IONIC EQUILIBRIUM IN MAIZE GRAIN DEPENDING ON THE FERTILISATION AND SOIL TYPE

RÓWNOWAGA JONOWA W ZIARNIE KUKURYDZY W ZALEŻNOŚCI OD NAWOŻENIA ORAZ TYPU GLEBY

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ABSTRACT

The research was performed over 2004-2009 based on the two-factor micro-plot experiment located at Wierzchucinek. Maize grown for grain in monoculture constituted the test crop. The aim of the present paper was to determine the effect of a varied sulphur fertilisation and Basfoliar 36 Extra as well as the soil type on the yield size and the ionic equilibrium of 'LG 2244' cultivar maize grain. The mean contents of cations in grain varied considerably and could be classified as follows: Mg >K >Ca > Na. Consequently, those contents, in general resulted in the narrowing of the value of ratios K/(Ca+Mg), Ca/Mg and K/Mg, and widening of the value of ratios K/Ca and K/Na. The interaction of the factors investigated differentiated the value of ratio K:Mg; one of the essential ionic ratios determining the quality of crops allocated to animal feed.

Key words: chemical composition, ionic equilibrium,maize grain, soil type, sulphur fertilisation

STRESZCZENIE

Badania prowadzono w latach 2004-2009 w oparciu o dwuczynnikowe doświadczenie mikropoletkowe zlokalizowane w Wierzchucinku Rośliną testową była kukurydza uprawiana na ziarno w monokulturze. Celem niniejszej pracy było określenie wpływu zróżnicowanego nawożenia siarką i Basfoliarem 36 Extra oraz typu gleby na wielkość plonu i równowagę jonową ziarna kukurydzy odmiany LG 2244. Średnie zawartości kationów w ziarnie były znacznie zróżnicowane i można uszeregować je w następującej kolejności: Mg >K >Ca > Na. Zawartości te w konsekwencji spowodowały na ogół zawężenie wartości stosunków K/(Ca+Mg), Ca/Mg i K/Mg, natomiast rozszerzenie wartości stosunków K/Ca i K/Na. Współdziałanie badanych czynników różnicowało wartość stosunku K/Mg - jednego z ważniejszych stosunków jonowych decydującego o jakości roślin przeznaczonych na paszę.

Słowa kluczowe: nawożenie siarką, równowaga jonowa, skład chemiczny, typ gleby, ziarno kukurydzy

