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ORIGINAL PAPER

PROPORTIONS OF NITROGEN AND SULPHUR IN SPRING RAPESEEDS DEPENDING ON FERTILIZATION WITH THESE ELEMENTS*

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Abstract

The study was based on a three-year field experiment conducted on degraded black soil, classified as class IIIb soil in the Polish soil valuation system, with neutral pH, high content of phosphorus and potassium, average content of magnesium, and low content of sulphur. The two-factor experiment was carried out in northern Poland (52°73′ N; 18°88′ E), in a split-block design with four replications. The preceding crop each year was sugar beet. The aim of the study was to evaluate the effect of varied levels of nitrogen (first factor – 0, 60, 120 and 180 kg ha^{-1}) and sulphur (second factor – 0, 20 and 60 kg ha^{-1}) applied to the soil and onto the leaves on the content and ratio of these elements in the seeds of the Star cultivar of spring rapeseed. Little variation was noted between growing seasons in the content of nitrogen and sulphur and in their proportions in the seeds. Application of nitrogen alone (without sulphur) and combined application of nitrogen with sulphur caused an increase in the nitrogen content in the seeds and in the N:S ratio. The sulphur content in the seeds of the plants fertilized with nitrogen and sulphur together was significantly higher than in the seeds of the plants fertilized with nitrogen alone and lower than in the plants fertilized with sulphur alone. The highest N:S ratios were obtained in the seeds of plants fertilized with nitrogen alone, and the lowest – following the application of sulphur alone. Application of nitrogen or nitrogen and sulphur caused an increase in the N:S ratio towards optimal values for fodder crops. The method of sulphur application did not significantly affect its content in the rapeseeds or the N:S ratio.

Keywords: *Brassica napus* L., content of nitrogen and sulphur in seeds, methods of sulphur application, N:S ratio.

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INTRODUCTION

Since the early 21st century, Poland has seen an increasing interest in the cultivation of rapeseed, largely owing to the use of its seeds not only for traditional purposes but also for production of biofuels (Tys et al. 2006). Mainly winter cultivars of rapeseed are grown in Poland. Spring cultivars of this species have less economic importance, as they produce lower yields (a difference of 35-40%) (Mrówczyński, Pruszyński 2008). Spring rapeseed, however, has numerous advantages. For example, it leaves a very good stand for cereal crops, has lower nutritional requirements and is less susceptible to disease than winter rapeseed, which generates lower costs (Rudko 2011). Interest in spring rapeseed usually increases following harsh winters, which cause frost damage to plants of winter varieties. In these conditions, spring rapeseed is sown in winter rapeseed plantations on which the herbicides used preclude cultivation of spring cereals (Mrówczyński, Pruszyński 2008). Moreover, the seeds of spring rapeseed cultivars are of good quality. Their fat content is similar to that of winter rapeseeds but they contain more total protein and less fibre and glucosinolates (Rudko 2011).

Spring rapeseed belongs the *Brassicaceae*, which have high nutritional requirements for sulphur. Until recently this nutrient was not considered in the agrotechnical procedures for rapeseed because its content in the soil was sufficient, often even exceeding the nutritional requirements of the plants. As a result of the reduction in emissions of SO_2 compounds from anthropogenic sources, which began in Poland with the political and economic transformation in the 1990s, the content of available sulphur in the soils has been continually decreasing (Barczak 2010, Gaj, Klikocka 2011, Przygocka-Cyna, Grzebisz 2017). According to the newest monitoring data (Siebielec et al. 2017), as many as 94% of soil samples (203 profiles) from various regions of Poland were classified as having low content of sulphate sulphur (VI) available to plants. Progressive sulphur deficiency affects other countries as well (Scherer 2001, Stern 2005, Jamal et al. 2010).

Proper nitrogen metabolism in the plant is not possible without an adequate supply of sulphur, which performs specific physiological functions. Numerous studies confirm that utilization of nitrogen from fertilizers and its efficiency are greater provided an optimal supply of sulphur to the plants (Barczak 2010, Jamal et al. 2010, Podleśna 2013, Skwierawska et al. 2016).

Considering the increased interest in rapeseed cultivation observed in Poland in recent years, as well as the growing deficiency of sulphur in Polish soils, a study was undertaken to evaluate the effect of varying levels of nitrogen and sulphur applied to the soil and onto the leaves on the content and proportions of these nutrients in the seeds of spring rape.

MATERIALS AND METHODS

Characteristics of the field experiment

A three-year (2010-2012) field study was conducted in the village of Kaźmierzewo (northern Poland, 52°73' N; 18°88' E) on degraded black soil classified as defective wheat complex, class IIIb (IUSS Working Group WRB 2015). The pH_{KCl} of the soil was 6.5-7.1 (neutral reaction). The content of available forms of phosphorus ranged from 175 to 198 mg P_2O_5 kg^{-1} (high), potassium – from 125 to 195 mg K_2O kg^{-1} (high), magnesium from 35 to 38 mg Mg kg^{-1} (average), and sulphur from 1.90 to 1.96 mg $S\text{-}SO_4^{-2}$ kg^{-1} (low). The soil had a regulated water regime. The Star cultivar (DLF Trifolium, Denmark) of spring rapeseed (*Brassica napus* L)., an open-pollinated variety, was used in the study. The preceding crop in each year was sugar beet.

