in agreement with the study by Rastija et al. [2012]. The highest Mn_c year-to-year variability was recorded for stem. In 2016 its concentration was almost halved compared to 2014. It showed a significant relationship with Mn_c in maize grain. The pattern of Mn_c in other vegetative organs of maize, i.e. husk leaves and the corncob were very similar, stressing its considerable drop in the dry 2015.

The total uptake of Mn in maize at harvest (Mn_{tot}) was driven by the interaction of the application method and the BDs rate (Fig. 2). The advantage of the broadcast over the row method of BDS application was the most prominent for the rate of $3.2 \text{ t}\cdot\text{ha}^{-1}$. The average Manganese Harvest Index (MnHI) was 15%, showing a slight increase in response to BDS application. It increased at the expense of Mn_a in leaves, but only for plants with the broadcast applied BDS. Plants grown on plots with the row applied BDS showed a highly stabile structure of Mn partitioning among maize organs. The Manganese Harvest Index (MnHI) can be very well predicted based on its concentration and/or accumulation in certain maize organs:

$$\text{MnHI} = 12.8 + 3.11\text{GR}_c - 0.12\text{LE}_c \text{ for } R^2 = 0.76 \text{ and } n = 72 \quad [3]$$

$$\text{MnHI} = 13.2 + 0.31\text{GR} - 0.04\text{ST} - 0.06\text{LE} \text{ for } R^2 = 0.94 \text{ and } n = 72 \quad [4]$$

These two equations clearly inform that any increase in Mn concentration or accumulation in leaves results in the MnHI decrease. The application of BDS in the highest rates can change this negative trend through a modification in the pattern of dry matter allocation [Przygocka-Cyna 2017].

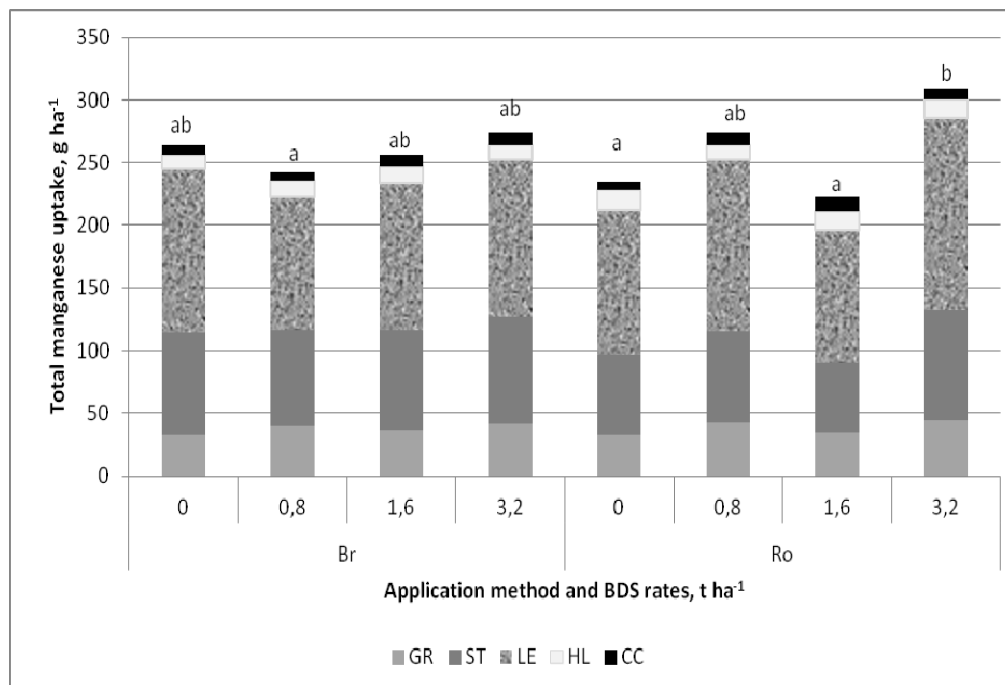
The prediction of grain yield based on Mn_c concentration in maize parts was limited only to grain, being, however, weak ($r = 0.31^{**}$). Much higher predictive strength was exerted by Mn accumulation in grain and the corncob:

$$\text{GY} = 6.53 + 0.06\text{GR} + 0.15\text{CC} \text{ for } R^2 = 0.48 \text{ and } n = 72 \quad [5]$$