STRESZCZENIE ROZSZERZONE

W produkcji paszowej kukurydzę można przetwarzać na kiszonkę z całych roślin, ziarna, oraz kolb. O jakości przydatności roślin jako surowca w przemyśle produkcyjnym decyduje nie tylko jej skład chemiczny, ale również równowaga jonowa (Niewczas, Mitek, 2010)
W związku z powyższym w latach 2004-2009 w oparciu o dwuczynnikowe doświadczenie mikropoletkowe przeprowadzono badania, których celem było określenie wpływu zróżnicowanego nawożenia siarką (20 i 40 kg S·ha^{-1}) i Basfoliarem 36 Extra oraz typu gleby(czarnoziem, gleba płowa, gleba bielicowa, czarna ziemia) na wielkość plonu i równowagę jonową ziarna kukurydzy. Obiektami pierwszego czynnika były cztery gleby (n=4: czarnoziem, gleba płowa, gleba bielicowa i czarna ziemia) różniącymi się właściwościami fizykochemicznymi, którymi zgodnie z ich profilami genetycznymi napełniono betonowe cembry. Drugim czynnikiem (n=5) było zróżnicowane nawożenie siarką i Basfoliarem 36 Extra (B): 20 kg S·ha^{-1} – S_1, 40 kg S·ha^{-1} – S_2, 20 kg S·ha^{-1} + Basfoliarem 36 Extra (S_1+B), 40 kg S·ha^{-1} +Basfoliar 36 Extra(S_2 +B) oraz obiekt bez nawożenia siarką i Basfoliarem 36 Extra (kontrola). Na podstawie zasobności gleb, pobrania jednostkowego i spodziewanego plonu ustalono poziom nawożenia mineralnego określony jako RBF (ang. Recommended Balanced Fertilization), który odpowiadał optymalnej dawce azotu, fosforu i potasu wynoszącej odpowiednio:120 kg·N·ha^{-1}, 80 kg·P_2O_5·ha^{-1} i 160 kg K_2O·ha^{-1}. Siarkę zastosowano doglebowo w postaci siarczanu (VI) sodu przed siewem kukurydzy, Basfoliar 36 Extra, płynny nawóz azotowy (36,3% N) z wysoką zawartością magnezu (4,3%) i mikroelementami (Mn – 1.35%, Cu – 0.27%, B – 0.027% Zn 0.013%, Mo – 0.0067%) stosowano dolistnie w fazie piątego liścia, łącząc ten zabieg z dokarmianiem roślin roztworem mocznika (20 kg N·ha^{-1}). W 2009 roku zebrano plon ziarna kukurydzy i oznaczono w nim podstawowy skład chemiczny (K, P, Mg, Ca, Na) oraz obliczono wartości stosunków jonowych i wagowych. Uzyskane wyniki poddano analizie statystycznej i obliczono współczynniki korelacji prostej oraz regresji liniowej. Stwierdzono, że typ gleby niezależnie od zastosowanego nawożenia istotnie determinował zawartości fosforu, potasu i magnezu w ziarnie kukurydzy, średnio istotnie najwyższe zawartości stwierdzono w ziarnie uprawianym na czarnej ziemi. Natomiast zastosowane nawożenie istotnie modyfikowało tylko zawartości fosforu i magnezu w ziarnie kukurydzy. Zastosowane nawożenie siarką oraz siarką łącznie z Basfoliarem 36Extra na tle NPK wpływało na ogół na rozszerzenie wartości stosunków K/(Ca+Mg i K:Mg w ziarnie kukurydzy w stosunku do obiektu gdzie stosowano wyłącznie NPK. Średnie zawartości kationów w ziarnie kukurydzy były znacznie zróżnicowane i można uszeregować je w następującej kolejności: Mg >K >Ca> Na. Zawartości te w konsekwencji spowodowały na ogół zawężenie wartości stosunków K/ (Ca+Mg), Ca/Mg i K/Mg, natomiast rozszerzenie stosunków K/Ca i K/Na. Składniki mineralne (K, Ca, Mg, Na i P) spełniają istotną rolę w żywieniu kukurydzy. Potas wykazuje antagonistyczne działanie z kationami wapnia, magnezu oraz sodu, nadmierne jego ilości w glebie a tym samym w roślinie prowadzą do naruszenia równowagi jonowej na skutek obniżenia zawartości sodu, wapnia i magnezu, efektem czego jest pogorszenie jakości roślin. Potwierdzeniem tego faktu jest wysoka zależność pomiędzy zawartością K a zawartością magnezu w ziarnie kukurydzy, gdzie współczynnik wynosił r=0.74 Można obliczyć, że wzrost zawartości magnezu w ziarnie kukurydzy o

0.2 jednostki (0.2 mmol·kg^{-1}) spowodował porównywalny przyrost zawartości K o: 0.44 mmol·kg^{-1} g·kg^{-1}.

INTRODUCTION

In animal feed production the maize can be processed into silage from entire plants, grain, and kolb. The grain of that crop constitutes a high-energy animal feed, it can be applied as basic animal feed and as a supplementary feed, especially in the nutrition of poultry, fattening pigs, cattle and sheep. The quality and the applicability of maize as raw material in the production industry are determined not only by its chemical composition but also the ionic equilibrium (Janukowicz, 2007, Krzywy, et al., 2001, Krzywy, et al., 2002).
With that in mind, research has been performed to determine the effect of a varied sulphur fertilisation (20 and 40 kg S·ha^{-1}) and Basfoliar 36 Extra and the soil type (Haplic Phaeozems, Orthic Luvisols, Orthic Podzols, Mollic Gleysols) on the yield size and the ionic equilibrium of the maize grain.

