Journal of Elementology ISSN 1644-2296

Wierzbowska J., Sienkiewicz S., Światły A. 2021.
Content of micronutrients in grain and straw of common maize fertilized with urea-ammonium nitrate solution with added P, Mg or S.
J. Elem., 26(4): 807-827. DOI:10.5601/jelem.2021.26.3.2184

RECEIVED: 6 September 2021
ACCEPTED: 16 September 2021

ORIGINAL PAPER

CONTENT OF MICRONUTRIENTS IN GRAIN AND STRAW OF COMMON MAIZE FERTILIZED WITH UREA-AMMONIUM NITRATE SOLUTION WITH ADDED P, Mg OR S*

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Abstract

A field experiment was conducted in 2015-2017, in the Production and Experimental Station located in Bałcyny (51.6667°N, 18.1667°E). The surface area of a plot for harvest was 450 m^2. The following nitrogen fertilizers were applied in the experiment: UAN – 32%N, UAN+S – 26% N + 3% S, UAN+P (medium) – 26% N and 11% P_2O_5, UAN+P (starter) – 21% N and 18% P_2O_5, UAN+Mg – 20% N + 4% Mg. It has been demonstrated that the content of micronutrients in maize grain is modified more by the atmospheric conditions (year of cultivation) than by the tested fertilization. The highest content of Zn, Mn and B was determined in the grain harvested in the second year of the experiment, when total rainfall was slightly higher than the long-term average. In turn, when the rainfall was deficient in the first year, maize contained the highest levels of Cu and Fe. Fertilization had no effect on the content of copper and manganese in grain, while nitrogen fertilization lowered the content of B and Fe. The content of micronutrients in maize straw also depended on the year of cultivation and the relationships looked similar. Concentrations of B, Cu, Zn, Mn and Fe in maize straw were differentiated more by the applied fertilization. Significantly the highest amounts of B, Cu, Zn, Mn and Fe were removed with the maize aerial mass in 2016, when the meteorological conditions favoured the growth of this plant. The unit uptake of micronutrients for the production of 1 t of grain was also more considerably affected by the weather conditions than by the applied fertilization. The contribution of grain to the accumulation of micronutrients varied significantly between the years, and ranged for particular elements as follows: B – from 35 to 44%, Cu – from 28 to 34%, Zn – from 42 to 52%, Mn – from 7 to 13% and Fe – from 15 to 17%.

Keywords: UAN, *Zea mays* L., removal of micronutrients, micronutrients accumulation in grain.

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* The study was financed from a grant funded by GRUPA AZOTY ZAKŁADY AZOTOWE " PUŁAWY "SA with its seat in Puławy, titled "Determining the agricultural and economic efficiency of spring fertilization of winter oilseed rape, winter wheat and common maize with ammonium nitrate-urea solution enriched with macronutrients (P, Mg and S)", and by the University of Warmia and Mazury in Olsztyn, Faculty of Agriculture and Forestry, Department of Agricultural and Environmental Chemistry (grant no. 30.610.003-110).

INTRODUCTION

Being one of the three major cereals, maize plays an important role in ensuring food safety for people and producing animal feeds (DeFries et al. 2015). It is distinguished by high yielding potential and versatile use. A great advantage of this crop is its ability to produce high yields in different environmental conditions. In 2020, the total maize cultivation area in Poland was over 1.42 million hectares (https://rejestrupraw.arimr.gov.pl/#).

Nitrogen fertilization is one of the ways to improve the yields of crops, and the availability of this element determines maize productivity (Zhu, Chen 2002, Liang et al. 2020). Maize grain yield depends on the intensity of photosynthesis, and a nitrogen deficit usually has a negative effect on the efficiency of this process (Olszewski et al. 2014). Compared with other anions, the concentration of phosphates in the soil solution is very small (Mollier, Pellerin 1999), and low temperatures after the emergence of plants additionally hinder the uptake of water and nutrients, especially phosphorus (Mozafar et al. 1993). Magnesium is easily leached, particularly from acid soils, and the uptake of Mg^{2+} by plant roots can be made more difficult because of the competition of other cations. A deficit of this element is becoming an increasingly significant factor that limits plant production (Gaj et al. 2018). Additional supply of N together with Mg may increase production, but the effectiveness of applied NPK fertilizers suffers considerably when sulphur is deficient (Tirupathi et al. 2016, Ariraman et al. 2020).).

Micronutrients play an important part in plant nutrition. Crops need small amounts of these elements, same as farm animals or humas (Gupta et al. 2008, Nuss, Tanumihardjo 2010). Measures taken to increase the accumulation of nutrients in grain include genetic improvements, conventional plant breeding and agronomic treatments (Welch, Graham 2002, Gu et al. 2015, Tuhy et al. 2015). Micronutrients also act as co-factors and participate in many metabolic pathways; furthermore, they are essential for the proper functioning of photosynthetic and respiratory processes (El-Mekser et al. 2014). Many plants are particularly sensitive to deficits of trace elements in soil. As for maize, a consequence of a deficit of micronutrients is the crop's lower yield (Salem, El-Gizawy 2012). Micronutrients such as Cu, Zn, Fe and Mn present in grain have a direct influence on the quality of food and fodder (Gupta et al. 2008).

A large increase in yield often leads to a decrease in the content of micronutrients in maize grain (Enakiev et al. 2018). This can be explained by the dilution effect, when greater yields mean a lower concentration of micronutrients per biomass unit. The aim of this experiment has been to evaluate the impact of fertilization with urea-ammonium nitrate (UAN) solution with added P, Mg or S on the content of micronutrients in maize grain and straw.

MATERIALS AND METHODS

Description of the experiment

The experiment was conducted in 2015-2017. It was set up on production fields owned by the Production and Experimental Enterprise located in Bałcyny (51.6667°N, 18.1667°E). The surface area of a plot for harvest was 450 m^2. In each year, the experiment was set up on lessivé soil formed from medium clay (WRB 2015). It had the following parameters: slightly acid reaction (pH in 1 mol dm^{-3} KCl ranged from 5.70 to 6.33), the C-org. content was between 12.5 and 1.32 g kg^{-1}, and the concentrations of available forms of P and K (by the Egner-Riehm method) and Mg (by the Schachtschabel method) were as follows: P – 97.8-135.3, K – 182.7-224.1 and Mg – 52.0-82.0, while the content of $S\text{-}SO_4^{2-}$ was within 4.0-14.0 mg kg^{-1}. The concentrations of available forms micronutrient were as follows: B – 0.31-0.48, Cu – 1.78-4.40, Zn – 4.18-6.85, Mn – 180.8-198.0 and Fe – 1550-1700 mg kg^{-1} (Ostrowska et al. 1991). The experiments were laid out in a random-block design with 4 replicates (Table 1).

Table 1

Design of the experiment

Number of object	Date of application	
	before sowing (100 kg N ha^{-1})	4–6 leaf phase (14-16 BBCH) (80 kg N ha^{-1})
I.*	control, no nitrogen fertilization	
II.*	ammonium nitrate	urea
III.*	UAN	urea
IV.*	UAN	UAN
V.*	UAN + S	UAN + Mg
VI.**	UAN + P(medium)	UAN + P(medium)
VII.***	UAN + P(starter)	UAN + S
VIII.***	UAN + P(starter)	UAN + Mg

* pre-sowing dose of phosphorus (37.36 kg P ha^{-1}) in the form of granulated fertilizer

** pre-sowing dose of phosphorus (4.18 kg P ha^{-1}) in the form of granulated fertilizer

*** pre-sowing fertilization with phosphorus in a liquid form

The following nitrogen fertilizers were applied in the experiment: UAN – 32%N, UAN+S – 26% N + 3% S, UAN+P (medium) – 26% N and 11% P_2O_5, UAN+P (starter) – 21% N and 18% P_2O_5, UAN+Mg – 20% N + 4% Mg.