Two experiments were carried out side by side in one field, with different doses and methods of sulphur application. The control treatment with no sulphur or nitrogen application was located between them. Both experiments were set up in a split block design with four replications. The area of the plots for harvest was 18 m^2. The experimental factors (n=2) were the nitrogen application dose (kg N ha^{-1}): 0 (control), 60, 120 and 180) – factor A, and sulphur application dose (kg S ha^{-1}): 0 (control), 20 and 60) – factor B. In both experiments, nitrogen was applied in the same form and at identical amounts, but in the first experiment sulphur was applied to the soil before sowing and in the second one it was applied as top dressing (foliar application). In both experiments, nitrogen was applied in split applications of 60 kg N ha^{-1}. In all treatments with nitrogen, the first portion was applied before sowing in the form of ammonium nitrate containing 34% N (17.0% $N\text{-}NH_4^+$ and 17.0% $N\text{-}NO_3^-$) with an addition of 2% CaO, 4% MgO and 0.2% boron. In each type of fertilization, 30 kg N ha^{-1} was applied. In the treatments with 120 kg N ha^{-1}, nitrogen was also applied 3-4 weeks before flowering (second application – BBCH 50-52), and in the treatments with 180 kg N ha^{-1}, before flowering (second application – BBCH 50-52) and at the start of flowering (third application – BBCH 61-63). The second and third portions were applied exclusively in the form of ammonium nitrate. In the treatments where sulphur was applied to soil before sowing, both doses of sulphur were applied at the same time, i.e. following the levelling of the field. In the experiment with the foliar application of sulphur, the application was split: in all fertilized treatments 20 kg S ha^{-1} was applied once at emergence (BBCH 13-16), and in the treatments with 60 kg S ha^{-1}, 20 kg S ha^{-1} was additionally applied after stem formation (BBCH 35-38) and 20 kg S ha^{-1} at the start of flowering (BBCH 61-63). Apart from these differences in sulphur application times, the agrotechnical procedures were identical in the two experiments. Sulphur was applied in the form of anhydrous sodium sulphate (22.5% S). Due to the high soil richness in macronutrients, low doses of phosphorus and potassium were used. Prior to winter ploughing, a compound fertilizer was applied, with 60 kg K_2O ha^{-1}, 30 kg P_2O_5 ha^{-1} and 48 kg MgO ha^{-1}. In each growing season, chemical plant protection was carried out according to recommendations by the Institute of Plant Protection (https://www.ior.poznan.pl).

Weather conditions

The Selyaninov hydrothermal coefficient was calculated for each month during the spring rape growing period, using this formula:

$$K = P / 0.1 \Sigma T,$$

where: P – sum of monthly precipitation in mm, T – sum of monthly air temperature >0°C

The most favourable weather conditions for the growth and development of spring rapeseed were noted in the first year of the experiment (Table 1). After sowing, rapeseed growth benefited from regular showers in both April and May, favourable rainfall distribution in June, and high levels of rainfall in July. The precipitation total was high in May of the second year, but its

Table 1

Temperature and precipitation distribution throughout the field experiment

Month	Study year	Temperature (°C)	Precipitation (mm)	Selyaninov coefficient
April	I	5.7	28.7	1.68
	II	10.0	29.5	0.98
	III	9.8	83.5	2.84
	long term	7.2	32.0	1.48
May	I	12.9	80.1	2.00
	II	15.2	57.8	1.23
	III	14.0	45.6	1.05
	long term	13.0	49.0	1.22
June	I	17.4	85.9	1.65
	II	18.9	83.0	1.46
	III	17.7	53.6	1.01
	long term	16.1	68.0	1.41
July	I	18.7	110.7	1.91
	II	17.9	100.6	1.81
	III	21.5	36.8	0.55
	long term	18.0	71.0	1.27
August	I	19.9	15.1	0.24
	II	15.5	65.8	1.37
	III	17.4	53.8	1.00
	long term	17.4	51.9	0.96

distribution was unfavourable; rain at the start of the month was followed by a nearly four-week dry period, during the rosette-formation stage. In contrast, heavy rainfall in late July and early August resulted in lodging, particularly on the plots with the highest nitrogen application doses. In the third year of the experiment, rainfall was low in three successive months. Total precipitation from May to July was only 136.0 mm (65% of the long-term average for those months), resulting in significantly lower Selyaninov coefficients for that growing season.

Chemical research

The content of potassium and phosphorus available for plants was determined in soil samples by the Egner-Riehm method, while the magnesium content was assessed by the Schachtschabel method. S-SO_4^{2-} was determined by ICP-OES using an Optima 7300 DV spectrometer. Soil pH was determined in the soil suspension in 1 M KCl solution by the potentiometric method.