MATERIAL AND METHODS

The research was performed over 2004-2009 drawing on the two-factor microplot experiment located at the Experiment Station of the University of Technology and Life Sciences at Wierzchucinek in the vicinity of Bydgoszcz (53^{o}26' N, 17^{o}79' E), made in concrete containers, 0.8 m^{2} each, filled with four soils (Haplic Phaeozems, Orthic Luvisols, Orthic Podzols, Mollic Gleysols) sampled from production fields of the Pomorze and Kujawy region, showing different physicochemical properties (Table 1).

Table 1 Physicochemical properties of soils prior to the establishment of the field experiment (2004)
Tabela Właściwości fizykochemiczne badanych gleb przed założeniem eksperymentu

Parameter Parametr			Soil type – Typ gleby			
			Haplic Phaeozems	Orthic Luvisols	Orthic Podzols	Mollic Gleysols
pH_{KCl}		–	6.70	5.60	5.30	6.50
Hh		mmol(+)·kg^{-1}	7.20	23.50	28.40	6.80
$C_{org.}$		g·kg^{-1}	15.6	6.2	7.7	13.2
N_{total}		g·kg^{-1}	1.44	0.46	0.88	1.39
C:N		–	11:1	13:1	10:1	9:1
According Egner-Riehm DL	P	mg·kg^{-1}	82	65	60	89
	K		122	84	95	148

The first factor covered the following treatments: four soils (n=4: Haplic Phaeozems, Orthic Luvisols, Orthic Podzols and Mollic Gleysols), the concrete containers were filled with compliant with their genetic profiles, while the second factor (n=5) – a varied fertilisation with sulphur and Basfoliar 36 Extra (B): 20 kg S·ha^{-1} – S_1, 40 kg S·ha^{-1} – S_2, 20 kg S·ha^{-1} + Basfoliar 36 Extra (S_1+B), 40 kg S·ha^{-1} + Basfoliar 36 Extra(S_2 +B) and non-sulphur fertilisation treatment and the control. All the fertilisation treatments involved a homogenous NPK fertilisation, respectively, in a form of triple superphosphate urea, 60% potassium salt. Sulphur was applied into soil in a form of sodium sulphate (VI) prior to maize sowing, Basfoliar 36 Extra, a liquid nitrogen fertiliser (36.3% N) with a high content of magnesium (4.3%) and microelements (Mn – 1.35%, Cu – 0.27%, B – 0.027% Zn 0.013%, Mo – 0.0067%) were applied as foliar fertilisation at the fifth-leaf phase, combining that treatment with plants fertilisation with urea solution (20 kg N·ha^{-1}). All the experiment treatments involved the use of homogenous NPK fertilisation (120 kg·N·ha^{-1}, 80 kg·P_2O_5·ha^{-1} and 160 kg K_2O·ha^{-1}). The agrotechnical practises, cultivation jobs and plant protection treatments applied were compliant with the maize-growing-for-grain guidelines. In 2009 there were collected maize grains for which the basic chemical composition (K, P, Mg, Ca, Na) was defined compliant with the methods applied at the Chemical-Agricultural Experiment Station and the values of ionic and weight ratios were calculated. The results were verified with the statistical analysis and the method of variance was applied using the Tuckey semi-intervals and for the level of confidence = 0.05 there were also calculated the coefficients of simple correlation and linear regression.

RESULTS AND DISCUSSION

The maize grain yield size ranged from 351.41 to 658.4 g·plot^{-1} and it was significantly determined with the soil type, fertilisation applied as well as the interaction of the factors (Table 2). On average the highest yield (573.32g) of maize grain was found for Mollic Gleysols, while the application of the fertilisation factors investigated, the highest yield was recorded having applied the dose of 40 kg·ha^{-1} of sulphur (S_2) against NPK.

