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ORIGINAL PAPER

EFFECT OF SULFUR-CONTAINING FERTILIZERS ON THE QUANTITY AND QUALITY OF SPRING OILSEED RAPE AND WINTER WHEAT YIELD*

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Abstract

Sulfur deficiency in soils is one of the most important problems of contemporary agriculture. Balanced fertilization (which means fertilization adjusted to plant requirements, soil properties, and weather conditions) is essential for maximizing yield, while simultaneously maintaining its high quality. The aim of a two-year field experiment was to determine the effect of sulfur fertilization on the yield quantity and quality. Two plants differing in sulfur requirements were cultivated: spring oilseed rape (first year of the research) and winter wheat (second year). During each year, sulfur was added at two levels of intensity (single dose and double dose), in the form of two mineral fertilizers containing sulfate sulfur (A: ammonium sulfate; B: a mixture of ammonium nitrate and ammonium sulfate) and one fertilizer containing elemental sulfur (C). A single dose of sulfur for spring oilseed rape and winter wheat amounted to 25 kg ha^{-1} and 12.5 kg ha^{-1}, respectively, and a double dose equalled 50 kg ha^{-1} and 25 kg ha^{-1}, respectively. Sulfur doses were adjusted to the requirements of the plants. The plants were harvested at full maturity. Dry matter yield of rape seeds and wheat grains was determined, and quality analyses were conducted. Fertilizer C had the lowest and fertilized B showed the highest yield-forming effect. Sulfur fertilization did not considerably affect the fatty acid content in spring rape seeds but increased the glucosinolate content. The highest content of compounds that form vitamin E was shown in seeds after fertilization with a double dose of sulfur. The starch content in winter wheat grains decreased after sulfur fertilization, but the gluten content increased. The lowest activity of amylolytic enzymes was found in grains of plants fertilized with a double dose of elemental sulfur.

Keywords: sulfur, fatty acids, glucosinolates, tocopherols, tocotrienols, gluten, starch.

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INTRODUCTION

Sulfur plays crucial functions in physiological processes (Skwierawska et al. 2016). It is a component of amino acids and is involved in enzymatic and redox processes in cells (Kopriva 2014). A reduction in yield quantity and quality (e.g. an increase in the content of non-protein nitrogen) occurs under conditions of sulfur deficiency (Tunçtürk et al. 2011, Sager 2012). Moderate sulfur doses (at which plants show the highest photosynthetic activity) are best for plants. Plants of *Brassicaceae* family (e.g. oilseed rape) are particularly sensitive to sulfur deficiency, but also cereal plants, especially wheat, increase the quantity and quality of grain yield after sulfur application. Plants take up sulfur from the soil solution mostly as sulfates. They can also take up sulfur from the air, in the form of sulfur dioxide (SO_2). Sulfur absorbed this way is important only in industrial areas, where SO_2 is an air pollutant (Hřivna et al. 2001, Lošák et al. 2011, Skwierawska et al. 2016).

In Poland, similarly to many countries of Central and Western Europe, systematic reduction in the amount of sulfur returning onto soil surface has been observed since the 1990s (Eurostat). As a result, most agricultural soils have a low content of sulfates, which is one of the most important problems of contemporary agriculture (Scherer 2009, Degryse et al. 2017, Monitoring… 2019).

The aim of the research was to determine the effect of fertilization with sulfur (sulfate and elemental) on the quantity and quality of yield of spring rape seeds and of winter wheat grains.

MATERIAL AND METHODS

A field experiment was carried out in 2012-2013 at the experimental station of the University of Agriculture, located in Krakow-Mydlniki (N 50.091568, E 19.857655). The experiment was established on typical brown soil classified as good wheat complex, with the granulometric composition of silt loam. The soil had a slightly acid reaction, and a low content of sulfate and total sulfur, according to criteria given by Kabata-Pendias et al. (1995).