After harvest, the content of the following elements was determined in the rape seeds from all treatments:

- total nitrogen (N_{tot}) by the Kjeldahl method using a Kjeltec 2200 Foss,
- total sulphur by ICP OES (Inductively Coupled Plasma Optical Emission) Spectrometry following mineralization of the samples in a mixture of concentrated acids, i.e. nitric (V) and chloric (VII) acids in a 4:1 ratio.

The results were used to calculate the N:S ratio.

Analysis of variance was performed on the results of the chemical assays using Statistica 8.0 software (StatSoft, USA). Significance of differences between means for each fertilizer treatment were determined by the Tukey's range test (p<0.05).

RESULTS AND DISCUSSION

The mean nitrogen content in the seeds of spring rapeseed grown under conditions of varied application of nitrogen and sulphur showed relatively little variation between years of the study, ranging from 34.4 to 35.0 g kg^{-1} (Table 2). The mean content was 34.8 g kg^{-1} for both sulphur application treatments (soil and foliar). The experimental factors caused an overall significant increase in the content of nitrogen in the rape seeds (Figure 1). The nitrogen application doses (kg ha^{-1}): 60, 120 and 180 in the absence of sulphur application caused an increase in nitrogen with respect to the control, on average by 1.6%, 2.5% and 6.3%, respectively. The seeds of plants fertilized with 60 kg S ha^{-1} applied to the soil without nitrogen accumulated significantly more nitrogen than the seeds of unfertilized plants (on average

Table 2

Nitrogen content in spring rape seeds (g kg^{-1})

($kg N ha^{-1}$) – A^+	Years of study												Average from years			
	I				II				III							
	($kg S ha^{-1}$) – B^{++}			mean	($kg S ha^{-1}$) – B^{++}			mean	($kg S ha^{-1}$) – B^{++}			mean	($kg S ha^{-1}$) – B^{++}			mean
	0	20	60		0	20	60		0	20	60		0	20	60	
	soil fertilizer of sulphur															
0	31.81	33.59	35.22	33.50	32.21	33.83	35.46	33.80	32.00	34.12	35.81	34.01	32.01	33.81	35.51	33.81
60	32.33	33.80	36.50	34.21	32.60	34.11	36.60	34.40	32.63	34.58	36.80	34.70	32.52	34.20	36.60	34.41
120	32.50	34.10	36.51	34.40	32.79	34.60	36.81	34.70	33.01	34.71	37.02	34.91	32.80	34.50	36.82	34.70
180	33.41	37.82	36.50	35.91	34.21	38.12	36.80	36.38	34.40	38.22	37.00	36.50	34.02	38.01	36.77	36.30
Mean	32.51	34.83	36.18	34.51	32.95	35.17	36.42	34.83	33.01	35.41	36.61	35.02	32.81	35.10	36.40	34.79
$LSD_{p<0.05}$	A-n.s., B-2.08, A×B-n.s.				A-n.s., B-1.92, A×B-1.54				A-2.40, B-1.92, A×B 2.02				A-0.47, B-0.29, A×B-0.37			
	foliar fertilizer of sulphur															
0	31.81	33.02	32.00	32.31	32.20	33.08	32.32	32.50	32.02	32.61	32.30	32.51	32.01	32.90	32.21	32.37
60	32.30	34.60	36.33	34.41	32.61	34.92	36.59	34.71	32.60	35.42	36.78	34.93	32.52	35.02	36.60	34.71
120	32.49	35.81	36.77	35.02	32.80	36.21	37.28	35.43	33.00	36.20	37.84	35.68	32.81	36.11	37.30	35.41
180	33.41	36.80	38.20	36.14	34.19	37.00	38.21	36.47	34.41	37.33	38.71	36.82	34.00	37.03	38.40	36.48
Mean	32.50	35.01	35.80	34.45	32,95	35.30	36.10	34.78	33.01	35.39	36.41	34,91	32.84	35.27	36.13	34.75
$LSD_{p<0.05}$	A-3.09, B-2.40, A×B-1.76				A-2.88, B-2.25, A×B-n.s.				A-3.04, B-2.56, A×B-2.23				A-0.48, B-0.32, A×B-0.43			

n.s.– not significant; A^+ – nitrogen fertilization; B^{++} – sulphur fertilization

