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ORIGINAL PAPER

THE RESPONSE OF SPRING RYE (*SECALE CEREALE* L.) TO NPK AND S FERTILIZERS. THE CONTENT AND UPTAKE OF MACROELEMENTS AND THE VALUE OF IONIC RATIOS*

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Abstract

The study aimed to analyze the effect of nitrogen and sulfur fertilization on the content and uptake of macronutrients in the dry matter (DM) of spring rye grain. The field experiment was carried out on Cambisols soil (WRB 2015) with a low sulfur content, in south-eastern Poland. The effects of fertilization with N (factor I) 0, 30, 60, 90 kg ha^{-1} and fertilization with S (factor II) 0, 40 kg ha^{-1} were investigated. The analysis showed that spring rye responded positively to N and S. N fertilization. Better grain yield was obtained after applying 90 kg N ha^{-1} (3.684) and adding 40 kg S ha^{-1} (3.230 t ha^{-1}). In the mentioned combination, the rye grain contained the most macronutrients, with the exception of P, and the uptake of the elements was also the most advantageous. The addition of S in the dose of 40 kg S ha^{-1} improved the effect of N and the yield of rye grain, in addition to which the content and uptake of macronutrients in the dry matter of rye grain were higher. The best yield of spring rye grain and the content and uptake of all macronutrients, except for potassium (K), in dry matter (DM), were recorded in the 2011 growing season, when the optimal distribution of precipitation was observed. Significant correlations were also found between the grain yield and the content and uptake of all the studied macronutrients, except for the correlation between the grain yield and the K content. Generally, a positive correlation was found between the content and uptake of macronutrients, except for

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the content of P. Fertilization with N significantly reduced the mass ratios of K^+:Ca^{2+}, K^+:Mg^{2+} and the mass and mole ratio of K^+:(Ca^{2+}+Mg^{2+}), and increased the mass ratio of Ca:P. By contrast, the addition of S significantly reduced the mass ratios of K^+:Ca^{2+} and K^+:(Ca^{2+}+Mg^{2+}) and increased that of Ca:P.

Keywords: nitrogen, sulphur, rye, yield, macroelement ratios in grain.

INTRODUCTION

In modern agriculture, mineral fertilization is the basic yield factor in plant cultivation, and the most important method of increasing the content of elements in arable crops (Klikocka et al. 2020). Over the past decade, cereal products have become staple food in human nutrition, improving human and animal health. According to the food pyramid developed by the National Food and Nutrition Institute, low-processed cereal products are the base of the pyramid, thus being essential elements in the human diet. In Poland, cereal products are very important as they account for nearly 50% of the daily requirement. They also contain the necessary mineral elements, especially potassium (K), phosphorus (P), magnesium (Mg), iron (Fe), zinc (Zn) and copper (Cu) – Pieczyńska et al. 2011.

Rye is one of the basic crops from which bread and animal feed are made (Zawojski et al. 2014). Russia, Poland and Germany in particular are the largest producers of rye in Europe. The total rye cultivation area in these three countries accounts for 57.66% of world rye production. Poles and Belarusians consume the most rye, on average 29.9 kg per capita per year. Cereals and cereal products in the daily diet currently provide humans with almost 30% of energy and protein, and 54% of carbohydrates. Moreover, they are a varied source of bioactive substances and nutrients (Narolski 2016, Podleśna et al. 2018, Klikocka et al. 2020).

The available studies show that the addition of sulfur to NPK fertilization has a positive effect on the increase in the content of macro- and microelements in potato tubers and cereal grains (Klikocka et al. 2014, 2015, 2017*a*, 2017*b*). Supplementing NPK fertilization with sulfur is important because deficiencies of this element in the soil are observed in many regions of Europe and the world (Potarzycki 2003, Klikocka, Marks 2018). Due to low SO_2 emissions in the air and sulfur deficiency in the soil, sulfur fertilization is necessary in order to improve the volume and quality of agricultural plant production (Tabak et al. 2019). In Poland, SO_2 emission (deposition) per 1 ha decreased from a very high level of over 130 kg S in the 1980s to no more than 18.7 kg SO_2 ha^{-1} recorded currently (Szulc 2008, Brodowska 2013, Klikocka et al. 2015). Minitoring studies conducted by IUNG in Puławy showed that in 2015 in Poland, 91.7% of soil profiles (198 profiles) had a low content (I) of sulphate sulfur (Siebielec et al. 2017).