The experiment, conducted in a randomized block design, comprised eight treatments in four replications. Doses of nutrients were adjusted to the requirements of the test plants (Table 1). Sulfur was added at two levels of intensity (S1, S2), in the form of commercially available mineral fertilizers: ammonium sulfate (24% S), a mixture of ammonium nitrate and ammonium sulfate (13% S), and elemental sulfur (90% S). Nitrogen was

Table 1

Doses of nutrients in the field experiment (kg ha^{-1})

Test plant	N	P	K	S1	S2
Spring rape	100 + 40*	32.7	132.8	25	50
Winter wheat	80 + 40*	26.2	116.2	12.5	25

* fertilization at two dates

added in the form of ammonium nitrate and, in some of the treatments, partially with sulfur fertilizers (the first dose of nitrogen was applied on 4th April 2012 and 12th April 2013, the second dose – on 20th May 2012 and 14 May 2013). Phosphorus and potassium were added before sowing (20th October 2011 and 14th September 2012) in the form of enriched superphosphate and potassium chloride. Spring oilseed rape (*Brassica napus* L.) of the variety Markus (year 2012) and winter wheat (*Triticum aestivum* L.) of the variety Wydma (years 2012-2013) were the test plants. The crops were protected according to the principles of integrated plant protection. The weather conditions during the experiment are shown in Figure 1.

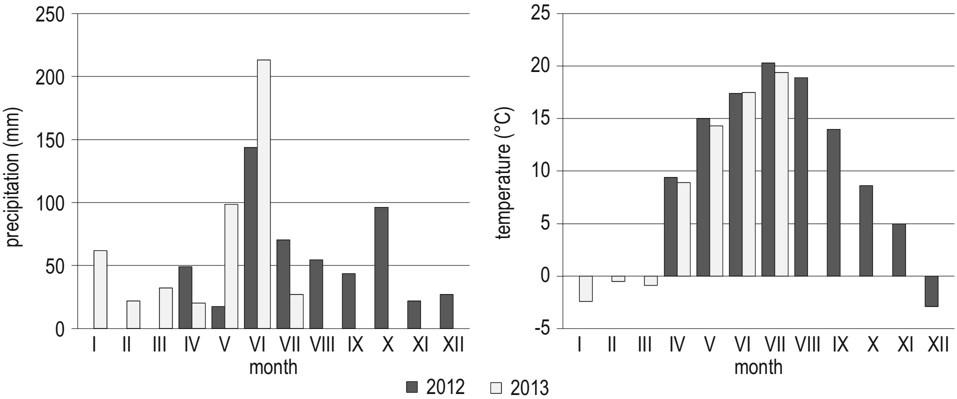

Fig. 1. Total atmospheric precipitation and mean air temperature in individual months of spring oilseed rape and winter wheat growth

Dry matter yield of oilseed rape seeds and wheat grains was determined after plant harvest. Laboratory analyses were conducted in the University of Agriculture in Krakow, and also in the National Research Institute of Animal Production in Aleksandrowice. Crude fat content in rape seeds was determined by the weight method, using a Büchi B-811 apparatus, and glucosinolate content was determined by the HPLC (high-performance liquid chromatography) method using a HPLC Agilent 1100 Series apparatus equipped with a UV detector, according to the procedure adopted in the accredited laboratory of the Institute of Animal Production in Krakow-Balice. The content of tocopherols (α, β, γ, δ) and tocotrienols ((α, β, γ, δ) in the rape seeds was determined by the HPLC method (Panfili et al. 2003), on an Agillent 1100 apparatus with a fluorescent detector. The content of fatty acids (palmitic, stearic, oleic, linoleic, linolenic) was determined by gas chromatography, according to PN-EN ISO 12966-2:2011. Starch content in wheat grains was determined by the enzymatic method (AOAC Method 996.11), while quantity and quality of wet gluten were determined by the Gluten Index method according to Perten, standard ICC No. 155 (PN-EN ISO 21415--2:2015), and determination of the falling number was done according to PN-EN ISO 3093:2010.