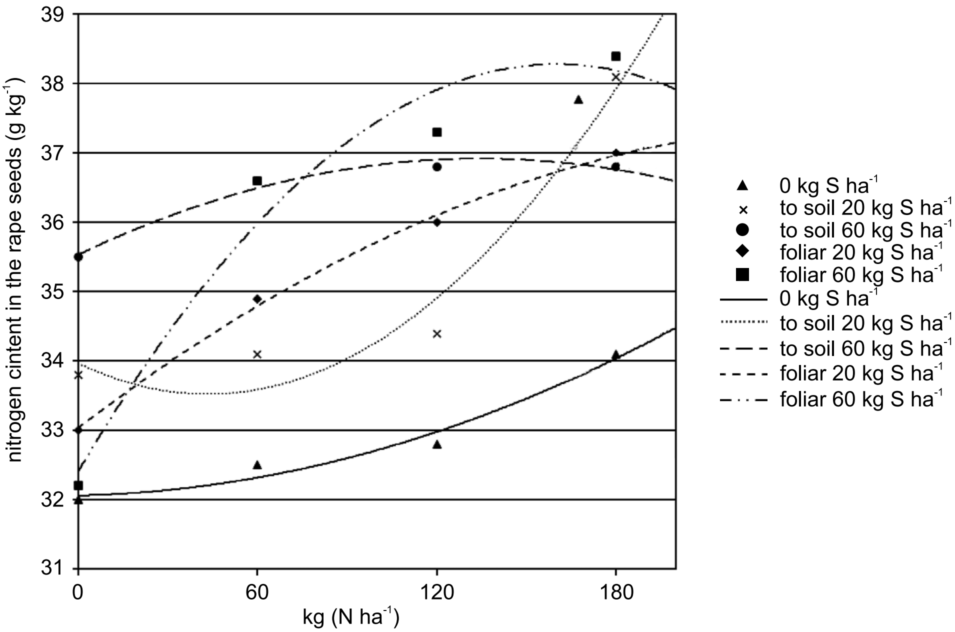

Fig. 1. Relationship between the nitrogen content in seeds of spring rapeseed and fertilization with nitrogen and sulphur - means for three years

by 10.9%). In the treatment with foliar application of sulphur, only the dose of 20 kg S ha^{-1} significantly increased the nitrogen content (on average by 2.8%). The highest content of this element in the rapeseeds, on average for the three years of the study, was obtained following the combined application of 180 kg N ha^{-1} and 20 kg S ha^{-1} (soil application) or 180 kg N ha^{-1} and 60 kg S ha^{-1} (foliar application). The beneficial effect of sulphur fertilization on the nitrogen content is illustrated by regression curves (Figure 1), the lowest line corresponds to the control, and the highest lines to the soil and foliar application of 60 kg S ha^{-1}. The effect of fertilization with nitrogen and sulphur on the accumulation of nitrogen in plants of the *Brassicaceae* family, in both the vegetative parts and the seeds, has been confirmed by Tomar, Singh (2007) and Jan et al. (2010). The beneficial effect of sulphur on the nitrogen content results from the fact that it is a component of numerous important nitrogen compounds, i.e. protein amino acids (methionine, cystine and cysteine), which play a key role in the formation of the secondary and tertiary structure of proteins. The primary product of the incorporation of sulphur into organic compounds in the plant is cysteine, which is the precursor of other sulphur amino acids (Gaj, Klikocka 2011, Wielebski 2015), and also takes part in the formation of the active centre of numerous enzymes (De Kok et al. 2003).

Over 90% of the total sulphur accumulated in plants is estimated to be in the form of sulphur amino acids (Gaj, Klikocka 2011). Sulphur exerts a strong effect on nitrogen metabolism (De Kok et al. 2003, Jamal et al. 2010), in particular by increasing the rate at which nitrogen taken up by the plant is transformed into protein (Rice 2007). Sulphur-containing ferredoxin has an important role in this process. The mean sulphur content in the spring rapeseeds, depending on the year and the means of sulphur application, ranged from 10.4 to 10.6 g kg^{-1} (Table 3). Accumulation of this element in the seeds of *Brassicaceae* is much greater than in the seeds of other species. For example, spring barley grain contains 1.05-1.13 g kg^{-1} of sulphur and narrow-leafed lupine contains 2.26-3.44 g kg^{-1} (Barczak 2010). The sulphur content in triticale grain is 1.40-1.76 g kg^{-1}, in potato tubers 1.21-1.37 g kg^{-1} (Klikocka, Sachajko 2011), and in maize grain 0.76-0.86 g kg^{-1} (Filipek-Mazur et al. 2013). The significantly highest content of this element in rapeseeds results not only from its high protein content, but also from the presence of sulphur-rich glucosinolates, which are secondary metabolites. The sulphur content in crops, besides genetic factors, is determined by the content of its available forms in the soil, by moisture and temperature conditions, and by the plantation's proximity to industrial and urban centres (Gaj, Klikocka 2011).

The most important nutrient influencing sulphur function in the plant is nitrogen (Jamal et al. 2010, Siaudinis 2010, Przygocka-Cyna, Grzebisz 2017, Varenyiova et al. 2017). Fertilization with nitrogen alone had no significant effect on the sulphur content in rapeseeds in any year of the study. However, a slight reduction in the sulphur content was observed in both sulphur application treatments. While the amount of nitrogen applied increased – in both the plants fertilized with nitrogen alone and in combination with sulphur (Figure 2) – differences with respect to the control were not confirmed statistically.