The literature on the subject reports that the so-called sulfur-loving plants, such as *Brassicaceae* (rapeseed), garlic, onion, sugar beet, potato, *Fabaceae*, maize, as well as wheat, respond favorably to sulfur fertilization (Klikocka 2011*a*, *b*). So far, however, no field research has been conducted on sulfur fertilization of spring rye. As shown in the literature, sulfur metabolism is closely related to nitrogen metabolism in plants. And this is not only a physiological and biochemical issue, but also an environmental one (Narolski 2016). Research shows that sulfur deficiency reduces the use of nitrogen by crops. This observation substantiates the following working hypothesis: sulfur used in the cultivation of spring rye increases the efficiency of nitrogen fertilization by improving the yield and improving the ionic ratios in the grain, which indirectly affects human and animal health. In order to verify this hypothesis, a field experiment was conducted in 2009-2011 in order to determine the yield, content and uptake of macronutrients in spring rye of the Bojko variety. The first experimental factor was nitrogen fertilization, and the second one included the addition of sulfur fertilizers to N fertilization.

At present, there is no information on the addition of sulfur to N fertilization on the content of macronutrients: phosphorus (P), potassium (K), magnesium (Mg) and calcium (Ca) in the grain and on the value of ionic ratios in the grain of spring rye. Therefore, in the present field study, the significance and role of sulfur and nitrogen fertilizers for spring rye grown on Cambisols were analyzed (WRB 2015).

MATERIALS AND METHODS

Field experiments

A randomised split-plot field experiment (in four replications) was conducted in 2009-2011 in the village of Malice, in south-eastern Poland (50°42′ N, 23°15′ E), on Cambisols (WRB 2015). The soil was made up of light silty sand (68% sand, 31% silt, and 1% clay). The soil had a slightly acidic reaction (pH_{KCl} = 5.6) and a mean content of available P (52.1 mg kg^{-1}; Double--Lactate extraction, pH 3.6 (1:50 m/v), mean content of K (84.5 mg kg^{-1}; extracted as P) and Mg (34.5 mg kg^{-1}; extracted by 0.0125 mol L^{-1} $CaCl_2$ (1:10 m/v ratio). The measurement of $S\text{-}SO_4$ content was also low (12.4 mg kg^{-1}; extracted by 0.025 m L^{-1} KCl) – Narolski (2016).

The field experiment focused on the Bojko cultivar of spring rye (*Secale cereale* L.). The basis for determining the number of doses of nitrogen fertilizers was the technological requirements of spring rye. Three doses of fertilizer were used to determine yield grain and calculate the optimal dose using the regression equation. On the other hand, sulfur in an increased amount of 40 kg ha^{-1} was used due to its low content in the soil ($S\text{-}SO_4$ – 12.4 mg kg^{-1}). It was assumed that sulfur fertilization (II-order factor) would demonstrate the additive effect of sulfur on nitrogen fertilization. Spring rye was fertilized with N and S, as shown in Table 1. Nitrogen was

Table 1

Doses of nitrogen (N) and sulphur (S)

Fertilizer	Total dose	Time and Dose of Fertilization		
		spring, before sowing	BBCH† 30-31	BBCH 55-59
	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})	(kg ha^{-1})
Nitrogen (N)	0	-	-	-
	30	30	-	-
	60	30	30	-
	90	30	30	30
Sulphur (S)	40	30	-	10

† BBCH – Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie. Meier U. 2018. Growth stages of mono- and dicotyledonous plants BBCH Monograph. Julius Kühn-Institut (JKI) Quedlinburg 2018, 204 pp. DOI: 10.5073 / 20180906-074619

added in the form of ammonium nitrate (NH_4NO_3 – 34% N, including ammonia N (N-NH_4) – 17.0% and nitrate N (N-NO_3 – 17.0%). Sulphur was used in two ways: (I) prior to rye sowing – as kieserite ($MgSO_4 \times H_2O$: 5.1% Mg and 20.0% S), and (II) during the vegetative growth phase as a foliar application of Epsom salts (magnesium sulphate heptahydrate $MgSO_4 \times 7H_2O$; 10.2% Mg and 32% SO_3) to rye plants (BBCH 55-59). Prior to sowing the rye, the soil was fertilized with phosphorus (39.6 kg P ha^{-1} as triple superphosphate granules $Ca(H_2PO_4)_2$) and potassium (83 kg K ha^{-1} as a potassium salt KCl).