Table 2 Maize grain yield (g·plot^{-1})
Tabela 2 Plon ziarna kukurydzy (g·poletko^{-1})

Object – Obiekt (II factor – II czynnik)	Soil type (I factor) – Typ gleby (I czynnik)				
	Haplic Pheozems	Orthic Luvisols	Orthic Podzols	Mollic Gleysols	Mean Średnia
NPK 0	522.65	372.60	510.28	493.96	474.88
NPK+S_1	439.24	439.27	639.33	679.60	549.36
NPK+S_2	549.85	658.45	538.33	554.23	575.22
NPK+S_1+B	460.02	520.22	471.31	591.56	510.78
NPK+S_2+B	581.97	351.41	520.88	547.22	500.37
Mean - Średnia	510.75	468.39	536.03	573.32	522.12
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0.05)}$ dla:	73.94	88.40	165.34	176.79	

Minerals (K, Ca, Mg, Na and P) play an essential role in maize nutrition (Sawicka, 1997). Potassium demonstrates a synergic interaction with nitrates and the antagonistic effect with calcium, magnesium and sodium cations (Brodowska, et al.,

2002, Kraus, 2000, Mehta, et al., 1983, Robins, 1993). Its excessive amounts in soil, however, and thus in the plant, disturb the ionic equilibrium as a result of a decrease in the content of sodium, calcium and magnesium; hence a deteriorated plant quality.
The contents of potassium in maize grain ranged from 64.91 mmol·kg^{-1}d.m. to 81.84 mmol·kg^{-1}d.m. (Table 3). The content, according to Sądej et al. (2003) in maize grain is 4.5 g· kg^{-1} of d.m., namely 192 mmol·kg^{-1}d.m., and as shown by research, it is least susceptible to changes due to mineral fertilisation.
The research showed that the soil type was the only one which significantly determined the content of the potassium parameter. On average the lowest content of potassium, irrespective of the fertilisation applied, was reported in the grain of maize grown in Haplic Phaeozems. The value was significantly 9% and 10% lower than the value reported for: Orthic Podzols and Mollic Gleysols, respectively.
Phosphorus is uptaken by the plants already from the beginning of the vegetation period all the way until grain ripening (Brogowski, et al., 1996, Jankowiak, et al., 1997). The contents of that nutrient in the maize grain researched ranged from 2.84 g·kg^{-1}d.m. to 4.23 g·kg^{-1}d.m. and they were significantly determined by the soil type, the fertilisation applied and the interaction of the factors (Tab. 3). The contents were similar to those reported by Sądej and Mazur (2003). On average the highest content of potassium was reported for grain derived from the plants grown in Mollic Gleysols, while lower in Orthic Podzols, Orthic Luvisols and Haplic Phaeozems, respectively 6%, 5% and 5% lower. It was also found that the highest mean content of that parameter was recorded for the grain from the treatment with a higher dose of sulphur 40 kg·ha^{-1} (S_2) against the fixed NPK fertilisation. It was significantly 6% higher both than the content recorded for the control and after a combined application of a lower dose of sulphur and Basfoliar 36 Extra (S_1+B). The most favourable effect of the interaction of the soil type and the fertilisation factor was recorded in Mollic Gleysols following the application of a higher dose of sulphur (S_2) and Basfoliar 36 Extra, while the lowest effect of the interaction was reported for Orthic Podzols after the application of the identical fertilisation.
The content of calcium in maize grain depended significantly neither on the factors applied nor on their interaction and it ranged from 24.02 mmol·kg^{-1}d.m. to 33.09 mmol·kg^{-1} d.m. (Table 3). The highest mean content of calcium was recorded for the grain from thee plants grown in Haplic Phaeozems and it was 10%, 11% and 12% higher than the content recorded in the grain from Orthic Luvisols, Mollic Gleysols and Orthic Podzols, respectively.
Magnesium determines the production applicability of plants considerably and, next to potassium and calcium, affects the setting of the grain and the corncob, which also conditions the enhancement of the wheat quality [Rabikowska1999, Kulczycki et al. 2001]. The content of that macroelement in the grain ranged from 69.01 mmol·kg^{-1}d.m. to 96.42 mmol·kg^{-1}d.m. (Table 3). The content of magnesium was significantly determined by both b the soil type and the fertilisation applied as well as by the interaction of the two experiment factors.
On average the highest contents of magnesium was found in the grain of maize grown in Mollic Gleysols 15% higher than the content in the grain of maize grown in Haplic Phaeozems. The most favourable effect of the fertiliser factor was observed after the application of a higher sulphur dose, namely 40 kg S·ha^{-1} against the fixed NPK fertilisation, while the strongest effect of the interaction on the content of magnesium was found after the application of a higher sulphur dose (S_2) in Orthic Podzols (96.42 mmol·kg^{-1}s.m.), while the poorest – in Orthic Luvisols after the application of a lower sulphur dose (S_1) and Basfoliar (67.20 mmol·kg^{-1}d.m.).