Table 3. Manganese profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Mn concentration (g·kg ⁻¹ DW)						Plant parts – Mn accumulation (g·ha ⁻¹)						TOT-Mn	MnHI (%)
		GRc	STc	LEc	HLc	CCc	GR	ST	LE	HL	CC				
Years (Y)	2014	3.9 b	12.1 b	97.3 c	17.9 ab	6.2 b	41.8 b	96.0 b	182 c	18.7 b	11.1 b	350 b	12.0 a		
	2015	4.7 c	11.4 b	56.4 a	17.3 a	4.2 a	49.7 c	89.0 b	68 a	11.4 a	6.8 a	225 a	22.0 b		
	2016	2.6 a	7.4 a	78.7 b	19.8 b	5.7 a	22.7 a	41.3 a	121 b	9.6 a	8.4 a	203 a	11.6 a		
F test value		73.9***	37.3***	45.5***	3.5*	25.6***	101.2***	107.5***	74.0***	71.7***	35.8***	97.7***	116.8***		
Application Method (AM)	Br	3.8	11.2 b	73.6 a	17.0 a	5.1	37.7	80.9 b	120	12.3 a	8.3 a	259	15.1		
	Ro	3.7	9.4 a	81.4 b	19.7 b	5.6	38.4	70.0 a	128	14.2 b	9.3 b	260	15.3		
F test value		0.1	13.0***	4.9*	11.5**	4.0	0.2	10.8**	1.2	8.9**	5.9*	0.0	0.1		
BDS rate (R)	0.0	3.9 ab	10.1	70.3 a	18.7	5.1	33.3 a	72.2 a	123	13.4	7.2 a	249 a	14.3		
	0.8	4.0 b	10.7	82.7 ab	17.7	5.1	41.0 bc	74.9 ab	121	12.4	8.4 ab	258 ab	15.7		
	1.6	3.2 a	9.5	72.4 ab	19.1	5.8	35.5 ab	67.9 a	111	14.0	10.0 c	239 a	15.5		
	3.2	4.0 ab	10.9	84.5 b	17.8	5.5	42.4 b	86.7 b	140	13.2	9.4 bc	291 b	15.3		
F test value		5.9**	1.9	4.2*	0.8	1.9	7.6***	5.9**	2.3	1.1	9.1***	6.0**	1.0		
F test value for the selected interactions															
AM x R		0.6	3.8*	5.4**	4.9**	5.2**	0.4	3.8*	2.5	2.9*	6.7***	4.1*	0.9		
Y x AM x R		5.9***	4.4**	2.4*	3.2*	4.4**	7.3***	3.3*	1.1	2.0	4.4**	2.2	3.0*		

Legend: Gr – grain; ST – stems; LE – leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; MnHI – manganese harvest index
 Numbers marked with the same letter are not significantly different, ***, **, * significance at 0.001; 0.01; 0.05, respectively



Legend: * – BDS rate, t·ha⁻¹; ** – method of BDS application: Br – broadcast, Ro – row
Numbers marked with the same letter are not significantly different

Fig. 2. The partitioning of manganese between maize organs at harvest

Zinc (Zn). The pattern of zinc concentration (Zn_c) variability in maize organs was completely different with respect to the previously described micronutrients (Table 4):

$$GR > CC > LE > ST > HL$$

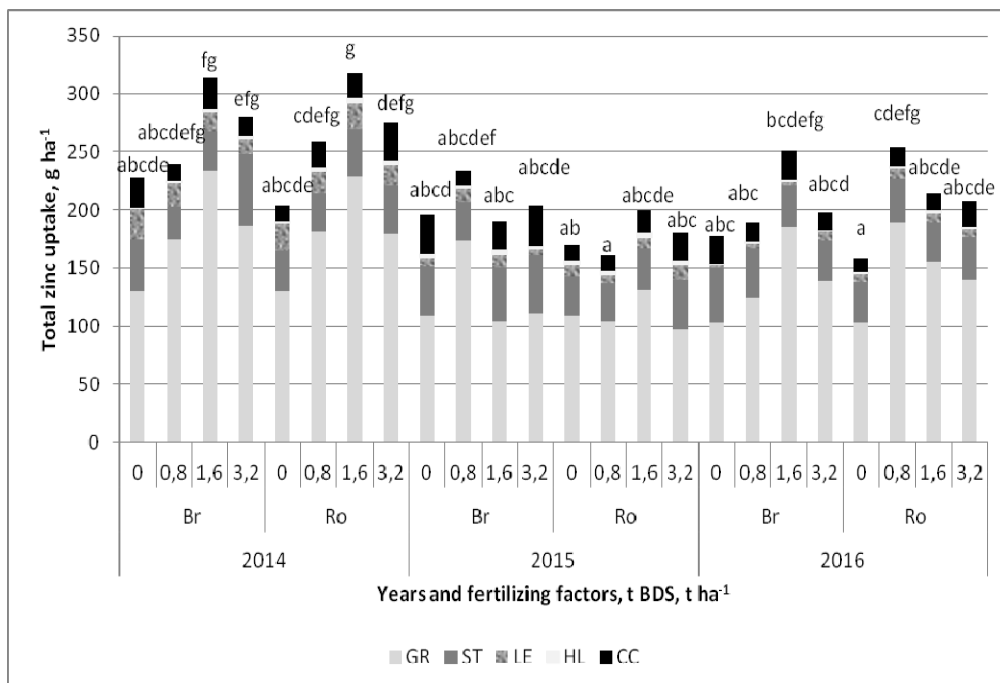
The concentration of Zn in grain was significantly driven by interactional effect of experimental factors and years. The impact of environment, i.e. weather, was decisive for Zn_c variability. In the dry 2015, it was lower by $\frac{1}{3}$, compared to other two years. The recorded Zn_c was low compared to data reported by Teklić et al [2013], but in the range presented by Li et al [2012]. As it results from the study, under suitable environmental conditions and simultaneous application of BDS in the rate 0.8-1.6 t·ha⁻¹, the Zn_c exceeded 20 mg kg⁻¹ DW. This value is the ranges frequently published [Teklić et al 2013]. A comparison of Zn_c pattern for grain with those observed for vegetative maize organs indicates the latter as Zn reservoirs for developing kernels. The yield of grain showed a positive, but low relationship with Zn_c in true leaves ($r = 0.46^{***}$).