The treatments carried out in the cultivation of spring rye were adequate with the current recommendations of integrated production (IP). Depending on the growing season and the current climatic and soil conditions, rye was sown between the last ten days of March and the first ten days of April. Rye grain was harvested in the BBCH 89-92 phase, which usually fell in the last ten days of July or the first ten days of August. Seeds were sown in the amount of 140 kg ha^{-1}, which resulted in the density of 350 plants per square meter. Before sowing, the grain was treated with Vitavax 200 FS in the amount of 300 ml 100 kg^{-1} (active substances: carboxin + thiram). In the tillering phase (BBCH 28), the herbicides Granstar 75 WG-tribenuron-methyl (20 g ha^{-1}) and Puma Super 069 EW-fenoxaprop-P-ethyl (1 l ha^{-1}) were used to control monocotyledonous and dicotyledonous weeds. The anti-fungus Stabilan 750 SL (chlormequat chloride) in an amount of 1.8 l ha^{-1} was also used in the BBCH 28 phase. No fungicides and insecticides were used, in accordance with the recommendations of the Institute of Plant Protection in Poznań.

Weather conditions

Table 2 presents the distribution of air climatic conditions during the plant growing season (March-August) in the years 2009-2011. Based on

Table 2

Selyaninov's hydrothermal coefficient in 2009-2011 and long-term averages from 1971-2005 (Zamość Research Station)

Years	Month (k)						Sum – Mean (Mar-Aug)		
	Mar	Apr	May	June	July	Aug	K	p	T
2009	5.3	0.5	2.4	2.1	0.4	0.8	1.3	349.1	2652
2010	1.8	1.1	2.0	1.1	2.1	1.3	1.6	443.4	2715
2011	1.2	1.1	0.7	1.0	2.7	2.3	1.6	414.6	2581
1971-2005	5.1	1.8	1.5	1.6	1.7	1.0	1.6	367.4	2353

K – Selyaninov's hydrothermal coefficient, K = (p×10)/∑t); p – precipitation (mm), t – temperature (°C).

atmospheric precipitation and air temperature, the Selyaninov's hydrothermal coefficient (K) was calculated. The data show that the growing season in 2009 was relatively dry (1.3), while the 2010 and 2011 seasons were optimal, but on the verge of wet (1.6).

Analysis and calculations

The grain yield (with a moisture content of 11%) was calculated after the wheat harvest in the BBCH 89-92 phase (Narolski 2016). Chemical analyses of the grain (in 2009-2011) for the content of P, K, Mg and Ca were performed at the Certified Research Laboratory of the Agricultural and Chemical Station in Lublin. The tests were carried out in accordance with Certificate No. AB 1186, which meets the PN-EN-ISO / IEC 17025-2005 standards. The grain of spring rye was mineralized with concentrated sulfuric acid, and the content of total phosphorus (P) in the filtrate was determined on the basis of the following reaction: ammonium heptamolybdate and antimony (III) potassium oxide tartrate react in an acidic environment with dialyzed and dilute phosphate solutions to form antimony-phospho-molybdate complexes. This complex is reduced to a deep blue colored complex by L (+) – ascorbic acid. The phosphorus content of the sample was measured at a wavelength of 880 nm on a SkalarSANplus analyzer. Potassium and calcium were determined by flame photometry on a Varian AA 240 FS. Magnesium was analyzed by the ASA method. The results obtained in this way enables the calculation of the following ionic (mass) ratios: K^+:Ca^{2+}, K^+:Mg^{2+}, K^+:(Ca^{2+}+Mg^{2+}), Ca:P, Ca^{2+}:Mg^{2+} and mole ratios of K^+:(Ca^{2+}+Mg^{2+}).

The analysis of variance (ANOVA) was performed using the Snedecor *F* test. Significance of differences was calculated using the Tukey's test (p=0.05), and differences between LSD were determined by *post-hoc* analysis. The Pearson's linear correlation analysis was used to determine the relationship between the yield and the content and uptake of macronutrients. Statistica 10 (StatSoft Inc.: Tulsa, OK, USA, 2010; StatSoft Polska, Sp.z o.o., Kraków, Poland 2010) and Excel 7.0 (2007 Microsoft Office System) were used to perform statistical analyses.

RESULTS AND DISCUSSION

The statistical analysis of the results showed a significant positive effect of nitrogen application on the yield of spring rye grain, and on the content and uptake of K, Mg and Ca in the dry matter of grain (DM), with the exception of P. The use of 60 and 90 kg N ha^{-1} significantly decreased the P content in grain. The analyzed features were also positively influenced by sulfur fertilizers. In the experiment, there was no interaction between N fertilization and S addition. However, there was a tendency for sulfur added to each N dose to increase the yield, content and uptake of P, K, Mg and Ca by the dry matter of grain (Table 3). According to Klikocka and Głowacka (2013), Woźniak and Stępniewska (2017), Klikocka and Marks (2018), Klikocka et al. (2018, 2020), the content and uptake of chemical elements is largely dependent on factors such as the species and variety of the crop, habitat conditions and agronomic factors (e.g. mineral fertilization).