The maize cultivar NK Borago (single hybrid), with large flex cobs, well filled with glassy flint kernels, was sown. It is an early variety (FAO 220) with excellent vernal vigour, recommended for cultivation on good soils, which warm up in the spring less rapidly (*Kukurydza* 2013). Plants of this maize cultivar are is also distinguished by good health.

In 2015 and 2016, maize was seeded in the last ten days of April, while in 2017 it was sown on 1 May, in the amount of 90,000 germinating kernels per 1 ha, in rows set 75 cm apart. In objects 2-8, nitrogen fertilization was applied in the quantity of 180 kg N ha^{-1}, split into two doses: 100 kg N ha^{-1} before sowing (BBCH 00) and 80 kg N ha^{-1} at the phase of 4-6 leaf (BBCH 14-16), in the forms defined in the design of the experiment. Before sowing, soil in objects 1-5 was enriched with 37.36 kg P ha^{-1} (as triple superphosphate). Soil in object 6, before sowing maize, was enriched with 4.18 kg P ha^{-1} in the solid form and 16.58 kg P ha^{-1} as UAN-P medium, while the remaining dose (16.58 kg P ha^{-1}) was applied as topdressing fertilization mainly in the form of UAN-P medium. In objects 7 and 8, the entire dose of phosphorus (37.36 kg P ha^{-1}) was applied in the liquid form (UAN+ P starter). All the objects were supplied 160.02 kg K ha^{-1} as 60% potassium salt before sowing the maize. At the 16-18 BBCH maize development phase, Insol Zn in a dose of 2 dm^3 ha^{-1} (100 g Zn ha^{-1}) was applied to maize leaves. Maize harvest took place in the last ten days of October in the first and second year of the experiment, being delayed until the second ten days of November in the last year due to heavy rainfalls.

Chemical analysis methods

During maize harvest, grain and straw samples were taken from each plot for chemical analyses. In the laboratory, the plant material was dried in the temp. of 60°C in a dryer with forced air circulation, ground (laboratory grinder Ika Werke M20), and wet mineralized (Büchi Speed Digester K-439) in a mixture of nitric (HNO_3) acid and chloric ($HClO_4$) acid (4:1 ratio) with the addition of hydrochloric acid (HCl). The content of Cu, Fe, Mn, Zn, was determined by atomic absorption spectrophotometry (AAS) on a Shimadzu AA-6800 apparatus (Ostrowska et al. 1991). To determine B content, plant material was dry mineralized (520°C) in the presence of calcium oxide (CaO), and the ash was dissolved in HCl (0.5 mol dm^{-3}). Boron content was determined colorimetrically on a Shimadzu UV – 1201 V apparatus with the use of azomethine-H (Benedycka, Rusek 1994). All contents of chemical elements are expressed in dry matter (temp. of drying 105°C).

Meteorological conditions

In the first and third year of the experiment, the emergence of maize plants proceeded during a period of relatively modest rainfalls (40% and 55% of the multi-year average rainfalls, respectively). The best conditions for plant emergence were noted in the second year of the study. During the second and third research year, the weather conditions in June, that is the time when maize plants go through vegetative development, ensured adequate moisture and the air temperature was close to the long-term average. However, during the first year, the atmospheric precipitations were much below the long-term mean (Table 2).

Table 2

Characteristics of the meteorological conditions during the experiment

Month	Average daily air temperature (°C)			Long-term average (1981-2010)	Rainfalls (mm)			Long-term average (1981-2010)	Selyaninov hydrothermal coefficient (K*)		
	2015	2016	2017		2015	2016	2017		2015	2016	2017
April	7.2	8.8	6.7	**7.7**	23.4	33.1	52.1	**29.8**	1.08	1.26	2.59
May	12.1	14.8	13.1	**13.2**	25.4	70.8	34.0	**62.3**	0.68	1.53	0.84
June	15.7	18.0	16.7	**15.8**	43.0	66.3	109.9	**72.9**	0.91	1.23	2.19
July	18.0	18.5	17.3	**18.3**	71.0	138.6	106.1	**81.2**	1.27	2.41	1.98
Aug	21.3	17.5	18.7	**17.7**	13.0	71.9	54.8	**70.6**	0.19	1.32	0.95
Sept	14.2	14.7	13.5	**13.0**	51.2	17.1	211.1	**56.2**	1.19	0.39	5.21
Oct	6.6	6.9	9.4	**8.1**	20.8	96.3	160.3	**51.2**	1.01	4.51	5.52

***** K: 0 - 0.5 – drought, 0.6 - 1.0 – dry weather, 1.1 - 2.0 – wet weather, > 2.1 – very wet weather

In the first year of the experiment, when the lowest atmospheric precipitations during the vernal plant growth were noted, July was also characterized by the lowest value of the Selyaninov hydrothermal coefficient (K = 1.27) compared to the two subsequent years, when it reached 2.41 and 1.98, respectively (Bac et al. 1998). The end of maize flowering and beginning of the milk maturity stage occurred in August. During the first year, this month was marked by a drought, when the Selyaninov coefficient was barely 0.19, which was due to high air temperatures and low rainfall. During the second and third year of the experiment, this coefficient in August reached 1.32 (humid) and 0.95 (dry weather).

In September, the mean daily temperature in 2015-2017 was approximately the same as the long-term one. In the first year of the study, the total atmospheric rainfall in September did not diverge from the average for 1981-2010, whereas the second year was dry (K = 0.39). September and October 2017 noted the record high rainfalls (K = 5.21 and 5.52, respectively).

Statistical analysis

The results underwent statistical processing by applying analysis of variance (ANOVA) in a Statistica 12® software package. Differences between the means were compared with the Tukey's test at significance p<0.05.

RESULTS AND DISCUSSION

The highest B content (3.26 mg kg^{-1} d.m.) was determined in the first year of the experiment, in grain of maize grown in treatments UAN+S/UAN+Mg and UAN+P(starter)/UAN+Mg (Table 3). In turn, the lowest