Table 3 Content of minerals in the maize grain
Tabela 3 Zawartość składników mineralnych w ziarnie kukurydzy

Object – Obiekt (II factor – II czynnik)	Soil type (I factor) – Typ gleby (I czynnik)				
	Haplic Pheozems	Orthic Luvisols	Orthic Podzols	Mollic Gleysols	Mean Średnia
P content in grain corn – Zawartość P w ziarnie kukurydzy [g·kg^{-1}s.m.]					
NPK 0	3.412	3.421	3.404	2.925	3.290
NPK+S1	3.156	3.549	3.327	3.498	3.382
NPK+S2	3.275	3.395	3.660	3.677	3.502
NPK+S_1+B	3.489	2.993	3.395	3.267	3.286
NPK+S_2+B	3.412	3.293	2.839	4.229	3.443
Mean-Średnia	3.349	3.330	3.325	3.519	3.381
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0,05)}$ dla:	0.165	0.197	0.393	0.368	
K content in grain corn – Zawartość K w ziarnie kukurydzy [mmol(+)·kg^{-1}s.m.]					
NPK 0	2.540	3.090	3.035	2.870	2.884
NPK+S1	2.925	2.870	3.200	3.200	3.049
NPK+S2	2.870	2.980	2.980	3.035	2.966
NPK+S_1+B	2.870	2.650	2.980	2.980	2.870
NPK+S_2+B	2.650	2.870	2.870	3.200	2.898
Mean-Średnia	2.771	2.892	3.013	3.057	2.933
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0,05)}$ dla:	0.225	n.i.	n.i.	n.i.	
Ca content in grain corn – Zawartość Ca w ziarnie kukurydzy [mmol(+)·kg^{-1}s.m.]					
NPK 0	0.600	0.640	0.530	0.490	0.565
NPK+S1	0.550	0.510	0.565	0.525	0.537
NPK+S2	0.675	0.565	0.525	0.640	0.595
NPK+S_1+B	0.625	0.510	0.525	0.565	0.556
NPK+S_2+B	0.640	0.525	0.565	0.565	0.582
Mean-Średnia	0.618	0.550	0.542	0.557	0.567
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0,05)}$ dla:	n.i.	n.i.	n.i.	n.i.	
Mg content in grain corn – Zawartość Mg w ziarnie kukurydzy [mmol(+)·kg^{-1}s.m.]					
NPK 0	0.839	1.010	1.032	0.892	0.943
NPK+S1	0.871	0.968	1.054	0.989	0.970
NPK+S2	0.882	0.935	1.172	1.118	1.027
NPK+S_1+B	0.871	0.817	0.946	0.978	0.903
NPK+S_2+B	0.914	0.914	0.860	1.161	0.962
Mean-Średnia	0.875	0.929	1.012	1.028	0.961
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0,05)}$ dla:	0.077	0.092	0.183	0.172	
Na content in grain corn – Zawartość Na w ziarnie kukurydzy [mmol(+)·kg^{-1}s.m.]					
NPK 0	0.075	0.084	0.075	0.112	0.086
NPK+S_1	0.112	0.084	0.075	0.093	0.091
NPK+S_2	0.093	0.112	0.112	0.084	0.100
NPK+S_1+B	0.093	0.093	0.075	0.112	0.093
NPK+S_2+B	0.093	0.127	0.102	0.084	0.101
Mean-Średnia	0.093	0.100	0.088	0.097	0.083
$LSD_{(p=0.05)}$ for:	I	II	II x I	I x II	
$NIR_{(p=0,05)}$ dla:	n.i.	n.i.	n.i.	n.i.	

The content of sodium in the maize grain ranged from 3.26 mmol·kg^{-1}d.m. to 5.52 mmol·kg^{-1}d.m. and it was not significantly determined by the experimental factors (Table 3). The highest contents of the parameter were recorded for the grain of maize grown in Orthic Luvisols and in Mollic Gleysols.