The best grain yield occurred after the application of 90 kg N ha^{-1} (3.684 t ha^{-1}). In relation to the control variant (0 N), it increased by 1.049 t ha^{-1} (27.5%). The content of K, Mg and Ca in rye grain increased significantly

Table 3

The nitrogen (N) and sulphur (S) fertilization on content (g kg^{-1}) of macroelements in the spring rye grain and their uptake (kg ha^{-1})

Fertilization		Grain yield (t ha^{-1})	P		K		Mg		Ca	
S	N		content	uptake	content	uptake	content	uptake	content	uptake
0S (N × S)	0	2.2587*a*	4.167*a*	10.780*a*	4.033*a*	10.380*a*	1.217*a*	3.140*a*	0.250*a*	0.647*a*
	30	2.795*a*	4.067*a*	11.367*a*	4.167*a*	11.647*a*	1.383*a*	3.867*a*	0.317*a*	0.890*a*
	60	3.551*a*	4.000*a*	14.223*a*	4.233*a*	15.060*a*	1.467*a*	5.217*a*	0.350*a*	1.423*a*
	90	3.658*a*	3.933*a*	14.390*a*	4.333*a*	25.853*a*	1.510*a*	5.527*a*	0.383*a*	1.400*a*
40S (N × S)	0	2.682*a*	4.283*a*	11.490*a*	4.100*a*	10.963*a*	1.317*a*	3.527*a*	0.350*a*	0.940*a*
	30	2.918*a*	4.200*a*	12.253*a*	4.233*a*	12.343*a*	1.367*a*	3.993*a*	0.367*a*	1.073*a*
	60	3.611*a*	4.167*a*	15.040*a*	4.433*a*	16.017*a*	1.467*a*	5.293*a*	0.383*a*	1.387*a*
	90	3.709*a*	4.000*a*	14.840*a*	4.567*a*	16.940*a*	1.667*a*	6.180*a*	0.433*a*	1.610*a*
Mean (S)	0S	3.148*B*	4.042*B*	12.690*B*	4.192*B*	13.235*B*	1.394*B*	4.438*B*	0.325*B*	1.045*B*
	40S	3.230*A*	4.163*A*	13.406*A*	4.333*A*	14.066*A*	1.454*A*	4.748*A*	0.383*A*	1.253*A*
Mean (N)	0N	2.635*D*	4.225*A*	11.135*C*	4.067*D*	10.672*D*	1.267*D*	3.333*D*	0.300*D*	0.793*D*
	30N	2.857*C*	4.133*AB*	11.810*B*	4.200*C*	11.995*C*	1.375*C*	3.930*C*	0.342*C*	0.982*C*
	60N	3.581*B*	4.083*B*	14.632*A*	4.333*B*	15.538*B*	1.467*B*	5.255*B*	0.367*B*	1.315*B*
	90N	3.684*A*	3.967*B*	14.615*A*	4.450*A*	16.397*A*	1.588*A*	5.853*A*	0.408*A*	1.505*A*
Mean (Y)	2009	3.110*B*	4.113*A*	12.740*B*	4.575*A*	14.276*A*	1.419*A*	4.463*A*	0.319*C*	1.009*C*
	2010	3.142*B*	4.106*A*	12.881*B*	3.938*C*	12.420*B*	1.425*A*	4.541*A*	0.356*B*	1.131*B*
	2011	3.315*A*	4.088*A*	13.523*A*	4.275*B*	14.255*A*	1.429*A*	4.775*A*	0.377*A*	1.306*A*

Values marked with different letters (*A*, *B*, *C*, *D*) in the column differ significantly ($P < 0.05$).

proportionally to the dose of applied nitrogen, and was the highest at the dose of 90 kg N ha^{-1} (K – 4.450, Mg – 1.588, Ca – 0.408 g kg^{-1} DM) – Table 3. A reverse relationship was observed in the case of phosphorus. The content of the element (P) in the dry matter of rye grain after applying the medium and high dose was at 60 and 90 kg N ha^{-1} (P – 4.083 and P – 3.967 g kg^{-1} DM, respectively). The use of the highest dose of N (90 kg N ha^{-1}): K – 16.397, Mg – 5.833 and Ca – 1.505 kg ha^{-1} had a significant effect on the uptake of K, Mg and Ca by dry matter. On the other hand, the highest P uptake by dry grain weight (DM) was recorded for the doses of 60 and 90 kg N ha^{-1} (P – 14.632 and 16.514 kg ha^{-1}, respectively) – Table 3.