Table 3

Content of micronutrients in common maize grain

Number of object	B			Cu			Zn			Mn			Fe		
	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017
mg kg^{-1} d.m.															
I.	2.88^{gh*}	3.10^{ijk}	2.43^{bc}	2.04d-g	2.05^{dh}	1.85^{bc}	19.50^{d}	20.69^{hi}	17.18^{a}	4.20^{a}	5.30^{d}	4.66^{bc}	29.02^{p}	$19.11^{e\text{-}g}$	18.69^{de}
II.	3.02^{hij}	3.17^{jk}	2.58^{cde}	1.83^{bc}	$1.99^{c\text{-}g}$	$2.06^{d\text{-}h}$	20.57^{gh}	21.70^{l}	20.09^{ef}	4.74^{bc}	5.74^{e}	4.82^{c}	23.42^{o}	20.58^{jk}	$19.74^{g\text{-}i}$
III.	2.88^{gh}	3.47^{l}	2.14^{a}	$2.04^{d\text{-}g}$	$1.93^{b\text{-}f}$	2.12^{gh}	$20.24^{e\text{-}g}$	$20.14^{e\text{-}g}$	19.98^{e}	4.56^{b}	6.05^{f}	4.69^{bc}	22.66^{n}	22.35^{n}	$18.90^{d\text{-}f}$
IV.	3.02^{hij}	2.80^{fg}	2.37^{b}	2.34^{ij}	1.81^{b}	$1.93^{b\text{-}}$	19.40^{d}	21.21^{jk}	$20.42^{e\text{-}g}$	4.25^{a}	6.41^{h}	4.54^{b}	21.98^{mn}	$19.47^{f\text{-}h}$	20.19^{ij}
V.	3.26^{k}	3.17^{jk}	2.60^{cde}	$1.90^{b\text{-}e}$	$1.95^{b\text{-}f}$	$1.94^{b\text{-}f}$	19.19^{d}	21.34^{kl}	18.46^{c}	4.69^{bc}	6.33^{gh}	4.20^{a}	21.14^{kl}	18.40^{cd}	15.80^{a}
VI.	2.88^{gh}	2.66^{def}	2.51^{bcd}	$2.09^{f\text{-}h}$	$2.07^{e\text{-}h}$	$1.94^{b\text{-}f}$	21.03^{ijk}	$21.11^{i\text{-}k}$	17.82^{b}	4.56^{b}	6.04^{f}	4.59^{bc}	21.98^{mn}	20.01^{hij}	17.96^{c}
VII.	2.73^{efg}	2.99^{hi}	2.36^{b}	2.46^{j}	$1.90^{b\text{-}d}$	1.84^{bc}	20.81^{hij}	$21.07^{i\text{-}k}$	20.14^{efg}	4.69^{bc}	6.12^{fg}	4.62^{bc}	21.08^{kl}	16.64^{b}	$18.90^{d\text{-}f}$
VIII.	3.25^{k}	2.88^{gh}	2.51^{bcd}	2.21^{hi}	$2.04^{d\text{-}g}$	1.47^{a}	$20.23^{e\text{-}g}$	$20.47^{f\text{-}h}$	21.08^{ijk}	4.67^{bc}	6.00^{f}	4.53^{b}	21.53^{lm}	17.94^{c}	$18.60^{c\text{-}e}$
Average	2.99^{A}	3.03^{A}	2.44^{B}	2.11^{B}	1.97^{A}	1.89^{A}	20.12^{B}	20.96^{C}	19.40^{A}	4.55^{A}	6.00^{B}	4.58^{A}	22.85^{B}	19.31^{A}	18.60^{A}
Average for fertilization															
I.	2.80^{AB}			1.98^{A}			19.12^{C}			4.72^{A}			22.27^{D}		
II.	2.93^{AB}			1.96^{A}			20.79^{A}			5.10^{A}			21.25^{AD}		
III.	2.83^{AB}			2.03^{A}			20.12^{AB}			5.10^{A}			21.30^{AD}		
IV.	2.73^{AB}			2.02^{A}			20.34^{AB}			5.07^{A}			$20.55^{A\text{-}C}$		
V.	3.01^{B}			1.93^{A}			19.66^{BC}			5.07^{A}			18.44^{B}		
VI.	2.68^{A}			2.03^{A}			19.99^{AB}			5.06^{A}			$19.98^{A\text{-}C}$		
VII.	2.69^{A}			2.07^{A}			20.67^{A}			5.14^{A}			18.87^{BC}		
VIII.	2.88^{AB}			1.91^{A}			20.59^{A}			5.07^{A}			19.36^{BC}		

* data marked with same letters do not differ significantly at $p<0.05$; I-VIII – number of object see Table 1

amount of this element was in grain of maize fertilized with UAN/urea and harvested in the third year of the study. Significant differences occurred in the content of B in maize grain in the individual years. The highest B content (3.03 mg kg^{-1} d.m.) was in maize grain collected in the first year, whereas the smallest B amount was found in grain of maize grown during an excessively wet year 2017. The applied fertilization significantly differentiated the B content of grain. Significantly the lowest B concentration was in grain of maize fertilized before sowing and then by topdressing with UAN+P(medium) and UAN+S(starter)/UAN+S (2.68 and 2.69 mg kg^{-1} d.m., respectively). Significantly the highest content of this element was in grain of maize fertilized with UAN+S/UAN+Mg (3.01 mg kg^{-1} d.m.).

Significantly the least of Cu (1.47 mg kg^{-1} d.m.) was determined in grain of maize fertilized with UAN+P(starter)/UAN+Mg and harvested in 2017 (Table 3). Significantly the highest content of this element (2.46 mg Cu kg^{-1} d.m.) was in grain of maize from the UAN+P(starter)/UAN+S treatment in the first year of the experiment. The weather conditions in the individual years of the study significantly differentiated the Cu content in grain. The highest Cu amount (2.11 mg kg^{-1} d.m.) was found in grain harvested in the dry 2015 year, while the least of this element accumulated in 2017 (by 10.5% less than in 2015). No significant effect of the applied fertilizers on the Cu content in grain was determined.

Significantly the highest Zn content (21.70 mg kg^{-1} d.m.) was determined in the second year of the experiment, in grain of maize fertilized with solid nitrogen fertilizers (ammonium nitrate/urea), while the lowest Zn content was in grain of maize from the control treatment (Table 3). Same as for B and Cu, significantly the lowest amount of Zn (19.40 mg kg^{-1} d.m.) accumulated in grain of maize harvested in the wet year 2017. In turn, the highest concentration of this nutrient (20.96 mg kg^{-1} d.m.) was in grain collected in the second research year. Compared to the control (19.12 mg kg^{-1} d.m.), the applied fertilization increased the Zn content in grain by 2.8% (UAN+S/UAN+Mg fertilization) up to 8.7% (ammonium nitrate/urea).

The highest Mn concentration was found in grain of maize fertilized before sowing and then by topdressing with UAN or with UAN+S before sowing and UAN+Mg topdressing (6.41 and 6.33 mg kg^{-1} d. m. respectively) in the second year of the study (Table 3). The least Mn (4.20 mg kg^{-1} d.m.) was accumulated in grain of maize fertilized with nitrogen (control) in the first year. The rainfalls and temperatures during the maize growing season significantly differentiated the content of this nutrient in grain. Similarly to B and Zn, the significantly highest Mn content (6.00 g kg^{-1} d.m.) was determined in maize grain harvested in the second year, when it was almost 10% higher than in the other years. The tested fertilizers did not have a significant effect on the Mn content in maize grain.

The significantly highest Fe content (29.02 mg kg^{-1} d.m.) was noted in grain of maize from the control treatment (without nitrogen fertilization) in the first year of the experiment (Table 3). The least of this element

(15.80 mg kg^{-1} d.m.) was in the third year, in grain of maize fertilized with UAN+S/UAN+Mg. Drought and high temperatures prevailing in 2015 caused significantly the highest accumulation of Fe in maize grain (22.58 mg kg^{-1} d.m.). In the following years, with higher precipitations, the content of Fe in grain was significantly lower (by 15.5 and 18.5%, respectively) than in the first year. Compared to the control treatment (22.27 mg kg^{-1} d.m.), nitrogen fertilization caused a decrease in the Fe content in maize grain. The least of this element was contained in grain of maize fertilized with UAN+S/ UAN+Mg (15.80 mg kg^{-1} d.m.), where its content was by 29% lower than in the control maize grain.

Significantly the highest concentration of B (6.56 mg kg^{-1} d.m.) was determined in the first year of the experiment in straw of maize fertilized with UAN before sowing and with urea by topdressing (Table 4). The least of this element (2.97 mg kg^{-1} d.m.) was found in the second year of the study in straw of maize fertilized with UAN+P(starter)/UAN+S. Most B was noted in maize straw obtained in the first year of the experiment (5.61 mg kg^{-1} d.m.), being by 30.5 and 29.6% lower in the two subsequent years, respectively. The applied fertilization significantly modified the B content in maize straw. The lowest B content (4.02 mg kg^{-1} d.m.) was determined in maize fertilized with UAN+P(starter)/UAN+Mg, while the highest content of this element (4.87 mg kg^{-1} d.m.) was found in straw of maize fertilized solely with solid nitrogen fertilizers (ammonium nitrate/urea).