The total Zn uptake by maize at harvest (Zn_{tot}) was significantly governed by interaction of experimental factors and years (Fig. 3). The interaction of the application method and BDS rates on the Zn_{tot} flourished the most in 2014. In this particular year, the highest Zn_{tot} , irrespectively of the application method, was recorded on plots fertilized with BDS of 1.6 t·ha⁻¹. In other years of the study, the effect of experimental factors was significant, but inconsistent. The contribution of grain in Zn_{tot} , termed as the Zinc Harvest Index ($ZnHI$) responded significantly to interaction

Table 4. Zinc profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Zn concentration (g·kg ⁻¹ DW)						Plant parts – Zn accumulation (g·ha ⁻¹)						TOT-Zn	ZnHI (%)
		GRc	STc	LEc	HLc	CCc	GR	ST	LE	HL	CC				
Year (Y)	2014	17.0 b	5.00 a	10.77 c	2.21 a	12.5	181 c	39.9	20.2 c	2.33 b	21.6 b	265 b	67.6 b		
	2015	11.2 a	5.00 a	8.03 b	4.70 b	13.4	118 a	39.3	10.0 b	3.12 a	21.8 b	192 a	61.1 a		
	2016	16.1 b	6.87 b	4.32 a	1.99 a	12.6	143 b	37.9	6.6 a	0.96 a	18.4 a	207 a	68.4 b		
F test value		48.7***	17.1***	101.0***	126.8***	1.00	51.1***	0.3	105.0***	105.0***	4.7*	52.1***	17.6***		
Application Method (AM)	Br	15.0	6.00 b	6.96 a	2.58 a	14.2 b	148	41.6 b	11.4 a	1.82 a	22.1 b	225	64.9		
	Ro	14.6	5.25 a	8.45 b	3.34 b	11.4 a	146	36.5 a	13.1 b	2.45	19.1 a	217	66.5		
F test value		0.6	6.3*	15.9***	24.2***	22.7***	0.2	5.2*	4.5*	26.5***	9.0**	1.7	2.2		
BDS rate (R)	0.0	13.5 a	5.61	7.48 ab	2.71 a	14.4 b	114 a	39.6 ab	13.2	1.89 a	20.3 b	189 a	60.5 a		
	0.8	15.8 b	5.26	8.49 b	2.73 a	9.8 a	158 bc	34.4 a	12.3	1.98 ab	16.0 a	223 b	70.2 b		
	1.6	16.3 b	5.58	8.07 ab	3.25 b	12.9 b	173 c	37.5 ab	12.5	2.39 b	22.2 b	248 c	69.1 b		
	3.2	13.6 a	6.05	6.79 a	3.17 ab	14.1 ab	142 b	44.7 b	11.0	2.27 ab	24.0 b	224 a	63.1 a		
F test value		8.1***	1.2	3.2*	3.4*	23.6***	24.5***	3.9*	1.3	3.7*	11.3***	15.5***	17.7***		
F test value for the selected interactions															
AM x R		0.1	0.8	2.6	0.3	23.6***	0.1	1.3	1.1	0.5	19.2***	0.8	3.7*		
Y x AM x R		5.2***	1.3	3.2*	4.0**	4.8***	5.1***	1.1	3.1*	2.2	3.9**	3.3**	3.0*		

Legend: Gr – grain; ST – stems; LE – leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; ZnHI – zinc harvest index
 Numbers marked with the same letter are not significantly different, ***, **, * significance at 0.001; 0.01; 0.05, respectively



Legend: * – BDS rate, t·ha⁻¹; ** – method of BDS application: Br – broadcast, Ro – row
Numbers marked with the same letter are not significantly different

Fig. 3. The partitioning of zinc between maize organs at harvest

of all studied factors. This index showed a strong variability, ranging from 56 to 66% for the N treatment. For BDS treatments, it ranged from 54 to 74%. The contribution of stem Zn in the Zn_{tot} was 3.5 times lower, but it was reversely correlated with ZnHI. Even greater differences were observed for the corncob, but it also showed a negative relationship with ZnHI. It means, that the increase of Zn_c in grain was at the expense of stem and corncob. The ZnHI can be satisfactorily predicted based on Zn_c or its accumulation in maize organs:

$$ZnHI = 67.7 + 1.52GR_c - 1.85ST_c - 0.73LE_c - 0.66CC_c \text{ for } R^2 = 0.84 \text{ and } n = 72 \quad [6]$$

$$ZnHI = 67.7 + 0.15GR - 0.32ST - 0.32LE - 0.34CC \text{ for } R^2 = 0.94 \text{ and } n = 72 \quad [7]$$

These two equations clearly indicate that any increase in Zn concentration in grains, concomitant with simultaneous decrease in vegetative parts of maize leads to higher ZnHI. The grain yield of maize showed a significant dependence on Zn_c in grain and husk leaves:

$$GY = 6.35 + 0.012GR + 0.83HL \text{ for } R^2 = 0.52 \text{ and } n = 72 \quad [8]$$

Copper (Cu). The order of maize organs with respect to copper concentration (Cu_c) at harvest was much less differentiated compared to other micronutrients (tab. 5):