Reference literature widely discusses the effects of N application on grain yield, the content of nutrients and grain quality (Podleśna et al. 2018). Generally, the applied doses of nitrogen (30, 60, 90 kg N ha^{-1}), independently of S fertilizer, increased the content of most macronutrients except phosphorus. Klikocka et al. (2018) concluded that 120 kg N ha^{-1} was a dose improving the content and uptake of K, Mg and Ca by spring wheat grains. However, as for P, Klikocka et al. (2018) observed that 90 and 120 kg N ha^{-1} doses tended to reduce the phosphorus content. Kozera et al. (2017) reported that a dose of 80 kg N ha^{-1} favourably modified the general mineral composition of spring barley grain (particularly the content of K, P and Mg) compared to the control plots. Brzozowska (2008) did not report any significant impact of N application on the content of macronutrients in the grain of winter wheat, except for nitrogen and potassium. According to Nogalska et al. (2012), grain yield correlates with differences in the plants' uptake of these elements.

The addition of fertilizer with sulfur to N fertilization improved the yield of rye grain by 2.53% (Table 3). It is a well-known fact that cereals, especially spring, are considered species with low S demand (Klikocka et al. 2020). Nevertheless, some researchers pointed to the need to fertilize spring cereals with sulfur, and noted the beneficial effect of S fertilizers on the yield of cereals (Podleśna 2013). The research carried out by Podleśna (2013) showed that the addition of 60 kg ha^{-1} of sulfur fertilizer to N fertilization increased the yield of winter wheat grain by 11%. Based on the research by Kozera et al. (2017), it does not seem beneficial to use high doses of S for spring cereals. However, in the case of soil with low sulfur content, it is worth considering the use of doses higher than recommended. The studies by Klikocka and Głowacka (2013) and Barczak and Nowak (2013) show that sulfur can be used in elementary and sulphate forms. Elemental sulfur in particular contributes to increasing the content of macronutrients in plants, and this form has a positive effect by improving plant resistance to fungal and bacterial diseases.

The content and uptake of macronutrients by rye grain dry matter increased significantly after adding 40 kg S ha^{-1} to N fertilization. Compared to the control group, the content and uptake increased respectively (%): for P – 2.90; 5.34, for K – 3.25; 5.91, for Mg – 4.13; 6.53 and Ca –15.14; 16.60

(Table 3). Barczak and Nowak (2013) noticed that the use of sulfur in mineral fertilization of oats resulted in a slight decrease in the share of P, K and Ca in the grain. On the other hand, the content of Mg increased compared to the control objects (0 S). On the other hand, Gondek and Gondek (2010) did not show statistically significant differences in the Mg content in wheat grain subjected to NPK fertilization supplemented with sulfur. Also Skwierawska et al. (2008) claimed that sulfur fertilizers did not have a significant effect on the P and K content in the dry matter of spring barley grain.

The addition of sulfur to N fertilization did not show any interaction. However, an additive effect was shown, as the supplementation of S to each N dose resulted in favorable improvement of the examined features. It was shown that the most favorable content and uptake by dry matter of rye grain occurred for K, Mg and Ca after using the combination of 60 and 90 kg N ha^{-1} plus 40 kg S ha^{-1}. It was shown that the content of P in the grain decreased with the increase of N doses, but the phosphorus content increased after the application of the S addition to each N dose (Table 3).

Interactions between minerals in agricultural crops are frequent. This is especially the case when one element is supplied to the soil, which improves the absorption and use of other components. According to Hiatt and Leggett (1974), this type of interaction occurs most often in the case of excessive concentrations of a single nutrient in a solution. Interactions between chemical elements can take place at the root surface or in the plant. They can be divided into two categories. The first involves interactions between ions that are capable of forming chemical bonds. In this case, the interactions are based on the formation or precipitation of complexes. Another category of interaction is between ions that are chemically similar in competing for adsorption, absorption, transport, and function on the surface of plant roots or in plant tissues. Such interactions are more commonly found between chemical elements. They have a similar size, load, coordination geometry and electronic configuration characteristics (Hiatt, Leggett 1974). At the cell membrane level, there are anion-cation and anion-anion interactions. with a similar concentration, but targeting only one component, the interaction is positive and characterized by synergy (Grzebisz 2008). If two chemical components are added at the same time, and the resulting yield is lower than after using a single component, the effect is negative (antagonistic). No interaction of a chemical element on the plant means no interaction.

In the present study, sulphur added to any dose of nitrogen independently increased the yield, content and uptake of P, K, Mg and Ca in dry grain matter (DM). Such a yield-increasing factor, here a fertilizer, implies an additive effect of S. The additive interaction between nutrients is generally manifested in weight (or yield) constantly increasing due to applying another factor (Randall et al. 1981). The assimilation of N and S by plants is closely correlated (Hopkins 2015). Nitrogen nutrition has a strong regulating impact on the assimilation of sulphur and vice versa. The N to S ratio in proteins is deemed to be a reliable indicator of sulphur supply in plants. Randall et al. (1981) demonstrated that the N:S ratio in wheat grain proteins varied from 12 to 25 due to variations in the supply of N and S.