Significantly the highest concentration of Cu (6.66 mg kg^{-1} d.m.) was determined in straw of maize harvested in the second year of the study from the UAN+S/UAN+Mg treatment (Table 4). Significantly less Cu (3.05 mg kg^{-1} d.m.) was in the first year in straw of maize fertilized with UAN+P(starter)/ UAN+Mg and UAN+P(starter)/UAN+S in the third year (3.09 mg kg^{-1} d.m.). Similarly to maize grain, the Cu content in straw was significantly varied in the years of the study. Significantly the highest Cu content (5.43 mg kg^{-1} d.m.) was determined in straw of maize harvested in the second year, whereas the amount of Cu in straw in the other years was lower by 20.5 and 29.5%, respectively in 2015 and 2017. Considering the fertilization treatments, straw of maize fertilized with UAN+P(starter)/UAN+Mg and the control maize contained significantly the least Cu (3.93 and 4.11 mg kg^{-1} d.m., respectively). The highest content of this element was found in straw of maize fertilized exclusively with solid fertilizers or with UAN before sowing and urea in a topdressing application (5.06 and 5.01 mg kg^{-1} d.m., respectively).

Maize straw from the control and from the treatment fertilized with UAN+P(starter)/UAN+Mg in the first year of the experiment contained the least of Zn, namely 12.31 mg kg^{-1} d.m. (Table 4). Over 2.5-fold more of this element was accumulated in straw of maize from the treatment fertilized with UAN in the second year of the experiment. Same as in grain, the Zn content in maize straw varied in the years of the study. The highest Zn content (21.33 mg kg^{-1} d.m.) in maize straw was detected in the second year of the experiment, which was by 17.3% and 15.5% more than in the first and

Table 4

Content of micronutrients in common maize straw

Number of object	B			Cu			Zn			Mn			Fe		
	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017	2015	2016	2017
mg kg^{-1} d.m.															
I.	5.24^{h}	4.43^{f}	2.95^{a}	3.93^{e}	4.79^{h}	3.60^{cd}	12.31^{a}	15.67^{c}	12.61^{a}	33.83^{cd}	44.95^{g}	33.67^{ed}	144.86^{n}	96.08^{hi}	90.79^{fg}
II.	6.20^{j}	4.57^{fg}	3.84^{cd}	4.54^{g}	5.13^{i}	5.51^{jk}	23.95^{l}	31.10^{n}	25.51^{m}	75.55^{l}	105.87^{n}	53.18^{i}	168.81^{o}	78.53^{b}	98.88^{i}
III.	6.56^{k}	3.91^{d}	3.69^{c}	5.13^{i}	5.48^{j}	4.41^{fg}	20.17^{ij}	22.29^{k}	20.63^{j}	70.82^{k}	74.03^{l}	29.32^{b}	129.05^{l}	85.01^{de}	112.02^{k}
IV.	5.90^{i}	4.26^{e}	3.83^{cd}	4.80^{h}	5.01^{hi}	3.36^{b}	15.13^{c}	19.85^{hi}	18.99^{fg}	45.17^{g}	75.48^{l}	35.75^{de}	133.46^{m}	76.31^{ab}	98.39^{hi}
V.	5.31^{h}	3.84^{cd}	3.69^{c}	3.81^{de}	6.66^{l}	3.49^{bc}	15.53^{c}	17.46^{d}	15.20^{c}	37.25^{ef}	43.61^{g}	25.77^{a}	107.58^{j}	83.34^{d}	87.68^{ef}
VI.	5.24^{h}	3.91^{d}	3.25^{b}	4.19^{f}	5.49^{j}	3.58^{bc}	19.52^{gh}	25.01^{m}	14.47^{b}	49.86^{h}	81.49^{m}	39.80^{f}	129.63^{lm}	79.02^{bc}	82.51^{cd}
VII.	5.75^{i}	2.97^{a}	3.32^{b}	5.14^{i}	5.72^{k}	3.09^{a}	22.32^{k}	20.24^{ij}	18.67^{ef}	68.62^{jk}	54.97^{i}	34.16^{cd}	128.79^{l}	77.03^{b}	94.60^{gh}
VIII.	4.72^{g}	3.32^{b}	4.20^{e}	3.05^{a}	5.13^{i}	3.62^{cd}	12.31^{a}	19.01^{fg}	18.21^{e}	31.80^{bc}	66.25^{j}	31.58^{bc}	107.13^{j}	72.88^{a}	96.26^{hi}
Average	5.61^{C}	3.90^{B}	3.59^{A}	4.32^{B}	5.43^{C}	3.83^{A}	17.65^{A}	21.33^{B}	18.04^{A}	51.61^{B}	68.33^{C}	35.40^{A}	131.17^{C}	81.03^{A}	95.14^{B}
Average for fertilization															
I.	4.20^{AB}			4.11^{A}			13.53^{D}			37.49^{B}			110.58^{AB}		
II.	4.87^{B}			5.06^{B}			26.85^{E}			78.20^{D}			115.41^{B}		
III.	4.72^{AB}			5.01^{B}			21.03^{B}			58.06^{A}			108.70^{AB}		
IV.	4.66^{AB}			4.39^{AB}			17.99^{AC}			52.13^{AC}			102.72^{AB}		
V.	4.28^{AB}			4.65^{AB}			16.06^{A}			35.54^{B}			92.86^{A}		
VI.	4.13^{AB}			4.42^{AB}			19.67^{BC}			57.05^{A}			97.05^{AB}		
VII.	4.02^{A}			4.65^{AB}			20.41^{B}			52.58^{AC}			100.14^{AB}		
VIII.	4.08^{AB}			3.93^{A}			16.51^{A}			43.21^{BC}			92.09^{A}		

* data marked with same letters do not differ significantly at p<0.05; I-VIII – number of object, see Table 1

third year, respectively. Fertilization significantly increased the Zn content in maize straw. Same as in grain, the least Zn (13.53 mg kg^{-1} d.m.) was in maize straw harvested from the control. The highest Zn content was found in straw of maize fertilized with solid nitrogen fertilizers (ammonium nitrate/urea), which contained twice as much of this element as straw from the control maize.

Manganese is an element that is much more abundant in straw than in grain. Significantly the highest Mn content (105.87 mg kg^{-1} d.m.) accumulated in straw of maize fertilized with solid nitrogen fertilizers (ammonium nitrate/urea) and grown in the second year (Table 4). The least Mn (25.77 mg kg^{-1} d.m.) accumulated in straw of maize fertilized with UAN+S/UAN+Mg and in the 3rd year of the study. Same as in grain, most Mn in straw (68.33 mg kg^{-1} d.m.) was determined in the 2nd year, while the straw content of this element was by as much as 46.2% lower in the last year of the experiment. Nitrogen fertilization generally increased the Mn content of maize straw. It was only in straw of maize fertilized with UAN+S/UAN+Mg that the content of this nutrient was similar to that in the control treatment straw. Fertilization with solid nitrogen fertilizers (ammonium nitrate/urea) resulted in the highest straw content of Mn, over two-fold higher than determined in straw of plants from the control treatment and the one fertilized with UAN+S/UAN+Mg.