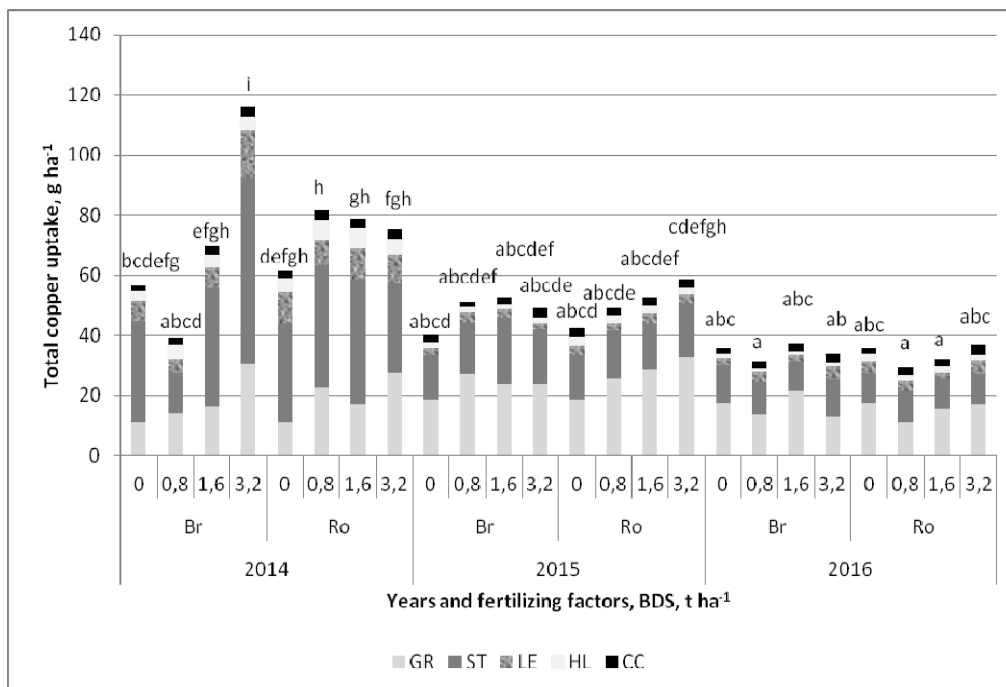
$$HL \geq LE > ST > GR > CC.$$

The Cu_c in grain, averaged over all factors, was within the frequently published range [Teklić et al 2013]. It was a year-to-year variable, but at the same time it was not affected by interaction of experimental factors, in spite of a positive response to the highest BDS rate. The Cu_c

Table 5. Copper profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Cu concentration (g·kg ⁻¹ DW)						Plant parts – Cu accumulation (g·ha ⁻¹)						TOT-Cu	CuHI (%)
		GRc	STc	Lec	HLc	CCc	GR	ST	LE	HL	CC				
Year (Y)	2014	1.74 a	4.57 b	4.94 b	4.40 b	1.58	18.7 a	36.7 c	9.40 b	4.62 c	2.74	72.2 c	26.4 a		
	2015	2.32 b	2.17 a	2.45 a	2.89 a	1.57	24.8 b	17.1 b	3.00 a	1.92 b	2.55	49.4 b	49.8 b		
	2016	1.82 a	1.93 a	2.40 a	2.63 a	1.63	15.9 a	10.7 a	3.70 a	1.23 a	2.42	33.9 a	46.7 b		
F test value		19.3***	87.4***	127.0***	51.7***	0.2	28.6***	103.9***	129.4***	199.3***	1.6	152.0***	76.0***		
Application method (AM)	Br	1.93	3.02	2.99 a	2.58 a	1.54	19.2	22.2	5.06	2.06 a	2.44	51.0	40.6		
	Ro	1.99	2.76	3.53 b	4.03 b	1.65	20.4	20.8	5.68	3.12 b	2.70	52.7	41.3		
F test value		0.6	2.1	13.3***	88.6***	1.4	1.5	0.8	3.0	52.1***	3.0	0.9	0.2		
BDS rate (R)	0.0	1.86 a	2.67 a	2.87 a	3.24	1.61	15.8 a	19.7 ab	5.15 a	2.40	2.27 a	45.3 a	38.1		
	0.8	1.85 a	2.56 a	3.15 a	3.30	1.50	19.0 ab	18.2 a	4.56 a	2.65	2.43 ab	46.8 a	41.8		
	1.6	1.89 a	3.18 b	3.04 a	3.40	1.55	20.4 bc	23.2 ab	4.84 a	2.72	2.68 ab	53.8 b	41.6		
	3.2	2.24 b	3.14 b	3.99 b	3.27	1.71	24.0 c	25.1 b	6.92 b	2.59	2.90 b	61.5 c	42.2		
F test value		5.3**	3.2*	11.4***	0.2	1.0	11.8***	4.2*	8.9***	0.9	3.5*	16.9***	1.3		
F test value for the selected interactions															
AM x R		1.2	6.7***	5.5**	4.0*	0.8	0.6	6.7***	6.0**	2.4	0.7	6.3***	2.9*		
Y x AM x R		1.7	6.3***	8.1***	0.6	0.5	2.4*	7.1***	6.7***	0.4	0.5	12.3***	0.8		

Legend: Gr – grain; ST – stems; LE – husk leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; CuHI – copper harvest index
 Numbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05, respectively



Legend: * – BDS rate, t·ha⁻¹; ** – method of BDS application: Br – broadcast, Ro – row
Numbers marked with the same letter are not significantly different