Results on yield quantity were subjected to a univariate analysis of variance. Significance of variance was determined by the Duncan's test ($\alpha \leq 0.05$), with the use of Statistica 10 software (StatSoft, Inc.).

RESULTS AND DISCUSSION

Amount of yield of oilseed rape seeds and wheat grain

The applied fertilization significantly influenced the amount of yield of rape seeds and wheat grains (Table 2). The fertilized plants gave significantly higher yield than the control plants (non-fertilized). Fertilization with a double dose of the mixture of ammonium nitrate and ammonium sulfate was the most beneficial (rape seed yield higher by 40% and wheat grain higher by 31%). Plant yield depended on the type of a fertilizer (including

Table 2

Oilseed rape seed and wheat grain yield

Treatment	Rape seed yield (Mg d.m. ha^{-1})	Wheat grain yield (Mg d.m. ha^{-1})
No fertilization (control)	4.31*a**	5.51*a*
NPK	5.51*cd*	6.59*b*
NPK + S1 (ammonium sulfate)	5.55*cd*	6.87*bc*
NPK + S1 (mixture of ammonium nitrate and ammonium sulfate)	5.74*de*	6.61*b*
NPK + S1 (elemental sulfur)	5.08*b*	6.63*b*
NPK + S2 (ammonium sulfate)	5.44*cd*	6.77*bc*
NPK + S2 (mixture of ammonium nitrate and ammonium sulfate)	6.02*e*	7.20*c*
NPK + S2 (elemental sulfur)	5.32*bc*	6.78*bc*

* Mean values in the columns marked with the same letters do not differ statistically significantly at a significance level $\alpha \leq 0.05$; according to the Duncan's test.

the chemical form of sulfur), and usually not on the applied sulfur dose. Hřivna et al. (2002) showed an increasing level of sulfur in soil as a result of sulfur fertilization and, due to this, an increase in winter rape seed yield.

Szulc et al. (2014) confirmed the purposefulness of sulfur fertilization of oilseed crops in regions of reduced industrial emissions and on soils with low sulfur availability. We observed a significant effect of fertilization on oilseed rape yielding, but the effect of the type of a fertilizer was stronger than the effect of increasing a sulfur dose from 25 kg to 50 kg ha^{-1}. Wielebski (2015) published that plants of the *Brassicaceae* family require sulfur doses of 40-80 kg S ha^{-1}, even though a study from 2011 showed that the effect of doses of 15-30 kg S ha^{-1} was not worse than the effect of 60 kg S ha^{-1}. Eriksen, Mortensen (2002) point to a beneficial effect of sulfur fertilization on the quantity and quality of cereal yield. The sulfur dose of 12.5 kg ha^{-1} applied in our research was sufficient to achieve a good wheat yield. Lepiarczyk et al. (2013) also showed that higher doses did not improve the production effect. The relatively good sulfur supply in wheat that we observed, even in the treatment fertilized only with NPK, can be a result of a very good preceding crop (sulfur from spring rape post-harvest residues had time to partially mobilize because of favorable hydrothermal conditions). Klikocka et al. (2016) showed an increase in grain yield of spring wheat cultivated on soil with low sulfur content and fertilized with 50 kg S ha^{-1} in combination with nitrogen doses ranging from 40 kg to 120 kg ha^{-1}. Withers et al. (1997) obtained the highest increase in spring barley yield after application of 10 kg S ha^{-1}, but they recommend doses even twice as high as economically justified. A positive effect on the increase in winter wheat grain yield due to sulfur fertilization was also confirmed by Xie et al. (2017).