Similarly to Mn, a higher content of Fe was determined in straw than in grain. The highest Fe content in straw (168.81 mg kg^{-1} d.m.) appeared in the first year of the study after fertilizing maize plants with ammonium nitrate/urea (Table 4). The least of this nutrient (72.88 mg kg^{-1} d.m.) accumulated in the second year in straw of maize fertilized with UAN+P(starter)/UAN+Mg. Like in grain, most Fe (131.17 mg kg^{-1} d.m.) accumulated in straw in the first year. In the subsequent years, the Fe concentration in straw was significantly lower, less by 38.2 in the second and by 27.5% in the third year. On average per fertilization treatment, significantly most Fe (115.41 mg kg^{-1} d.m.) accumulated in straw of the maize fertilized with solid nitrogen fertilizers (ammonium nitrate/urea). The least of this element was in straw from the plots fertilized with UAN+S/UAN+Mg and UAN+P(starter)/UAN+Mg (92.86 and 92.09 mg kg^{-1} d.m., respectively).

In this study, the content of B in maize grain (2.14 - 3.26 mg B kg^{-1} d.m.) was approximately the same as its range (1.44 - 3.20 mg kg^{-1}) given by Wróbel and Korzeniowska (2007) or Mickiewicz and Wróbel (2008). However, concentrations of B determined in straw in the course of our experiment tended to be lower than provided by Mickiewicz and Wróbel (2008) (5.44 to 7.84 mg kg^{-1}). In a study by Wróbel and Mickiewicz (2009), boron fertilization significantly increased the yields of maize grain but did not increase the concentration of this element in grain.

In our research, the content of Cu in maize grain was similar to values determined by Meller and Bilenda (2013), where grain of maize fertilized with biomass ash contained between 1.99 and 2.97 mg Cu kg^{-1}. Stanisławska-

-Głubiak et al. (2012) reported that the content of Cu in maize green mass varied from 8.50 to 9.50 mg kg^{-1}. Meller and Jarnuszewski (2015), who studied the chemical composition of plants grown on post-bog soils fertilized with NPK + Zn or Cu, concluded that the content of Cu in maize green mass ranged from 1.86 to 7.78 mg kg^{-1}.

In this study, the content of Zn in maize grain and straw was similar to that given in the literature. Depending on the type of soil and soil cultivation methods, the Zn content in maize grain varied from 13.90 to 27.29 mg kg^{-1} (Wróbel, Korzeniowska 2007, Mickiewicz, Wróbel 2008). When biomass incineration ash is used for agricultural purposes such as fertilization, the Zn content in maize grain has been determined at 3.21 to 37.70 mg Zn kg^{-1} (Meller, Bilenda 2013). In turn, a study by Wieremiej (2016) showed that the Zn content in maize grain ranged from 21.79 to 31.60 mg kg^{-1}. More Zn accumulated in grain of maize fertilized with mineral than with organic fertilizers. Depending on the P and K fertilization levels, the Zn content in maize grain varied from 13.30 to 16.32 mg kg^{-1} (Bąk et al. 2016). As for the vegetative organs of maize, most Zn was accumulated by cob cores (17.11 - 28.00 mg kg^{-1}) and stems (14.10 - 19.14 mg kg^{-1}), while cob cover leaves contained between 5.07 and 7.24 mg Zn kg^{-1}, and the other leaves had 5.02 to 6.45 mg Zn kg^{-1}. Depending on the type and method of soil cultivation and applied fertilization, the content of Zn in maize straw ranged from 17.60 to 79.30 mg kg^{-1} (Wróbel, Korzeniowska 2007, Wieremiej 2016).

In grain of maize fertilized with biomass ash, the content of Mn varied from 9.50 to 10.90 mg kg^{-1}, whereas in green mass the amounts of Mn ranged from 28.2 to 41.4 mg kg^{-1} (Meller, Bilenda 2013). A several-fold higher amount of Mn (712 - 1225 mg kg^{-1}) in maize green mass was determined by Stanisławska-Glubiak et al. (2012). An addition of sulphur to phosphate rock (phosphate-sulphur fertilizers) caused a considerable increase in the content of Mn in plant tissues. In turn, Meller and Jarnuszewski (2015) maintained that the content of Mn depended on the type of soil on which maize grew. Green mass of maize grown on muck soil taken from gley soil contained 6.13 mg Mn kg^{-1}, while the Mn content in maize green mass obtained on muck taken from organic soil reached 13.0 mg kg^{-1}.

Compared with the literature data, the Fe content in maize grain determined in our experiment was relatively small. Meller and Bilenda (2013) showed that fertilization of maize with biomass ash had a weak influence on the Fe content in grain. In their study, maize grain from the control treatment had 59.4 mg Fe kg^{-1}, while that yielded by maize fertilized with ash contained from 51.0 to 63.8 mg Fe kg^{-1}. Biomass ash had a stronger effect on the Fe content of maize green mass, raising it by over 40% in comparison with the control plants. In the experiment conducted by Wieremiej (2016), the lowest Fe concentration (18.42 mg kg^{-1}) was found in grain of maize grown without fertilization, while the highest one (113.6 mg kg^{-1}) was in grain of maize fertilized with layer hen manure. As for straw, the least Fe (211.3 mg kg^{-1}) was in maize fertilized with NPK mineral fertilizers, while the highest Fe content in straw (794.5 mg kg^{-1}) accumulated after fertilization with fermented bovine manure.

Guo et al. (2020) concluded that an adequate dose of N (120-180 kg N ha^{-1}) could increase concentrations of Fe and Mn in contemporary cultivars of maize, without compromising grain yields. In turn, higher N doses decrease concentrations of Cu and Zn in maize grain. It is therefore necessary to design an optimal nitrogen management strategy so as to enrich maize grain with essential elements while maintaining high yields of grain produced by modern cultivars of this crop. According to Losak et al. (2011), nitrogen fertilization applied to maize on highly fertile soils with high pH did not affect grain yield, nor did it depress the uptake and concentrations of micronutrients in maize grain and straw. The content of Cu, Fe, Mn and Zn in phytomass as well as the Fe:Zn and Fe:Mn ratios were adequate for maize plants.

Among micronutrients accumulated in aerial mass, maize accumulates the highest quantities of Fe and Zn, but lower amounts of Mn and Cu (Losak et al. 2011). Application of fertilizers containing micronutrients (especially Zn and Fe) in maize cultivation should be recommended if their levels in soil or plants are low.

Significantly the highest removal of B, Cu, Zn, Mn and Fe with yield of aerial biomass of maize was observed in 2016 (93.58, 105.57, 565.5, 1126.0 and 1457 g ha^{-1}, respectively), when the course of meteorological conditions ensured the highest grain and straw yields (Figure 1). In the first and in the third year of the study, the removal of B was by over 40% lower. The removal of Cu was lower by as much as 60% in 2015 and 54% in 2017. The removal of Zn was 1.7-fold lower in 2017 and as much as 2.3-fold lower in 2016. The removal of Mn in the first and third year was over three-fold lower than in 2016 (353.6 and 328.2 g ha^{-1}, respectively). Significantly less Fe (940.0 g Fe ha^{-1}) was taken up by maize in the third year of our experiment, when the growing season was excessively wet.

The tested fertilization did not have a significant effect on the removal of B, Cu and Fe with the yield of maize aerial mass (Figure 2). However, a tendency for higher uptake of these nutrients occurred under the influence of fertilization. The removal of B and Cu with the yields of maize grain and straw was 58.44 and 52.40 g ha^{-1}, respectively. The highest uptake of these elements (75.66 and 71.13 g ha^{-1}, respectively) by maize was determined for the treatment fertilized with ammonium nitrate/urea. Also, the highest Fe removal with maize yield (1242 g ha^{-1}) was observed after fertilization with solid nitrogen fertilizers (ammonium nitrate/urea). Maize fertilized with UAN+P(medium)/UAN+P(medium) or UAN+S/UAN+Mg absorbed by about 20% less of this element. It was only in the case of Zn and Mn that fertilization differentiated their removal. The least of these elements was determined in aerial mass of the control maize (262.2 and 386.4 g ha^{-1} respectively for Zn and Mn). Same as for other elements, significantly most Zn (485.4 g ha^{-1}) and Mn (930.8 g ha^{-1}) was taken up by maize fertilized with ammonium nitrate/urea.