Fig. 4. The partitioning of copper between maize organs at harvest

was significantly higher in the dry 2015 compared with other years. It is in agreement with Rastija et al. [2012], who showed a triple increase in Cu_c in grain harvested in a very dry 2013, compared to 2014, with ample water supply. The reverse trends, but only with respect to 2014, were observed for Cu_c concentrations in vegetative parts of maize. The effect of the application method was observed for true leaves and husk leaves. For these two organs, a much higher Cu_c was recorded for plants grown on the plot with the row applied BDS. The effect of increasing BDS rates on Cu_c was observed for grain, stems and true leaves. For leaves, the highest Cu_c was recorded in 2014; it was twice as high compared with other years. In this particular year, Cu_c responded significantly to interaction of application method and BDS rate. A progressive Cu_c increase was recorded for plants grown on the broadcast treated plots, whereas only up to 0.8 t·ha⁻¹ on plots with row applied BDS. The Cu_c pattern for stem was very similar to that for true leaves ($r = 0.73^{***}$), but showed a positive, yet weak relationship with the grain yield ($r = 0.34^{**}$).

The total Cu uptake at maize harvest (Cu_{tot}) ranged from 29 to 116 g·ha⁻¹ and was significantly driven by interaction of all factors (Fig. 4). The contribution of the grain Cu concentration in the Cu_{tot} , termed as the Copper Harvest Index ($CuHI$) was, on average, 41%, but ranging from 18 to 58%. The lowest values were recorded in 2014 and the highest in the years with stress, i.e. in 2015 and 2016. The effect of BDS was apparent in all years, but inconsistent. The $CuHI$ was in balance with Cu relative contribution ($Cu_{\%ST}$) in the Cu_{tot} . The same dependence was observed

for the relative contribution of true leaves and husk leaves in the Cu_{tot} . The obtained relationships clearly inform that these three maize organs are the direct source of Cu for the developing grains. The CuHI can be predicted based on both Cu concentration or on its accumulation in maize organs:

$$CuHI = 33.6 + 13.38GR_c - 4.16ST_c - 2.1LE_c \text{ for } R^2 = 0.88 \text{ and } n = 72 \quad [9]$$

$$CuHI = 36.7 + 1.12GR - 0.62ST - 1.75HL \text{ for } R^2 = 0.93 \text{ and } n = 72 \quad [10]$$

These two equations indicate that the excess of copper in vegetative maize parts leads to a decrease of its concentration in maize kernels. The Cu accumulated in grain and husk leaves followed the same pattern as recorded for zinc

$$GY = 6.62 + 0.013GR + 0.36HL \text{ for } R^2 = 0.57 \text{ and } n = 72 \quad [11]$$

The application of BDS, through a positive effect on CuHI, significantly affected the grain yield.

Cadmium (Cd). Cadmium concentration (Cd_c) in maize organs was several times lower compared to that of copper, and decreased in the following order (Table 6):

$$LE > GR > ST \geq HL = CC$$

The Cd_c in maize grain was the only plant part, which responded significantly to all studied factors (data not shown but available by the author). The vegetative maize organs did not act as a barrier for Cd movement to kernels as supposed by Carbonell et al. [2011]. The threshold value of Cd_c of $0.1 \text{ g}\cdot\text{kg}^{-1}$ was exceeded for all treatments, excluding the broadcast BDS treated plots in 2014. In this particular year, Cd_c was above the threshold value on plots with the row applied BDS. In the dry 2015, BDS application resulted in a significant increase of Cd_c compared to the N plot. The same trend was observed in 2016, characterized by a shortage of nitrogen supply. A very similar pattern was observed for the corncob. For leaves, Cd_c reached significantly higher values in years with water (2015) or N (2016) stress. In general, the row method of BDS application resulted in a significant increase in Cd_c . The same trend was observed for husk leaves. The stem Cd_c was affected by all studied factors, but it did not respond to the interaction between them. The grain yield showed a positive, but weak relationship with Cd_c in grain ($r = 0.36^{**}$). The obtained trends in Cd accumulation in maize parts are in agreement with data reported by Lavado et al [2007]. These authors showed a 3-time increase in Cd_c in both grain and shoot in response to the biosolids rate of $7.5 \text{ t}\cdot\text{ha}^{-1}$, but the threshold values were not exceeded.

The total Cd uptake by maize at harvest (Cd_{tot}) was significantly governed by the interaction of year and the method of BDS application (Fig. 5). Except for 2016, maize grown on plots with the row applied BDS accumulated considerably more cadmium. In 2014, the row applied BDS resulted in 40% increase in Cd accumulation. In the dry 2015, the average accumulation of Cd was significantly higher, but the relative increase, due to BDS application, was only 17%. The relative contribution of grain Cd in Cd_{tot} , termed as Cadmium Harvest Index (CdHI), was much higher in the years with stress, exceeding 50%. In 2015, it was above 50% only on plots with the row applied BDS. The observed increases in Cd uptake and its subsequent accumulation in grain, was due to its higher concentration in grain. A quite reverse impact of application method was recorded for the stem accumulated Cd. In the first two years, it was much lower on plots with the row applied BDS. The CdHI regression models based on Cd_c or its accumulation in maize organs fully corroborated the presented opinion:

$$CdHI = 32.3 + 241.5GR_c - 157.1ST_c \text{ for } R^2 = 0.88 \text{ and } n = 72 \quad [12]$$

$$CdHI = 43.7 + 19.9 - 20.0ST - 20.6LE \text{ for } R^2 = 0.88 \text{ and } n = 72 \quad [13]$$