With the contents of the minerals investigated, there were calculated the following values of the ionic ratios: K:(Ca+Mg), Ca:Mg, K:Mg, K:Ca, Na:K and weight ratio Ca:P. (Table 4).

The values of the ratios K:(Ca+Mg) are on average from 0.62 /1 to 0.77/1. The results diverge considerably from the data reported by Krzywy et al. (2002) according to which the ratio should be 2.2/1. Low values of that ratio result from the research material; the maize grain with a lower content of potassium, calcium and magnesium than the other parts of that plant (Sądej, et al., 2003). Interestingly, the values of the ratio K:(Ca+Mg) are most frequently referred to in the green matter of plants allocated to animal feed. It was found that in the grain of maize grown in Mollic Gleysols, after the application of 20 kg S·ha^{-1} there was noted a widening of the value of that ionic ratio, while its narrowing was reported in the grain of maize grown in Orthic Podzols, after the application of 40 kg S·ha^{-1}.

The values of the ratio Ca/Mg in the maize grain ranged from 0.27/1 to 0.46/1, (Tab. 4) and they were definitely narrowed, as compared with those reported by Krzywy et al. (2002). According to those authors the value of that ratio in animal feeds should be 3/1. The application of sulphur at the dose of 20 kg S·ha^{-1} narrowed the ratio in the grain of maize grown both in Haplic Phaeozems or in Orthic Luvisols. The value of that ratio Ca/Mg is determined by the content of magnesium in soil. Under the unbalanced fertilisation with that element the ionic equilibrium is disturbed both in soil and in the plant (Brodowska, et al., 2003).

The values of the ratio K/Mg in the maize grain were narrowed and ranged from 0.79/1 to 1.04 / 1 (Tab. 4). The narrowed value of that ratio was recorded in the grain of maize grown in Orthic Podzols following the application of NPK and sulphur at the dose of 40 kg S·ha^{-1}. A widened value of that ratio was recorded in the grain of maize grown in Phaeozems after the application of NPK and sulphur at the dose of 20 kg S·ha^{-1}. According to Brodowska et al. (2002), sulphur fertilisation increases the content of potassium and decreases the content of magnesium, which affects the relationship between those cations at the right level. A similar effect of sulphur was recorded in the present research, while Sądej (1999) found that a more favourable effect on the value of the ratio K/Mg is due to natural rather than mineral fertilisation. Krzywy et al. (2002) showed that widening the values of the ratio analysed can be due to increasing doses of mineral NPK fertilisers, since then there occurs a decrease in the content of magnesium in the plant, which coincides with the report by Kulczycki (2007).

The values of the ratios K/Ca are given in Table 4. The narrowed value of that ratio was noted in the grain of maize grown in Haplic Phaeozems after the combined application of NPK and sulphur at the dose of 40 kg ha and Basfoliar 30 Extra, while widening of the values of the ratio K/Ca was found in the grain of maize cultivated in Mollic Gleysols after a combined application of NPK and sulphur at the dose of 20 kg ·ha^{-1}. The present results are higher than the value reported in literature which, according to Krzywy et al. (2004) is 2/1. In the present research widening the value of the ratio K/Ca in the grain of maize grown in Mollic Gleysols could have been due to a low content of calcium in the grain or a high richness of the soils in available forms of potassium.

Table 4 Value of the ionic and weight ratios in the maize grain
Tabela 4 Wartości stosunków jonowych w ziarnie kukurydzy