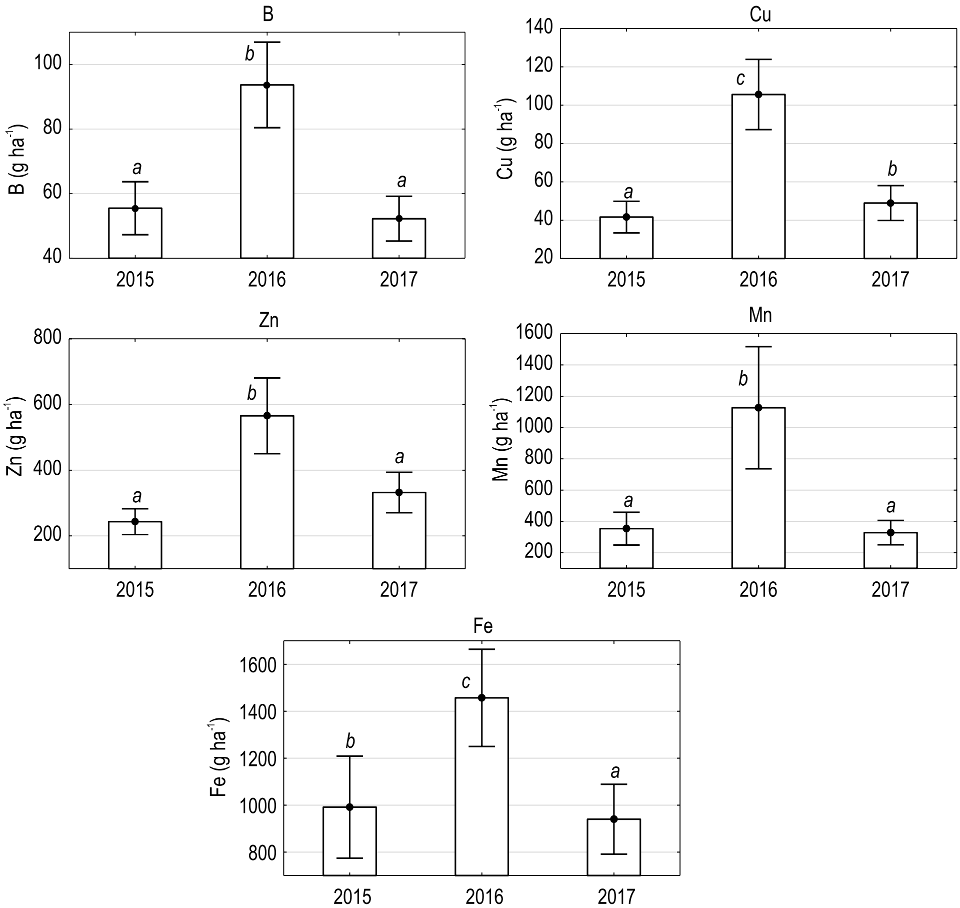

Fig. 1. Removal of micronutrients (mean ± standard deviation) with yield of maize aerial mass in each year of the experiment (data marked with same letters do not differ significantly at p<0.05

A significantly lower unit uptake of B (6,59 g t^{-1}) by maize was noted when the UAN+P(starter)/UAN+S fertilization variant was applied (Table 5). The lowest unit uptake of this element (8.34 g t^{-1}) occurred in the control treatment. Significantly less B (5.47 g**)** for production of 1 tonne of grain with an adequate amount of straw was take up by maize grown in the conditions of excessive moisture in the third year of the study, and most of this element (8.53 g t^{-1}) was accumulated by maize grown in the first year, which was characterized by the lowest amounts of rainfall and lowest maize yields.

Maize absorbed between 6.47 and 7.35 g t^{-1} Cu to produce 1 tonne of grain and an adequate amount of straw. The tested fertilization did not have a significant effect on the unit uptake of this nutrient. However, there was an observable tendency for the highest Cu unit uptake in the ammonium nitrate/urea treatment, and for the lowest one in the treatment fertilized with UAN+P

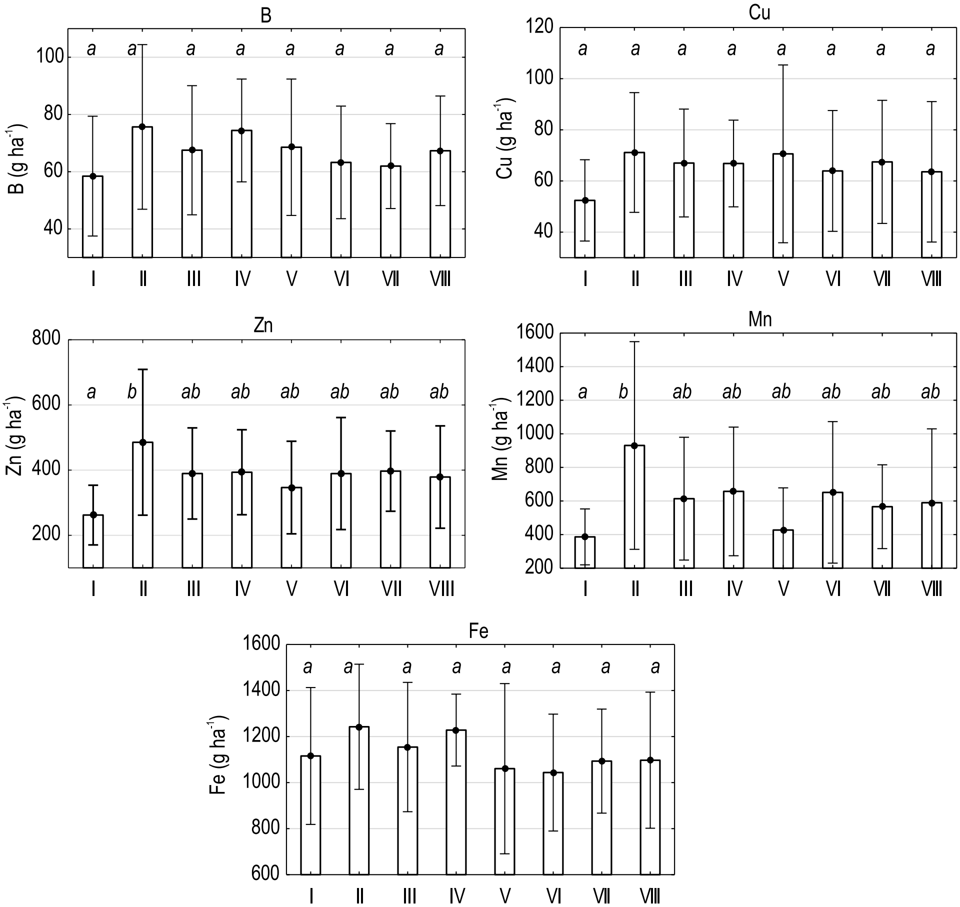

Fig. 2. Removal of micronutrients (mean ± standard deviation) with yield of maize aerial mass depending on fertilization (mean ± standard error; data marked with same letters do not differ significantly at p<0.05; I-VIII – number of object, see Table 1)

(medium) before sowing and by topdressing. Significantly the highest unit uptake of Cu (9.40 g t^{-1}) occurred in the conditions enabling the highest grain and straw yields, i.e. in 2016. The lowest unit uptake of this element (5.13 g t^{-1}) took place in the third year, which had abundant rainfalls.