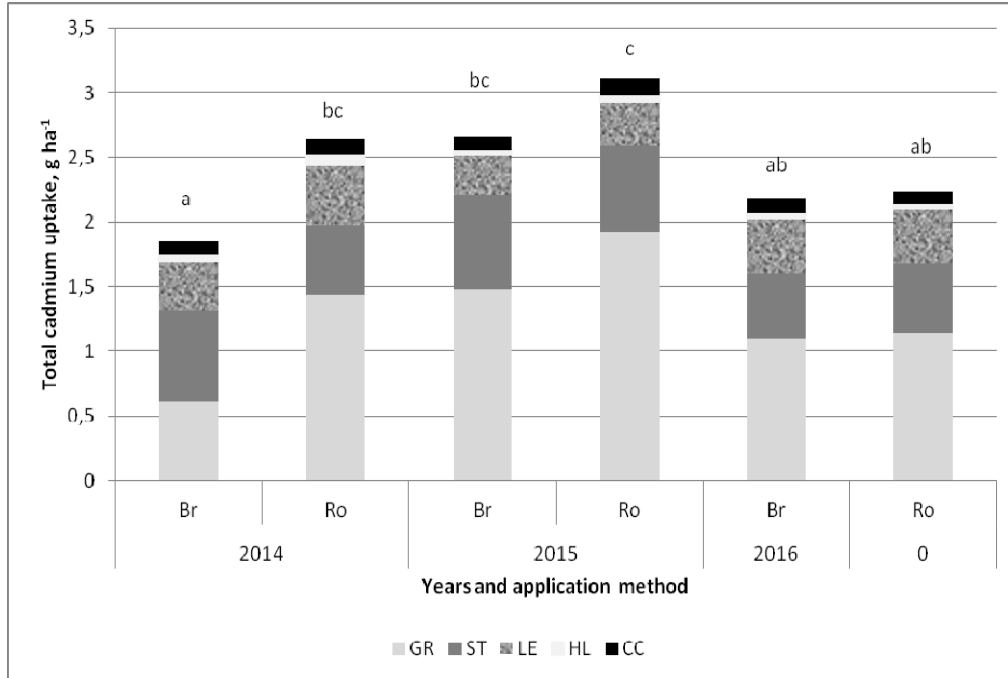
These two equations inform that Cd_c was the driving force of its accumulation in grain. This conclusion is also corroborated by Cd_{tot} calculation which indicated GR as a single predictor:

$$Cd_{tot} = 1.0 + 11.5GR_c \text{ for } R^2 = 0.80 \text{ and } n = 72 \quad [14]$$

Table 6. Cadmium profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Cd concentration (g·kg ⁻¹ DW)						Plant parts – Cd accumulation (g·ha ⁻¹)						TOT-Cd	CdHI (%)
		GRc	STc	Lec	HLc	CCc	GR	ST	LE	HL	CC				
Year (Y)	2014	0.09 a	0.08	0.22 a	0.07 ab	0.06	1.02 a	0.62 ab	0.42 b	0.07 b	0.11	2.25 a	42.8 a		
	2015	0.16 c	0.09	0.27 b	0.06 a	0.07	1.70 b	0.70 b	0.33 a	0.04 a	0.12	2.88 b	56.2 b		
	2016	0.12 b	0.09	0.28 b	0.08 b	0.07	1.12 a	0.52 a	0.42 b	0.04 a	0.11	2.21 a	47.8 a		
F test value		21.7***	3.0	8.7***	3.6*	1.1	20.0***	5.5**	7.9***	21.7***	0.4	13.2***	13.8***		
Application Method (AM)	Br	0.11 a	0.09 b	0.24 a	0.06 a	0.07	1.06 a	0.65	0.37	0.04 a	0.11	2.23a	45.0		
	Ro	0.14 b	0.08 a	0.27 b	0.08 b	0.07	1.50 b	0.58	0.41	0.06 b	0.12	2.66b	52.9		
F test value		21.6***	5.0*	6.6**	19.5***	0.2	21.8***	2.7	2.8	15.7***	1.2	13.0***	14.1***		
BDS rate (R)	0.0	0.07 a	0.08 a	0.23	0.06	0.06	0.64 a	0.58	0.39	0.04	0.09 a	1.74 a	33.7 a		
	0.8	0.14 b	0.10 b	0.28	0.07	0.08	1.42 b	0.69	0.40	0.05	0.12 b	2.69 b	50.8 b		
	1.6	0.15 b	0.08 a	0.25	0.07	0.07	1.65 b	0.59	0.37	0.05	0.12 b	2.78 b	57.6 b		
	3.2	0.14 b	0.08 a	0.26	0.07	0.07	1.42 b	0.60	0.40	0.05	0.11 b	2.58 b	53.7 b		
F test value		19.4***	3.7*	2.6	1.1	1.5	21.8***	1.3	0.7	0.7	4.2*	15.9***	25.0***		
F test value for the selected interactions															
AM x R		3.8*	1.0	4.1*	0.3	3.5*	3.6*	0.6	3.7*	0.4	2.6	2.6	1.9		
Y x AM x R		2.5*	1.4	2.0	0.2	2.5*	1.6	1.7	2.2	0.2	2.3	0.8	2.5*		

Legend: Gr – grain; ST – stems; LE – husk leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; CdHI – cadmium harvest index
 Numbers marked with the same letter are not significantly different; ***, **, * significance at 0.001; 0.01; 0.05, respectively