Object – Obiekt (II factor – II czynnik)	Soil type (I factor) – Typ gleby (I czynnik)			
	Haplic Pheozems	Orthic Luvisols	Orthic Podzols	Mollic Gleysols
	The values of the ratio – Wartość stosunku K/(Ca+Mg)			
NPK 0	0.66	0.69	0.70	0.75
NPK+S1	0.76	0.70	0.72	0.77
NPK+S2	0.70	0.73	0.62	0.63
NPK+S_1+B	0.72	0.74	0.74	0.70
NPK+S_2+B	0.64	0.73	0.73	0.66
	The values of the ratio – Wartość stosunku Ca/Mg			
NPK 0	0.43	0.38	0.31	0.33
NPK+S1	0.38	0.31	0.32	0.32
NPK+S2	0.46	0.36	0.27	0.34
NPK+S1+B	0.43	0.38	0.33	0.35
NPK+S2+B	0.42	0.34	0.43	0.29
	The values of the ratio – Wartość stosunku K/Mg			
NPK 0	0.94	0.95	0.91	1.00
NPK+S1	1.04	0.92	0.94	1.01
NPK+S2	1.01	0.99	0.79	0.84
NPK+S1+B	1.03	1.01	0.98	0.95
NPK+S2+B	0.90	0.98	1.04	0.86
	The values of the ratio – Wartość stosunku K/Ca			
NPK 0	2.21	2.53	2.99	3.08
NPK+S1	2.77	2.98	2.97	3.26
NPK+S2	2.26	2.76	3.04	2.48
NPK+S1+B	2.42	2.75	3.04	2.76
NPK+S2+B	2.17	2.88	2.54	2.96
	The values of the ratio – Wartość stosunku Na/K			
NPK 0	0.05	0.05	0.04	0.07
NPK+S1	0.06	0.05	0.04	0.05
NPK+S2	0.06	0.06	0.06	0.05
NPK+S1+B	0.05	0.06	0.04	0.06
NPK+S2+B	0.06	0.08	0.06	0.04
	The values of the ratio – Wartość stosunku Ca/P			
NPK 0	0.18	0.19	0.16	0.17
NPK+S1	0.17	0.14	0.17	0.15
NPK+S2	0.21	0.17	0.14	0.17
NPK+S1+B	0.18	0.17	0.16	0.17
NPK+S2+B	0.19	0.16	0.21	0.14

The values of the ionic ratios Na:K in the maize grain ranged from 0.04/1 to 0.08/1 (Table 4). Having applied the fertilisation investigated, one can conclude that the values of that ratio were, in general, similar to each other. According to Brodowska et al. (2002), sulphur fertilisers increase the percentage share of potassium and sodium in the sum of cations, which most probably did not differentiate the values of the ratio Na/K. According to Sienkiewicz et al. (2004), the application of mineral and natural fertilisers only slightly affected the content of sodium in the plant and thus the value of the ratio Na/K, which was found also in the present research.

The values of the ratio Ca/P ranged from 0.14/1 to 0.21/1 (Table 4). The experiment mean for the entire experiment was 0.17 and it was much lower than the value reported by Krzywy et al. (2002). It was found that the application of sulphur at the dose of 20 kg $\cdot ha^{-1}$ against NPK resulted in a clear narrowing of the value of the discussed weight ratio in the grain of maize grown in those soils, except for Orthic Podzols. As reported by Sądej et al. (2003), and from the present research, the maize grain demonstrates a high phosphorus content and a low content of calcium, unlike for the green parts of plants, where the ratio is 2/1. According to Krzywy et al. (2002), the application of mineral fertilisers, irrespective of the form of their nutrients, in general does not affect the value of the ratio Ca/P, which also coincides with the present results.

The contents of nitrogen, phosphorus, potassium, magnesium and sodium in the maize grain, in general, resulted in narrowing the values of ratios K/(Ca+Mg), Ca/Mg and K/Mg, and widening the values of the ratios K/Ca and K/Na. The soil type determined the values of the ionic ratios Ca/Mg and K/Ca in the maize grain; there was found widening of their values in the grain in Haplic Phaeozems and Mollic Gleysols, respectively.

The results on the contents of minerals were exposed to the analysis of simple correlation and linear regression. There were found significant positive correlations between the content of P and K and the content of magnesium in the maize grain the coefficients were r=0.62 and r=0.74 (Fig.1), respectively. One can calculate that an increase in the content of magnesium in the maize grain by 0.2 units (0.2 $mmol\cdot kg^{-1}$) caused a comparable increase in the content of K or P, respectively by 0.44 $mmol\cdot kg^{-1}$ or by 0.42 $g\cdot kg^{-1}$. The statistical analysis showed only a positive correlation between the value of the ratio Ca/P and the value of the ratio K/Mg in the grain maize and the coefficient of correlation is 0.52. The relationships are given in Fig. 2.