Significantly the least Zn per yield unit (36.51 g t^{-1}) was accumulated by the control maize. Fertilization improved the unit uptake of Zn, but it was only the maize fertilized with ammonium nitrate/urea that absorbed significantly the most (50.17 g t^{-1}) of this nutrient. Significantly the highest unit Zn uptake (50.20 g t^{-1}) occurred in the conditions enabling the acquisition of the highest grain and straw yield, i.e. in the second year of the experiment. In the other two years, the unit uptake of Zn was around 30% lower.

Significantly the lowest unit uptake of Mn (44.61 g t^{-1}) was determined in maize from the UAN+S/UAN+Mg treatment, while the highest (93.64 g t^{-1})

Table 5

Uptake of micronutrients by maize per 1 tonne of grain with an adequate amount of straw (g t^{-1})

Specification	B	Cu	Zn	Mn	Fe
Average for fertilization					
Control	8.34^{b}	7.29^{a}	36.51^{a}	53.12^{ab}	163.98^{b}
Amonium nitrate/urea	8.08^{ab}	7.35^{a}	50.17^{b}	93.64^{b}	138.03^{ab}
UAN/urea	7.24^{ab}	6.96^{a}	40.78^{ab}	62.9^{ab}	123.32^{ab}
UAN/UAN	7.99^{ab}	7.03^{a}	40.31^{ab}	65.53^{ab}	134.33^{ab}
UAN+S/UAN+Mg	7.52^{ab}	7.23^{a}	36.90^{a}	44.61^{a}	115.61^{a}
UAN+P(medium)/UAN+P(medium)	6.66^{a}	6.47^{a}	39.87^{ab}	63.93^{ab}	111.61^{a}
RSM+P(starter)/RSM+S	6.59^{a}	6.92^{a}	41.18^{ab}	58.65^{ab}	116.22^{a}
UAN+P(starter)/UAN+Mg	7.29^{ab}	6.51^{a}	39.47^{ab}	58.15^{ab}	118.53^{a}
Average for years of study					
2015	8.53^{B}	6.37^{B}	37.11^{A}	53.79^{B}	153.61^{C}
2016	8.39^{B}	9.40^{C}	50.20^{B}	99.49^{C}	130.90^{B}
2017	5.47^{A}	5.13^{A}	34.64^{A}	34.42^{A}	98.60^{A}

[*] data marked with same letters do not differ significantly at $p<0.05$

appeared after the application of solid nitrogen fertilizers (ammonium nitrate/urea). The highest unit Mn uptake (99.49 g t^{-1}) by maize was recorded in the second year of the study, being nearly three-fold lower in the third year. The least Fe (111.61 g t^{-1}) per 1 tonne of grain with an adequate amount of straw was absorbed by maize fertilized before sowing and by top-dressing with UAN+P(medium). In turn, the highest unit uptake of this element (163.98 g t^{-1}) was found in the control. The highest unit uptake of Fe (153.61 t^{-1}) took place in the first year of the experiment, when a large rainfall deficit occurred and the yields of grain and straw were the lowest. In turn, the lowest unit uptake of Fe (98.60 g t^{-1}) was noted in the third year, with abundant rainfalls.

The contribution of grain to the accumulation of micronutrients varied between the years (Figure 3). The lowest share of grain in the accumulation of B was determined in the hot and dry year 2015 (35%), while the highest one (44%) was in the excessively wet and cold year 2017. The share of grain in Cu accumulation ranged from 21% (in the second year) to 37% (in the third year). Significantly the highest share of grain in Zn accumulation was noted in the third year (56%) and the lowest (42%) was in the second year. Same as for Cu and Zn, the lowest contribution of grain to the accumulation of Mn (around 6%) was in the second year, whereas in the first and third year it reached 9 and 13%, respectively. The share of maize grain in the accumulation of Fe ranged from 15 to 19%. The least of this element was accumulated by grain in the first and second year, while its accumulation by grain was significantly higher in the third year.

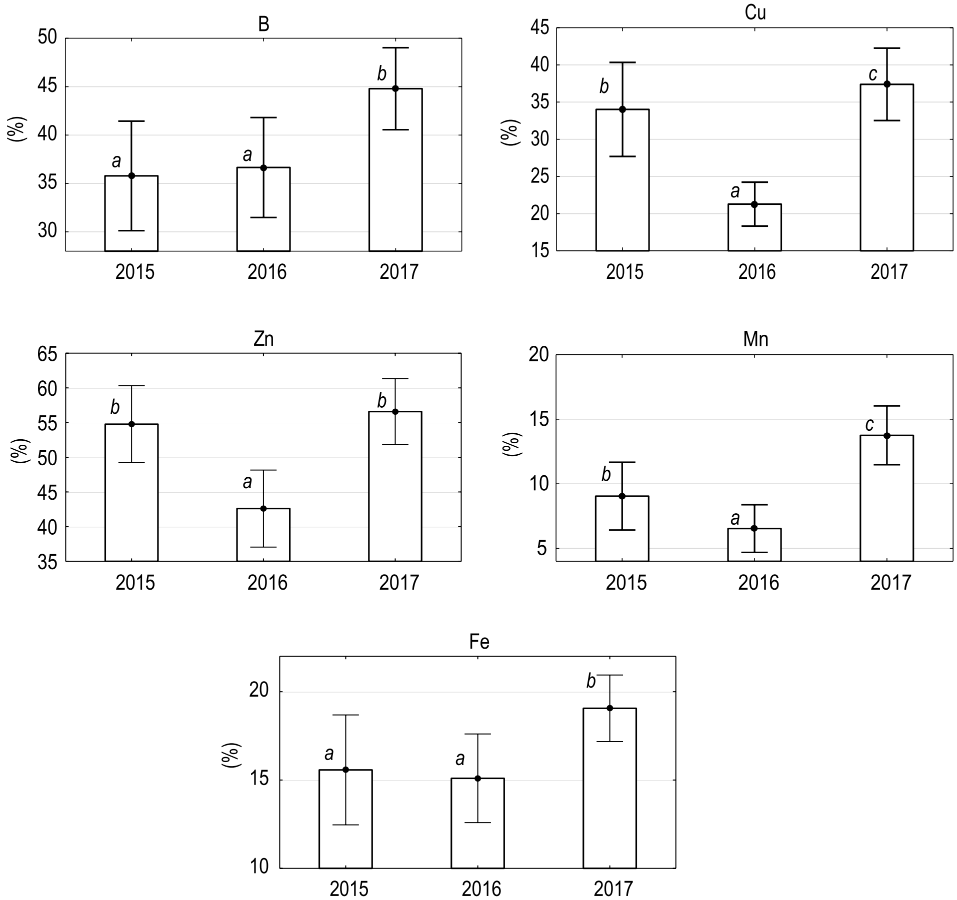

Fig. 3. Contribution of maize grain (mean ± standard error) to accumulation of micronutrients in each year of the study (data marked with same letters do not differ significantly at $p<0.05$)