Legend: * – BDS rate, t·ha⁻¹; ** – method of BDS application: Br – broadcast, Ro – row
 Numbers marked with the same letter are not significantly different

Fig. 5. The partitioning of cadmium between maize organs at harvest

The grain yield, as in the case of zinc and copper, can be predicted based on Cd accumulation in grain and husk leaves:

$$GY = 7.61 + 1.11GR + 19.65HL \text{ for } R^2 = 0.41 \text{ and } n = 72 \quad [15]$$

These sets of equations stress the importance of Cd_c in grain as a factor impacting both its accumulation in grain and yield. Any unfavorable growth conditions, like shortage of water or shortage of N supply, and also BDS application, as showed in this study, led to the increase in Cd grain concentration, creating, in turn, a health threat.

Lead (Pb). Lead concentration (Pb_c) in maize parts showed huge differences, and decreased in the following order (Table 7):

$$ST_c > HL_c > LE_c > CC_c > GR_c.$$

The order of maize organs is different than that presented by Lu et al. [2015] for maize grown on the long-term irrigated fields polluted with wastewater containing heavy metals. Those authors documented significantly higher Pb_c in leaves compared to stems. The above presented order of maize organs clearly shows that vegetative organs of maize acted as a barrier, preventing Pb accumulation in grain. This barrier, as indicated by strong differences in Pb_c values for respective maize organs, was much stronger compared to that described by Carbonell et al. [2011] for maize fertilized with municipal solid waste compost. The Pb_c in grain was significantly governed by interaction of all factors. The threshold value of 0.1 mg·kg⁻¹ DM was, on

Table 7. Lead profile of maize: concentration and partitioning among plant parts

Factors	Level of factor	Plant parts – Pb concentration (g·kg ⁻¹ DW)						Plant parts – Pb accumulation (g·ha ⁻¹)						TOT-Pb	PbHI (%)
		GRc	STc	Lec	HLc	CCc	GR	ST	LE	HL	CC				
Year (Y)	2014	0.14 a	3.00 a	0.58 b	3.16	0.34	1.52 a	23.7 b	1.09 b	3.31 c	0.59	30.2 b	5.18 a		
	2015	0.22 c	3.61 b	0.45 a	3.26	0.33	2.30 b	28.4 b	0.54 a	2.16 b	0.53	33.9 b	7.11 b		
	2016	0.16 b	3.64 b	0.59 b	2.90	0.35	1.43 a	20.2 a	0.92 b	1.39 a	0.53	24.5 a	6.08 ab		
F test value		75.9***	6.3**	5.5**	2.9	2.2	79.2***	10.0**	21.1***	105***	3.5	13.3***	9.6***		
Application method (AM)	Br	0.17	3.33	0.51	3.04	0.34	1.74	23.4	0.83	2.24	0.54	28.8	6.26		
	Ro	0.17	3.51	0.57	3.17	0.34	1.76	24.8	0.87	2.34	0.56	30.3	5.99		
F test value		0.1	1.2	2.0	1.0	0.0	0.2	0.8	0.4	0.7	1.3	1.1	0.6		
BDS rate (R) (t·ha ⁻¹)	0.0	0.18 ab	3.62	0.51	2.87 a	0.33	1.51 a	25.9	0.88	2.07 a	0.45 a	30.8	5.20 a		
	0.8	0.16 a	3.14	0.62	2.96 ab	0.33	1.66 ab	21.8	0.90	2.15 ab	0.54 b	27.0	6.31 ab		
	1.6	0.17 a	3.66	0.53	3.37 b	0.36	1.81 bc	25.3	0.81	2.52 b	0.62 c	31.1	5.99 ab		
	3.2	0.19 b	3.26	0.51	3.23 ab	0.34	2.01 c	23.4	0.82	2.42 ab	0.58 bc	29.2	7.01 b		
F test value		5.1**	2.4	2.0	3.8*	1.9	11.8***	1.5	0.4	3.8*	11.7***	1.5	4.3*		
F test value for the selected interactions															
AM x R		2.8	1.0	2.3	0.9	0.7	1.4	0.8	1.8	0.8	0.8	0.9	0.9		
Y x AM x R		7.1***	1.2	2.3*	0.9	0.6	5.2***	0.6	2.7*	0.8	1.5	0.6	2.7*		

Legend: Gr – grain; ST – stems; LE – husk leaves; HL – husk leaves; CC – corn cob; c – concentration; TOT – total accumulation; PbHI – lead harvest index
 Numbers marked with the same letter are not significantly different, ***, **, * significance at 0.001; 0.01; 0.05, respectively

average, exceeded in all years. In 2014, it was only slightly, but positively, affected by high rates of BDS. In the dry 2015, it showed much higher values, and at the same time a lower response to the BDS. In 2016, it was above the threshold value, but underwent the decrease in response to high rates of BD.

The general pattern of Pb_c in leaves was quite opposite to that presented for grain, being governed by interaction of all factors. The effect of experimental factors was inconsistent, showing, however, a strong increase in response to low or medium BDS rates in 2014, and 2016. A significantly higher Pb_c values were recorded in 2015. The Pb_c in husk leaves rose up only in response to increasing rates of BDS. Any significant response to studied factors was detected to the corncob. The grain yield showed a positive, but weak relationship with Pb_c in husk leaves.