Oilseed rape seed quality

Seeds of non-fertilized oilseed rape had the highest fat content (413 g kg^{-1} d.m.), which was a result of the concentration in a relatively small yield (Table 3). Among the fertilized treatments, seeds of rape fertilized with a double dose of elemental sulfur and a single dose of the mixture of ammonium nitrate and ammonium sulfate had the highest fat content. Rape seeds contained the most oleic acid (63.5-64.2%), followed by linoleic (21.0-21.6%), and the lowest amount of stearic acid (1.76-1.84%). No clear relationship between the applied fertilization and the profile of fatty acids was found.

Fertilization with mineral fertilizers without sulfur caused a 25% decrease in the glucosinolate content in rape seeds compared with the control, where that content was 11.4 mmol kg^{-1} d.m. (Table 3). Seeds of plants fertilized with sulfur contained 10-48% more glucosinolates than seeds of rape fertilized with mineral fertilizers without sulfur.

The highest total content of vitamin E constituents (462-540 mg kg^{-1} d.m.)

Table 3

Qualitative parameters of rape seeds

Treatment	Fat content (g kg^{-1} d.m)	Fatty acid content (%)					Glucosinolate content (mmol kg^{-1} d.m.)
		palmitic	stearic	oleic	linoleic	linolenic	
No fertilization (control)	413	4.47	1.80	64.24	21.01	8.48	11.4
NPK	392	4.52	1.81	63.74	21.42	8.50	8.6
NPK + S1 (ammonium sulfate)	382	4.50	1.78	64.07	21.09	8.56	12.2
NPK + S1 (mixture of ammonium nitrate and ammonium sulfate)	391	4.55	1.78	63.71	21.37	8.40	10.0
NPK + S1 (elemental sulfur)	377	4.59	1.82	63.47	21.55	8.57	12.7
NPK + S2 (ammonium sulfate)	384	4.48	1.76	63.68	21.40	8.68	9.5
NPK + S2 (mixture of ammonium nitrate and ammonium sulfate)	389	4.54	1.84	63.99	21.12	8.51	9.6
NPK + S2 (elemental sulfur)	396	4.55	1.82	64.11	21.06	8.46	11.3

was found in seeds of rape fertilized with a double dose of both sulfur forms and with a single dose of elemental sulfur (Figure 2). In relation to control seeds, there was a 58% increase in the content of α-tocopherol in the seeds of plants fertilized with a single dose of elemental sulfur, a 61% increase in the seeds of plants fertilized with a double dose of ammonium sulfate, and as much as an 81-82% increase in the seeds of plants fertilized with a double dose of elemental sulfur and a mixture of ammonium nitrate and ammonium sulfate. Seeds of rape fertilized with both doses of elemental sulfur and a double dose of sulfate sulfur also contained the most γ-tocopherol (20-42% more than in control seeds). A reverse relationship was observed in the case of the β-tocopherol content. The highest amount was found in seeds of non-fertilized plants, and fertilization, especially with a double dose of sulfur, led to a decrease in the content even by 30%. Variation in the δ-tocopherol content was low.

An effect of fertilization on the content of tocotrienols (especially β-tocotrienol) in rape seeds was also observed (Figure 2). Seeds of non-fertilized rape contained 2.8 mg β-tocotrienol in 1 kg d.m., whereas seeds of rape fertilized with both doses of elemental sulfur and a double dose of sulfate sulfur contained 8-10 times more of the compound. As a result, the percentage of toco-