Both soil and foliar application of sulphur without nitrogen significantly affected the sulphur content in the rapeseeds. In each year of the study, even the dose of 20 kg S ha^{-1} caused a significant increase with respect to the control: for each application variant, the difference was 13.4% on average. It was only in the third year of the study that a significant difference was noted between the effect caused by 20 and 60 kg S ha^{-1}; it was 4.4-4.5% on average for both methods of sulphur application. The content of this element in the seeds of rape plants fertilized with both nitrogen and sulphur was higher overall than in the seeds of plants fertilized with nitrogen alone, and lower than in the seeds of plants fertilized with sulphur alone. In contrast to the study by Podleśna (2013) on winter rapeseed, no marked effect of the methods of sulphur application was noted on its content in the seeds of spring rape in any year of the study.

The difference in the content of sulphur in the seeds from the treatments with both N and S versus its content in the seeds of plants grown without sulphur and nitrogen reached 12.4% in the case of soil application and 17.5% in the case of foliar application. The data obtained in this study confirm the results of another investigation, where the sulphur content in crops was

Table 3

Sulphur content in spring rape seeds (g kg^{-1})

(kg N ha^{-1}) – A^{+}	Years of study												Average from years			
	I				II				III							
	(kg S ha^{-1}) – B^{++}			mean	(kg S ha^{-1}) – B^{++}			mean	(kg S ha^{-1}) – B^{++}			mean	(kg S ha^{-1}) – B^{++}			mean
	0	20	60		0	20	60		0	20	60		0	20	60	
	soil fertilizer of sulphur															
0	9.61	10.40	11.10	10.37	9.70	11.41	11.89	11.00	9.72	11.21	11.90	10.94	9.72	11.00	11.61	10.78
60	9.63	10.91	11.10	10.55	9.70	10.40	11.05	10.38	9.61	10.60	11.62	10.61	9.60	10.61	11.22	10.48
120	9.50	10.51	11.11	10.37	9.82	10.50	10.91	10.41	9.50	10.30	11.51	10.44	9.60	10.40	11.22	10.41
180	9.51	10.51	11.00	10.34	9.41	10.50	10.82	10.24	9.71	10.33	10.89	10.31	9.50	10.40	10.89	10.26
Mean	9.56	10.58	11.10	10.41	9.66	10.70	11.17	10.51	9.64	10.61	11.48	10.58	9.61	10.60	11.24	10.48
$LSD_{(p<005)}$	A-n.s., B-0.75, A×B-n.s.				A-n.s., B-0.60, A×B-n.s.				A-0.49, B-0.55, A×B -0,67				A-0.45, B-0.30, A×B-0,28			
	foliar fertilizer of sulphur															
0	9.61	10.81	10.91	10.44	9.70	11.11	11.63	10.81	9.72	11.01	11.72	10.82	9.70	11.01	11.41	10.71
60	9.61	11.11	11.20	10.64	9.70	10.82	11.40	10.64	9.61	10.91	11.61	10.71	9.61	10.89	11.41	10.70
120	9.50	10.89	11.20	10.53	9.82	10.70	10.81	10.44	9.50	10.55	11.70	10.58	9.61	10.71	11.20	10.51
180	9.50	10.72	11.11	10.44	9.41	10.70	10.81	10.31	9.72	10.40	11.40	10.51	9.50	10.63	11.11	10.41
Mean	9.56	10.88	11.11	10.52	9.66	10.83	11.16	10.55	9.64	10.72	11.61	10.66	9.61	10.81	11.28	10.57
$LSD_{(p<0,05)}$	A-n.s., B-0.48, A×B-n.s.				A-0.59, B-0.55, A×B-0.49				A-n.s., B-0.41, A×B-n.s.				A-n.s., B-0.26, A×B-n.s.			

n.s. – not significant; A^{+} – nitrogen fertilization; B^{++} – sulphur fertilization

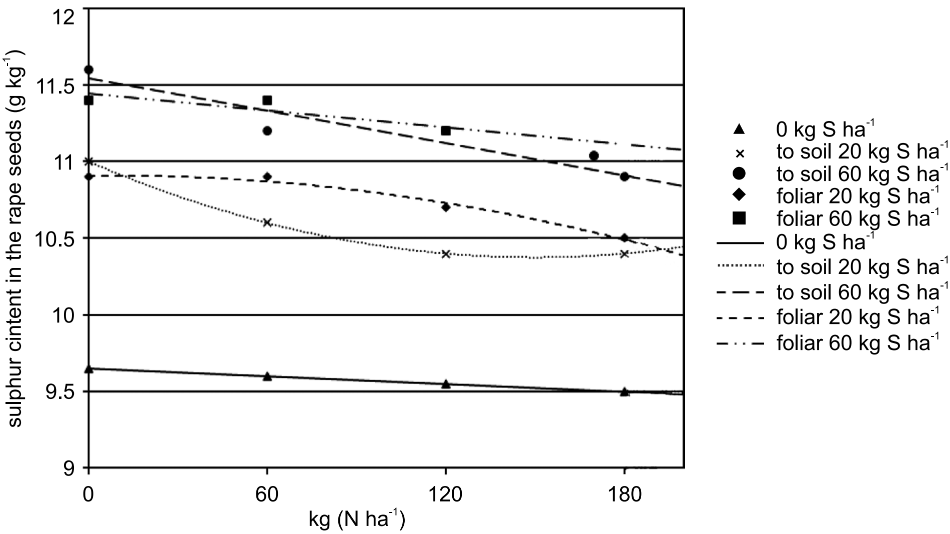

Fig. 2. Relationship between the sulphur content in seeds of spring rapeseed and fertilization with nitrogen and sulphur - means for three years