The total Pb uptake by maize at harvest (Pb_{tot}) was entirely driven by a year-to-year variability. It showed a positive, but weak response to Pbc in stem ($r = 0.34^{**}$). The contribution of Pb in grain, termed as the Lead Harvest Index (PbHI) showed a significant response to all studied factors. As a rule, PbHI was low, ranging from 3.5 to 8.5%. Its values responded to the method of BDS application, being, however, highly variable in consecutive years of study. The effect of BDS was more pronounced in years with favorable precipitation than in the dry 2015. The PbHI can be well predicted by both the Pb concentration and accumulation in maize parts:

$$PbHI = 4.45 + 32.8GR_c - 1.18ST_c \text{ for } R^2 = 0.69 \text{ and } n = 72 \quad [16]$$

$$PbHI = 5.86 + 1.31GR - 0.19ST - 0.3HL \text{ for } R^2 = 0.95 \text{ and } n = 72 \quad [17]$$

These two equations indicate stem as the maize parts governing lead accumulation in grain. Therefore, any growth conditions leading to the increase of stems biomass, in turn, negatively affect Pb accumulation in grain. It was the case of 2014. The grain yield of maize showed a significant dependence on lead accumulation in kernels and the proximate organs:

$$GY = 3.59 + 1.31GR + 0.48HL + 5.48CC \text{ for } R^2 = 0.69 \text{ and } n = 72 \quad [18]$$

This equation stresses the importance of vegetative parts of the cob as a barrier for lead transport to kernels.

CONCLUSIONS

1. The concentration of Fe, Zn, Cu, Cd in maize grain was significantly increased by the application of BDS, but modified by the course of weather or supply of nitrogen.
2. Water shortage (2015) resulted in a significant decrease of Fe, Zn, Cd concentration in grain. A reverse response was recorded for Mn, Cu, and Pb. Nitrogen shortage (2016) resulted in the decreased concentration of Mn.
3. The harvest indices (HIs) of studied elements, averaged over treatments and years, increased in the following order: $Zn > Cd > Cu > Fe > Mn > Pb$. The main reason for the HI year-to-year variability was water shortage (Mn increase; Zn, Cd - decrease); nitrogen shortage (Fe - increase) or both (Cu, Pb - decrease).
4. The effect of BDS on HIs of studied elements was always positive for grain and negative or neutral for other vegetative organs. Its increase was a result of the enlargement of the sink capacity of grain at the expense of stem and leaves (Fe, Cu, Cd); leaves (Mn); stem and husk leaves (Zn, Pb).
5. The stem was the maize organ limiting Fe accumulation in grain, but controlling the Pb reallocation to grain.
6. The grain yield of maize can be predicted by the concentration of studied elements, but a slightly higher predictability was exerted by their accumulation in grain and husk leaves (Zn, Cu, Cd, Pb); by grain and the corn cob (Mn); by stem and the corncob (positive), leaves (negative) for Fe.

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**PROFIL MINERALNY KUKURYDZY ZIARNOWEJ W STADIUM DOJRZAŁOŚCI
FIZJOLOGICZNEJ NAWOŻONEJ GRANULATEM POFERMENTACYJNYM
CZĘŚĆ II. MIKROELEMENTY I METALE CIĘŻKIE**

Synopsis. W pracy założono, że granulát pofermentacyjny z biogazowni rolniczej (BDS) zastosowany jako nawóz organiczny istotnie wpływa na rozdział suchej masy i pierwiastków śladowych (mikroelementy i metale ciężkie) między części rośliny nasiennej, co z kolei prowadzi do wzrostu plonu. Hipotezę tę zweryfikowano na podstawie serii eksperymentów polowych z kukurydzą, przeprowadzonych w latach 2014–2016 w miejscowości Brody, Polska. Eksperyment dwuczynnikowy składał się z metody aplikacji BDS (rzutowo i rzędowo) i dawki: 0; 0,8; 1,6; 3,2 t·ha⁻¹. Koncentracja pierwiastków śladowych w ziarnie zależała od współdziałania czynników doświadczalnych, głównie dawki BDS i warunków pogodowych. Susza (2015) spowodowała istotny spadek koncentracji Fe, Zn i Cd z jednoczesnym wzrostem koncentracji Mn, Cu i Pb w ziarnie. Indeksy żniwne (HIs) pierwiastków śladowych wzrastały w kierunku: Zn > Cd > Cu > Fe > Mn > Pb. Wartości His były wynikiem rozdziału pobranego składnika między ziarno a części wegetatywne kukurydzy takie jak łodyga i liście (Fe, Cu, Cd), liście (Mn), łodygę i liści okrywowe kolby (Zn, Pb). Łodyga okazała się organem kukurydzy istotnie warunkującym HI dla Fe, lecz jednocześnie kontrolującym realokację Pb do ziarna. Przeprowadzone badania wykazały, że całkowita akumulacja kadmu przez kukurydżę zależała od koncentracji tego składnika w liściach, która wzrastała w reakcji na suszę, czy też niedobór azotu, lecz także poprzez stosowanie granulowanego pofermentu. Każdy z tych czynników prowadził do przekroczenia wartości krytycznych koncentracji kadmu w ziarnie, wynoszącej 0,1 g·kg⁻¹ s.m..

Słowa kluczowe: granulát pofermentacyjny, metoda stosowania i dawka, części kukurydzy, mikroelementy, metale ciężkie, rozdział

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