The applied fertilization did not have a significant effect on the contribution of grain to the accumulation of B and Cu (Figure 4). The share of grain in B accumulation by maize ranged from 35% (UAN before sowing and in a topdressing application) to 42% (UAN(medium) applied pre-sowing and by topdressing). The contribution of grain to Cu accumulation varied from 28% (ammonium nitrate/urea) to 34% (pre-sowing and topdressing with UAN(medium)). Significantly the lowest share of grain in the accumulation of Zn (about 44%) was obtained after fertilizing maize with ammonium nitrate/urea. On the other hand, significantly the most of this nutrient (54%) was accumulated by grain of maize fertilized with UAN+P(starter)/UAN+Mg. Grain of maize fertilized with UAN+S/UAN+Mg accumulated significantly most Mn (13%). Significantly the lowest contribution of grain to the accumulation of this element (7%) was observed when maize was fertilized with ammonium nitrate/urea. Significantly the lowest (15%) share of maize grain

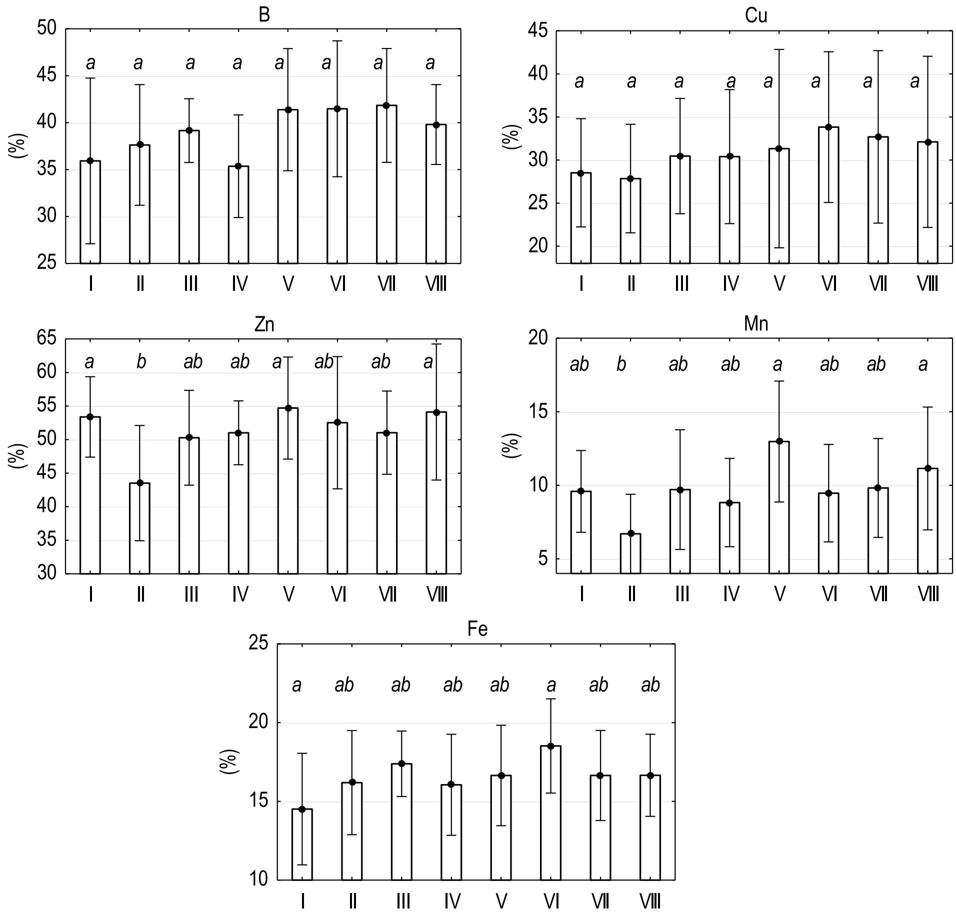

Fig. 4. Contribution of maize grain (mean ± standard error) to accumulation of micronutrients depending on fertilization (data marked with same letters do not differ significantly at $p<0.05$; I-VIII – number of object, see Table 1)

in Fe accumulation was determined in the control treatment, while significantly the most of this nutrient (17%) was accumulated by grain of maize fertilized pre-sowing and topdressing with UAN(medium).

According to Borges et al. (2009), the accumulation of micronutrients in maize aerial biomass follows this order of amounts: Zn > Mn > Cu > B. To produce one tonne of grain, maize needs: 0.9 g B, 19 to 20 g Cu, 42 to 46 g Mn and 100 to 194 g Zn. The removal of Zn with maize yield ranged from 308.2 g ha^{-1} (NPK fertilization) to 975.1 g ha^{-1} after the application of fermented bovine manure (Wieremiej 2016). The Fe removal rate by maize fertilized with fresh manure from broiler chickens was 994.4 g ha^{-1}, and as much as 8013 g Fe ha^{-1} when the plant was fertilized with fermented cattle manure.

The unit uptake of B determined in this study was much lower than reported by Grzebisz and Gaj (2007). Those authors demonstrated that maize could take up as much as 20 g B t^{-1} for producing 1 tonne of grain and an adequate amount of straw. However, the unit uptake of Zn determined in our experiment was similar to values given by other researchers. Depending on the volume of yields, Grzebisz and Gaj (2007) determined the Zn uptake by maize at 40 to 50 g t^{-1}. In another study, by Wieremiej (2016), the unit uptake of this nutrient by maize varied from 55.18 to 119.5 g t^{-1} depending on the applied fertilization. Wrońska et al. (2007) reported that the unit uptake of this nutrient by maize ranged from 49.62 to 51.44 g t^{-1}, and a dose of nitrogen or the time of Zn application and its doses had little effect on the Zn uptake. Wieremiej (2016), while investigating the effect of natural fertilizers on the unit uptake of Fe by maize, concluded that it varied from 210 (fertilization with fresh hen manure) to 803.5 g t^{-1} (fertilization with fermented bovine manure). These values are much higher than the ones established in our experiment.

In a study carried out by Bąk and Gaj (2016), depending on the level of phosphorus and potassium fertilization, the contribution of maize grain to the accumulation of Zn varied from 51.7 to 57.3%. According to Wieremiej (2016), the share of maize grain in the accumulation of this element varied from 23.6% (fertilization with fermented bovine manure) to 41.6% (fertilization with layer hen manure). According to this author, fertilization could also have affected the contribution of grain to Fe accumulation, namely grain from maize grown without fertilization accumulated 5.06% of this element, compared to as much as 29.7% when maize plants were NPK fertilized.

CONCLUSIONS

The content of micronutrients in maize grain was differentiated more by years of the study than by the applied fertilization. The highest Zn, Mn and B content was determined in grain harvested in the second year, when rainfalls slightly exceeded the long-term average. When there was a deficit of precipitations, in the first year, grain contained the highest levels of Cu and Fe. The tested nitrogen fertilizers did not have an effect on the grain content of copper and manganese. In response to nitrogen fertilization, the content of B and Fe in grain tended to decrease. Same as in maize grain, the content of micronutrients in straw depended on the year of cultivation, and the relationships were likewise similar. The concentrations of B, Cu, Zn, Mn and Fe were more highly differentiated by the applied fertilization in straw than in grain.

Significantly the highest B, Cu, Zn, Mn and Fe amounts were removed with the aerial mass yield of maize in 2016, that is a year when meteorological conditions were favourable for the cultivation of this crop. The tested fertilization did not have a significant effect on the removal of B, Cu and Fe with yield of aerial biomass, but significantly more Zn and Mn were accumulated by maize fertilized with ammonium nitrate and urea. The unit uptake of micronutrients to produce 1 tonne of grain was modified to a larger extent by the atmospheric conditions than by the applied fertilization.

The contribution of grain to the accumulation of micronutrients was significantly varied in the three years of the experiment, and equalled: B – from 35 to 44%, Cu – from 28 to 34%, Zn – from 42 to 52%, Mn – from 7 to 13% and Fe – from 15 to 17%.

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