In this field experiment, sulfur added to any nitrogen dose increased the grain yield and increased the content and uptake of P, K, Mg and Ca in the grain. As mentioned earlier, this is the additive effect of sulfur on nitrogen fertilization (Randall et al. 1981). It is a well-known fact that the metabolism of N and that of S are closely related (Hopkins 2015). The N to S ratio of proteins is considered to be a reliable indicator of the sulfur supply of plants. According to Randall et al. (1981), the N: S ratio in wheat grain proteins ranges from 12 to 25, and is modified by different amounts of N and S used in fertilization.

The research showed significant positive correlations between the yield of rye grain and the content and uptake by the grain of all macronutrients, except for potassium (K). As reported by Hiatt and Leggett (1974), a positive correlation occurs when the use of two chemical elements in the form of fertilizer increases the yield and its content and uptake of chemical components, compared to adding only one nutrient. Phosphorus (P), unlike Ca, Mg and K, is taken up in the form of an anion and interacts antagonistically with Ca and Mg in the soil. This is especially true in alkaline soils, where P forms sparingly soluble chemical bonds in the form of sediments. These deposits can be found on roots and other plant tissues. Then they are more soluble, because they are affected by the acidic biological environment of the plant (Aulakh, Pasrich 1997). According to the cited authors, there is a negative interaction between S and P, which affects the grain yield. The authors suggest that sulphates and phosphates may compete for uptake and translocation pathways, thus influencing the influx and flow of nutrients through the plant. Moreover, they add that P can reduce the availability of S in the soil, especially in the case of poor sulfur content.

The calculated correlation coefficients between the grain yield and the content of macronutrients decreased in the order Mg> Ca> K> P. On the other hand, the correlation between the grain yield and the uptake of macronutrients by grain DM showed the order P> Mg> K> Ca. As shown in the literature, low-yielding (low-growing) plants produce more minerals per unit weight of the plant compared to plants that grow taller and faster (high-yielding). The content of nutrients in the soil has no major influence on the described phenomenon. Thus, regardless of the content of nutrients in the soil Cakmak (2002) describes the phenomenon as a concentration-dilution phenomenon. This, however, was not confirmed in the present study.

In this study, a positive correlation was observed between all analyzed macroelements except P. There were no significant correlations between the content of K and Ca, P and K, and between P and Ca. On the basis of the correlation analysis, a negative relationship was found between the content of P and Mg (Table 4).

Table 4

Correlation coefficients between grain yield and content and uptake of makroelements by grain DM of spring rye

Features (n=24)	No	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Grain yield	(1)	**-0.578**	**0.978**	0.367	**0.928**	**0.803**	**0.964**	**0.587**	**0.850**
P – content	(2)	-	-0.394	-0.233	**-0.596**	**-0.439**	**-0.549**	-0.283	**-0.473**
P – uptake	(3)	-	-	0.348	**0.901**	**0.789**	**0.943**	**0.583**	**0.832**
K – content	(4)	-	-	-	**0.685**	**0.456**	**0.423**	0.280	0.383
K – uptake	(5)	-	-	-	-	**0.802**	**0.919**	**0.580**	**0.823**
Mg – content	(6)	-	-	-	-	-	**0.931**	**0.698**	**0.837**
Mg – uptake	(7)	-	-	-	-	-	-	**0.662**	**0.887**
Ca – content	(8)	-	-	-	-	-	-	-	**0.920**
Ca – uptake	(9)	-	-	-	-	-	-	-	-

Bold letters represent significant differences at P 0.05 ≥ 0.406; P 0.01 ≥ 0.517

In the present study, nitrogen fertilization considerably reduced the mass ratios of K^+:$Ca^{2+}$and K^+:Mg^{2+} and the mass and mole ratios of K^+:(Ca^{2+}+Mg^{2+}) – Table 5, Figure 1(*a-f*). In addition, the nitrogen application increased the mass ratio of Ca:P; however, with no influence on the Ca^{2+}:Mg^{2+} mass ratio. By contrast, the use of sulphur supplementation significantly reduced the

Table 5

The influencs of N and S fertilization on the ratios of macroelements in the grain of spring rye