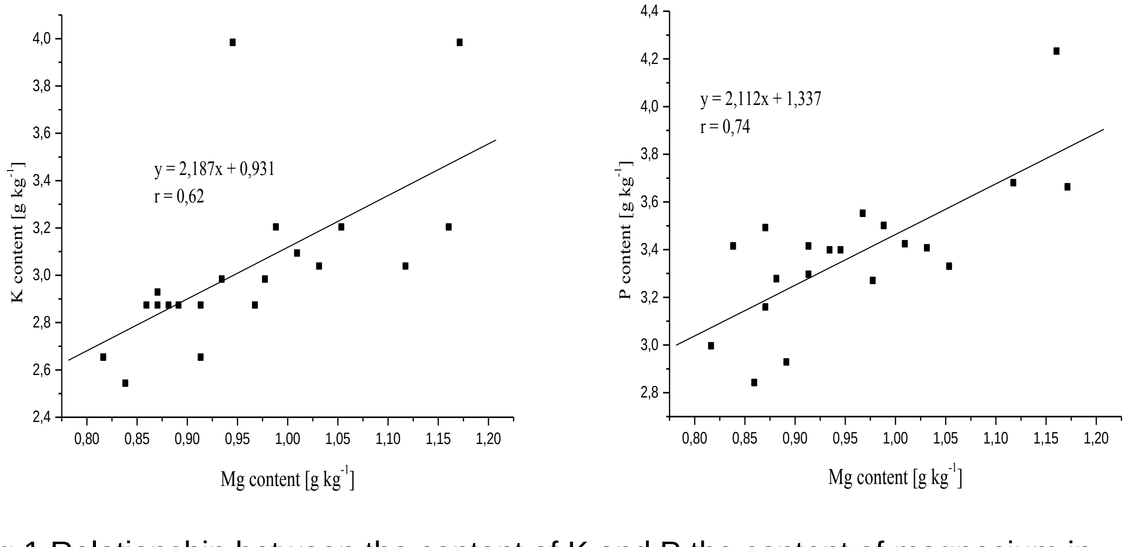

Fig.1 Relationship between the content of K and P the content of magnesium in maize grain

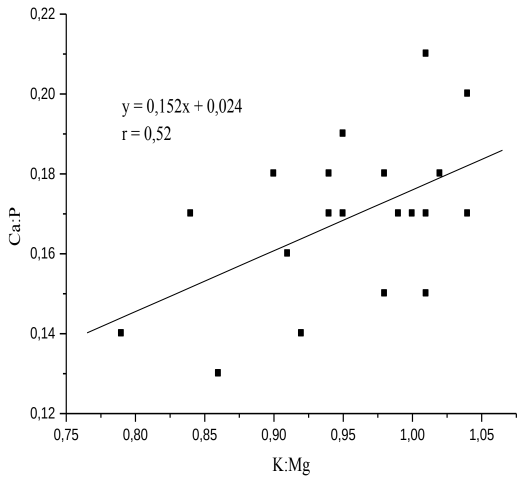

Fig.2 Relationship between the value of the ratio Ca/P and the value of the ratio K/Mg in the maize grain

CONCLUSIONS

1 The maize grain yield size was significantly modified by the soil type and by the sulphur fertilisation applied and with sulphur combined with Basfoliar 36Extra against fixed NPK fertilisation.
2 The soil type, irrespective of the fertilisation applied, determined the contents of phosphorus, potassium and magnesium in the maize grain significantly; the mean significantly highest contents were found in the grain in Mollic Gleysols, while the fertilisation applied significantly modified only the contents of phosphorus and magnesium in maize grain.
3 The sulphur fertilisation applied and sulphur combined with Basfoliar 36Extra against NPK, in general, widened the values of the ratios K/(Ca+Mg and K:Mg in the maize grain, as compared with the treatment with NPK only.
4 The mean contents of cations in the maize grain varied a lot and could be grouped in the following order: Mg >K >Ca> Na. The contents, as a result, narrowed the values of the ratios K/ (Ca+Mg), Ca/Mg and K/Mg, and widening of the ratios K/Ca and K/Na.

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