determined to be a consequence of its availability in the environment (Klikocka, Sachajko 2011, Podleśna 2013). The rate of absorption of sulphur from the soil solution and its physiological efficiency are affected not only by the content of sulphates (VI) in the environment but also by the efficiency of their assimilation and transport from the root system to the stem, mainly through the xylem (Rice 2007).

Numerous studies (Mathot et al. 2009, Jan et al. 2010, Siaudinis 2010, Filipek-Mazur et al. 2013, Barczak et al. 2016) indicate a strong interaction of sulphur and nitrogen as fertilizer components essential for the synthesis of amino acids, which in turn are components of proteins. A measure of the interaction between these nutrients is the N:S ratio, which is considered an important indicator of sulphur supply to plants (Zhao et al. 1997. Rice 2007, Mathot et al. 2009). In the seeds of the spring rape grown in this experiment, this average ratio averaged 3.3:1 (Table 4), and was much lower than in potato tubers (10.4-12.4:1) – Klikocka, Sachajko (2011), peas (15:1) – Gaines, Phatak (1982) and grassland biomass (9.2-12.6:1) – Grygierzec et al. (2015). Cereal grains generally have a higher N:S ratio than rapeseeds (Barczak 2010, Jamal et al. 2010, Klikocka, Sachajko 2011, Filipek-Mazur et al. 2013). The low value of this ratio in the seeds of spring rape is due to their high content of sulphur, which is a consequence of the significantly higher uptake of this nutrient by plants of the *Brassicaceae* family than by oilseed plants, potatoes, grasses and cereals. Przygocka-Cyna and Grzebisz (2017) emphasizes that the lower the value of this ratio, the more efficiently the plant metabolizes nitrogen, which in crop production is reflected by higher yield.

Table 4

N:S in spring rape seeds

Dose (kg N ha^{-1})	Years of study												Average from years			
	I				II				III							
	(kg S ha^{-1})			mean	(kg S ha^{-1})			mean	(kg S ha^{-1})			x	(kg S ha^{-1})			mean
	0	20	60		0	20	60		0	20	60		0	20	60	
	soil fertilizer of sulphur															
0	3.31:1	3.23:1	3.17:1	3.22:1	3.32:1	2.96:1	2.98:1	3.07:1	3.30:1	3.04:1	3.01:1	3.12:1	3.30:1	3.07:1	3.06:1	3.13:1
60	3.36:1	3.10:1	3.29:1	3.26:1	3.36:1	3.28:1	3.33:1	3.31:1	3.40:1	3.26:1	3.17:1	3.27:1	3.39:1	3.23:1	3.27:1	3.28:1
120	3.42:1	3.25:1	3.29:1	3.31:1	3.35:1	3.30:1	3.38:1	3.34:1	3.47:1	3.37:1	3.22:1	3.36:1	3.42:1	3.32:1	3.29:1	3.34:1
180	3.52:1	3.60:1	3.32:1	3.49:1	3.64:1	3.64:1	3.41:1	3.57:1	3.55:1	3.71:1	3.39:1	3.54:1	3.58:1	3.65:1	3.38:1	3.52:1
Mean	3.39:1	3.28:1	3.26:1	3.32:1	3.40:1	3.40:1	3.25:1	3.32:1	3.44:1	3.34:1	3.18:1	3.30:1	3.42:1	3.31:1	3.22:1	3.31:1
	foliar fertilizer of sulphur															
0	3.31:1	3.05:1	2.94:1	3.11:1	3.32:1	2.98:1	2.78:1	3.01:1	3.30:1	2.96:1	2.76:1	3.01:1	3.30:1	2.99:1	2.82:1	3.04:1
60	3.36:1	3.12:1	3.24:1	3.25:1	3.36:1	3.23:1	3.21:1	3.24:1	3.40:1	3.25:1	3.17:1	3.26:1	3.39:1	3.21:1	3.21:1	3.24:1
120	3.42:1	3.28:1	3.29:1	3.33:1	3.35:1	3.38:1	3.45:1	3.40:1	3.47:1	3.45:1	3.23:1	3.37:1	3.42:1	3.37:1	3.33:1	3.37:1
180	3.52:1	3.44:1	3.46:1	3.48:1	3.64:1	3.46:1	3.54:1	3.54:1	3.55:1	3.59:1	3.39:1	3.50:1	3.58:1	3.49:1	3.46:1	3.51:1
Mean	3.39:1	3.21:1	3.23:1	3.28:1	3.40:1	3.25:1	3.23:1	3.28:1	3.44:1	3.31:1	3.15:1	3.30:1	3.42:1	3.27:1	3.19:1	3.27:1