Fertilization		K:Ca	K:Mg	K: (Ca+Mg)		Ca:Mg	Ca:P
S	N	mass	mass	mass	mole	mass	mass
0S (N × S)	0 30 60 90	16.13*a* 13.62*b* 12.10*bc* 11.45*c*	3.31*a* 3.02*a* 2.89*a* 2.87*a*	2.75*a* 2.46*a* 2.33*a* 2.29*a*	0.91*a* 0.82*a* 0.78*a* 0.77*a*	0.21*a* 0.23*a* 0.24*a* 0.25*a*	0.06*a* 0.08*a* 0.09*a* 0.08*a*
40S (N × S)	0 30 60 90	11.71*c* 11.86*cd* 10.30*d* 10.86*d*	3.11*a* 3.10*a* 3.03*a* 2.75*a*	2.46*a* 2.44*a* 2.34*a* 2.19*a*	0.83*a* 0.82*a* 0.79*a* 0.73*a*	0.27*a* 0.27*a* 0.30*a* 0.26*a*	0.08*a* 0.09*a* 0.10*a* 0.11*a*
Mean (S)	0S 40S	13.32*A* 11.18*B*	3.02*A* 3.00*A*	2.46*A* 2.36*B*	0.82*A* 0.79*A*	0.23*B* 0.27*A*	0.08*B* 0.10*A*
Mean (N)	0N 30N 60N 90N	13.92*A* 12.74*AB* 11.20*B* 10.16*B*	3.21*A* 3.06*B* 2.96*BC* 2.81*C*	2.60*A* 2.45*B* 2.33*B* 2.24*C*	0.87*A* 0.82*B* 0.78*C* 0.75*C*	0.24*A* 0.25*A* 0.27*A* 0.26*A*	0.07*BC* 0.08*B* 0.10*A* 0.10*A*
Mean (Y)	2009 2010 2011	14.11*A* 11.25*B* 11.40*B*	3.23*A* 2.79*C* 3.01*B*	2.62*A* 2.23*C* 2.37*B*	0.87*A* 0.75*C* 0.80*B*	0.24*B* 0.25*AB* 0.27*A*	0.08*A* 0.08*A* 0.10*A*

Values marked with different letters (*A*, *B*, *C*, *D*) in the column differ significantly (P<0.05).

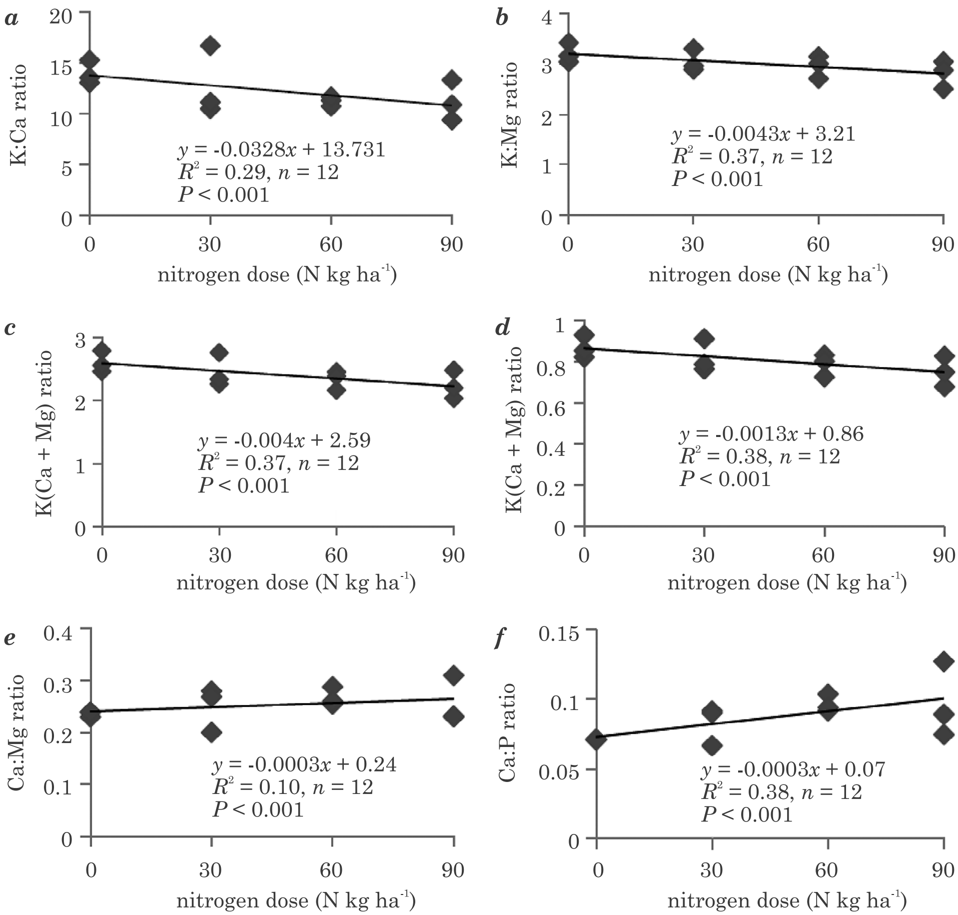

Fig. 1. Effect of nitrogen fertilization (N kg ha^{-1}) on ionic ratios in spring rye DM grain

mass ratios of K^+:Ca^{2+} and K^+:(Ca^{2+}+Mg^{2+}) and increased those of Ca^{2+}:Mg^{2+} and Ca:P. Sulphur addition had no significant influence on the K^+:Mg^{2+} mass ratio or on the mole ratio of K^+:(Ca^{2+}+Mg^{2+}) – Table 5. The values of macronutrient ratios are similar to those published by Kozera et al. (2017), Klikocka et al. (2018). According to Jankowska-Huflejt et al. (2009) and Gęsiński and Barczak (2021), excess potassium in animal feeds is more often reported than its deficit. An increased content of calcium (Ca) and magnesium (Mg), which can be antagonistic to potassium (K), facilitates maintaining a balance between uni-and bivalent ions (Hopkins 2015). As demonstrated by this experiment, the use of N and S fertilisers increased the content and uptake of both these essential nutrients by grain. Comparison of the results with data reported by Jarnuszewski and Meller (2013) and by Wołoszyk and Iżewska (2015), and with data for spring barley grain, implies that the mean values of K^+:Ca^{2+} in grain were excessively high and for Ca^{2+}:Mg^{2+} and Ca:P ratios – excessively low, but the K^+:$Mg^{2+}$and K^+:(Ca^{2+}+Mg^{2+}) can be considered optimum ratios. Interestingly, the value ranges of ionic ratios, notably K^+:Mg^{2+} and K^+:(Ca^{2+}+Mg^{2+}), were significantly extended after using S fertilisers.

It is worth bearing in mind that the content and uptake of micronutrients by rye grain in this experiment were exposed to the influence of atmospheric conditions in each growing season. It was shown that the distribution of weather factors in 2009 and 2011 was the most favorable for the content and uptake of P and Mg. In turn, the content and uptake of Ca by the grain was the most favorable in 2011. The validity of the above findings is supported by the research of Woźniak and Stępniowska (2017). These authors state that high sums of atmospheric precipitation favored the accumulation of P-phytate in the grain, while low precipitation had a positive effect on the content and uptake of K and Mg in the grain.

As shown in the present research, the content and uptake of macronutrients tended to be the least favorable in 2010. In this growing season, the potassium (K) content was comparable to the data from the remaining years of the study. In the growing season of 2010, the highest sum of atmospheric precipitation and the highest temperatures were recorded, which significantly exceeded the long-term average. According to Gilewska and Otręba (2008), long-term precipitation worsens pollination of flowers. This process requires moderately dry and warm weather. Moreover, excessively high rainfall combined with high temperatures favor the development of fungal diseases (Martyniak 2004). High temperatures in the generative stage of cereal development accelerate the aging process of the leaves and increase the respiration rate (Cakmak 2002), which directly reduces photosynthesis and assimilation. This phenomenon leads to poor seed filling. Weaker plants show a limited need for nutrients, which leads to the reduced transport of macronutrients from the leaves and stems to the grain. As reported by Klikocka et al. (2018), the lowest macronutrient uptake by spring wheat cultivated in the 2010 growing season reflects the occurrence of unfavorable weather conditions from shooting to heading, when nutrient uptake and growth processes are the most intensive. Under the weather conditions described above, N and S fertilization may have a limited impact on the size of the grain yield (Table 3).

CONCLUSIONS

The present fertilization experiment showed that the use of 40 kg S ha^{-1} in combination with 90 kg ha^{-1} nitrogen fertilizer, introduced to soil before sowing the grain of spring rye, was enough to ensure the optimal grain yield (6.684 t ha^{-1}), good K, Mg content, and Ca in grain, and had a beneficial effect on the uptake of the analyzed macronutrients. The results confirm the fact that the addition of sulfur to N fertilization is necessary for the effective growth of plants, in this case spring rye. As shown in our experiment, supplementation of S with NPK fertilizers effectively improves the chemical composition of spring rye grain macronutrients. In light of the research and the results obtained, it can be recommended to use S as an additive to nitrogen fertilizers for spring rye. It is also a method of agronomic biofortification by means of S fertilization with macronutrients (P, K, Mg and Ca), especially on soils with low sulfur content. Therefore, taking into account the current recommendations of plant production (IP) for spring rye cultivation, it is recommended to use 90 kg N ha^{-1}.

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