The N:S ratio in the rapeseeds was highly stable in the years of the study, with values ranging from 3.28 to 3.32:1. The fertilizers significantly affected the N:S value. Application of nitrogen alone caused an increase of this ratio in the seeds, on average from 3.30:1 (control) to 3.58:1 (180 kg N ha^{-1}). Application of sulphur without nitrogen decreased the value of the ratio to 3.06:1 in the case of soil application and to 2.82:1 in the case of foliar application. The highest N:S value (3.65:1) was obtained for the combination of 180 kg N ha^{-1} and 20 kg S ha^{-1} in the treatment with soil application of sulphur.

Application of nitrogen alone or with sulphur (180 kg N ha^{-1} + 20 kg S ha^{-1} and 180 kg N ha^{-1} + 60 kg S ha^{-1}) caused changes in the N:S ratio towards values considered optimal for rapeseeds, which is 4-5:1 according to Przygocka-Cyna and Grzebisz (2017) and 5:1 according to Zhao et al. (1997). This may be significant in assessment of the fodder value of rapeseed, which can be processed to extraction meal, a valuable component of concentrate feed for growing cattle.

In conclusion, little variation was noted between growing seasons in the content of nitrogen and sulphur in the seeds of spring rape. In treatments with the application of nitrogen alone (without sulphur), an increase in the application dose (kg N ha^{-1}): 60, 120 and 180) was generally accompanied by a significant increase in the content of this element in seeds in each growing season, while the sulphur content was stable. The highest nitrogen content in the seeds of plants fertilized with sulphur alone (without nitrogen) was obtained using 60 kg S ha^{-1} in the case of soil application and 20 kg S ha^{-1} in the case of foliar application. In every year of the study, the highest nitrogen content in the seeds from plants submitted to the foliar application of sulphur was obtained in response to the highest levels of the nutrients (180 kg ha^{-1} N and 60 kg S ha^{-1}), whereas in the case of soil application the optimum combination was 180 kg ha^{-1} N and 20 kg S ha^{-1}. The sulphur content in the seeds of plants fertilized with both nitrogen and sulphur was generally significantly higher than in the seeds of plants fertilized with nitrogen alone, and lower than in the seeds of plants fertilized with sulphur alone. The highest N:S ratios were obtained in the seeds of plants fertilized with nitrogen alone, and the lowest - following the application of sulphur alone. Application of nitrogen and nitrogen together with sulphur caused an increase of the ratio towards the optimal values for fodder crops. The methods of sulphur application did not significantly affect its content in the rapeseeds or the N:S ratio.

CONCLUSIONS

Application of nitrogen (kg N ha^{-1}: 0, 60, 120 and 180) and sulphur (kg S ha^{-1}: 0, 20 and 60) fertilization in a three-year field experiment carried out on degraded black soil with low sulphur content generally resulted in slight differences in the content of nitrogen and sulphur and in their proportions (N: S) in spring rapeseed. Fertilization with single fertilizing components, as well as their combined use, resulted in an increase in the content of a given ingredient in seeds. The consequence of nitrogen application, as well as the combined use of nitrogen and sulphur, was the broadening of the N:S ratio towards optimal values for crops grown for fodder use. The method of using sulphur (soil and foliar fertiliser) did not significantly affect the content of this element in spring rapeseed seeds or the N: S ratio value.

REFERENCES

Barczak B. 2010. *Sulphur as a nutrient determining the yield size and quality of selected crop species.* University of Technology and Science Publications, in Bydgoszcz, Poland, 144: 1-131. (in Polish)

Barczak B., Skinder Z., Piotrowski R. 2016. *Sulphur as a factor that affects nitrogen effectiveness in spring rapeseed agrotechnics.* Part II. Yield of seeds and protein. Acta Sci. Pol., Agric. 15(4): 3-14.

De Kok L.J., Castro A., Durenkamp M., Stuiver C. E., Westerman S. et al. 2003. *Sulphur in plant physiology.* Fert. Fertil., 2: 55-80.

Filipek-Mazur B., Lepiarczyk A., Tabak M. 2013. *Effect of nitrogen and sulphur fertilization on yield and chemical composition of maize grain.* II. *Nitrogen and sulphur content.* Fragm. Agron., 30(4): 29-35. (in Polish)

Gaines T.P., Phatak S.C. 1982. *Sulphur fertilization effects on the constancy of the protein N:S ratio in low and high sulphur accumulating crops.* Agron. J., 74: 415-418. DOI: 10.2134/ /agronj1982.00021962007400030004x

Gaj R., Klikocka H. 2011. *Multifunctional sulphur effect in plants – from nutrition to protection.* Prog. Plant Prot, 51(1): 33-44. (in Polish)

Grygierzec B., Luty L., Musiał K. 2015. *The efficiency of nitrogen and sulphur fertilization on yield and value of N:S ratio for Lolium × boucheanum.* Plant Soil Environ, 61(3): 137-143. DOI: 10.17221/1005/2014-PSE

Institute of Plant Protection https://www.ior.poznan.pl

IUSS Working Group WRB. 2015. *World reference base for soil resources 2014. International soil classification system for naming soils and creating legends for soil maps.* Update 2015. World Soil Resources Report 106. FAO, Rome, Italy. http://www.fao.org/3/i3794en/I3794en.pdf

Jamal A., Moon Y., Abdin M. 2010. *Sulphur – a general overview and interaction with nitrogen.* Austr. J. Crop Sci, 4(7): 523-529.

Jan A., Ahmad G., Arif M., Jan M.T., Marwat K.B. 2010. *Quality parameters of canola as affected by nitrogen and sulfur fertilization.* J. Plant Nutr, 33(3): 381-390. http://dx.doi.org/10.1080/01904160903470430

Klikocka H., Sachajko J. 2011. *Comprehensive evaluation of potato and spring triticale cultivation technology*. Acta Agroph, 195(4): 1-129. (in Polish)

Mathot M., Thélier-Huchéb L., Lambert R. 2009. *Sulphur and nitrogen content as sulphur deficiency indicator for grasses.* Eur. J. Agron., 30: 172-176. http://doi.org/10.1016/j.eja.2008.09.004

Mrówczynski M., Pruszyński S. 2008. *Integrated production of winter and spring oilseed rape. Multiannual program* 2006-2010. Poznań, Poland, Institute of Plant Protection. (in Polish)

Podleśna A. 2013. *Studies on the role of sulfur in shaping the mineral management, yield volume* *and yield quality by selected crops*. Monographs and Scientific Dissertations, 37, Institute of Soil Science and Plant Cultivation – State Research Institute, Puławy, Poland (in Polish)

Przygocka-Cyna K., Grzebisz W. 2017. *Sulphur balance in Poland – regional analysis*. Fragm. Agron. 34(1): 60-75.

Rice R. 2007. *The physiological role of minerals in the plant*. In: *Mineral Nutrition and Plant Disease*. Datnoff L.E. Elmer W.E., Huber D.M., (ed). St. Paul, Minnesota, USA, The American Phytopathological Society, 9-30.

Rudko T. 2011. *Cultivation of winter oilseed rape. Rape. Principles of cultivation*. Lublin, Poland, Institute of Agrophysics. (in Polish)

Scherer H.W. 2001. *Sulphur in crop production – invited paper*. Eur. J. Agron.,14: 81-111. doi.org/10.1016/S1161-0301(00)00082-4

Siaudinis G. 2010. *Effect of nitrogen and sulphur fertilization on the elemental composition and seed quality of spring oilseed rape*. Zemdirbyste – Agriculture, 97(4): 47-56. http://www.lzi.lt/ /tomai/97(4)tomas/97_4_tomas_str5.pdf

Siebielec G., Smreczak B., Klimkowicz-Pawlas A., Kowalik M., Kaczyński R. et al. 2017. *Report on the third stage of commissioned research 'Monitoring of chemism of arable soils in Poland in 2015-2017'*. Institute of Soil Science and Plant Cultivation – State Research Institute, Puławy, Poland. (in Polish)

Skwierawska M., Benedycka Z., Jankowski K., Skwierawski A. 2016. *Sulphur as a fertiliser component determining crop yield and quality*. J. Elem., 21(2): 609-623. DOI: 10.5601/jelem. 2015.20.3.992

Stern D. 2005. *Global sulphur emissions from 1850 to 2000*. Chemosphere, 58: 163-175. doi.org/ /10.1016/j.chemosphere.2004.08.022/

Tomar S.K., Singh K. 2007. *Response of Indian mustard (Brassica juncea) to nitrogen and sulphur fertilization under rainfed condition of Diara land*. Int. J. Agric. Sci., 3(2): 5-9.

Tys J., Jackowska I., Rybacki R. 2006. *Technological value of different varieties of rapeseed developed for bio-diesel*. Acta Agroph., 8(4): 1017-1030.

Varenyiova M., Ducsay L., Ryant P. 2017. *Sulphur nutrition and its effect on yield and oil content of oilseed rape (Brassica napus* L.). Acta Univ. Agric. Silvic., 65(2): 555-562. https://doi. org/10.11118/actaun201765020555

Wielebski F. 2015. *The role of sulphur as a factor affecting quantity and quality of yield of winter oilseed rape*. Oilseed Crops, 36: 39-59. DOI: 10.5604/12338273.1194981

Zhao F.J., Bilsborrow P.E., Evans E.J., McGrath S.P. 1997. *Nitrogen to sulphur ratio in rapeseed and rapeseeds protein and its use in diagnosing sulphur deficiency*. J. Plant Nutr, 20: 549-558. https://doi.org/10.1080/01904169709365273