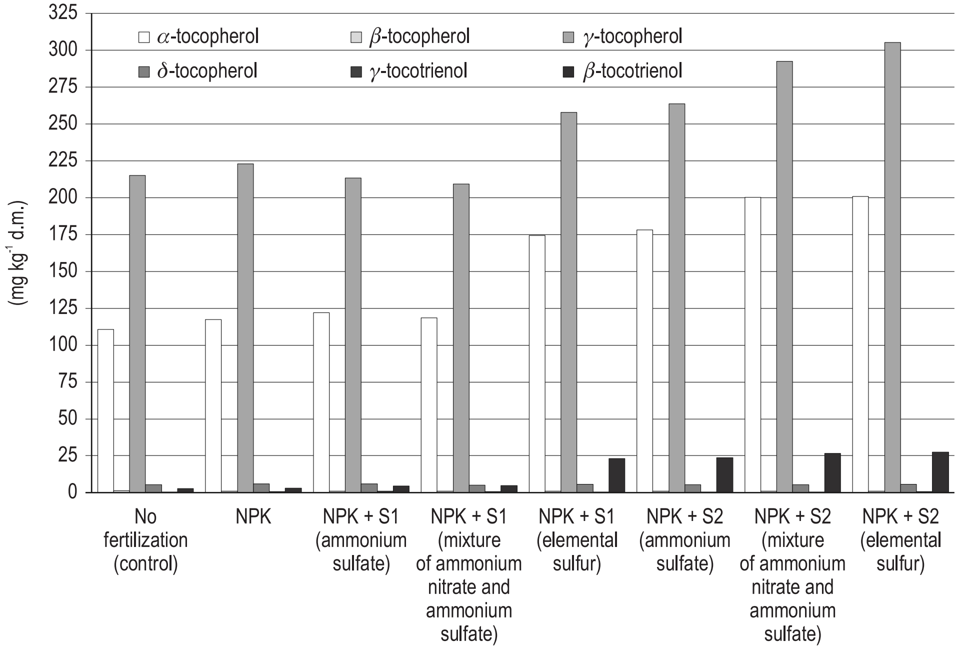

Fig. 2. Tocopherol and tocotrienol content in oilseed rape seeds

trienols in the group of compounds that form vitamin E increased by approximately 4%. No α- and δ-tocotrienols were detected.

The fat content in rape seeds is the fundamental criterion of their applicability in the oil industry. Rape oil is characterized by a low content of saturated acids, high content of oleic acid, and optimal share of linoleic and α-linolenic acids (Orsava et al. 2015). Fat content in rape seeds is conditioned genetically, but it depends also on methods of cultivation and harvest, fertilization, weather conditions. Krauze, Bowszys (2001) and Wierzbowska et al. (2012) showed an increase in the share of unsaturated fatty acids in fat after sulfur fertilization. We did not observe any clear relationship between the fertilization and the fatty acid profile. Šípalová et al. (2011) recorded no effect of combined nitrogen and sulfur fertilization on the linolenic acid concentration in camelina seeds. In our study, seeds of non-fertilized plants had the highest fat content, which was a result of its concentration in a small yield. Among the fertilized treatments, fertilization with a double dose of elemental sulfur and a single dose of the mixture of ammonium nitrate and ammonium sulfate gave the highest fat content. The positive effect of sulfur was also stated by Ahmad et al. (2007) and Lošák et al. (2010).

The glucosinolate content in plants depends primarily on genetic traits, but also on environmental conditions such as the available sulfur content in soil (De Pascale et al. 2007). Sulfur fertilization can increase the glucosinolate content in oilseed rape seeds (Ahmad et al. 2007), which is undesirable for double improved rape varieties. Wielebski, Wójtowicz (2003) showed that sulfur fertilization caused mainly an increase in the content of alkene glucosinolates, whereas Figas (2009) showed a tendency of increasing the total content of glucosinolates and content of alkene glucosinolates, particularly progoitrin, gluconapin and glucobrassicanapin. Rape seeds belong to the richest sources of vitamin E-active substances (tocochromanols). Their content depends mostly on soil and weather conditions as well as seed maturity (Dolde et al. 1999). We found that elemental sulfur (regardless of a dose) and other sulfur-containing fertilizers (at an increased dose) increased the content of tocopherols and tocotrienols in oilseed rape seeds. In the group of compounds that constitute vitamin E, tocotrienols are frequently considered as unimportant because their quantity is much smaller. Photosynthetically inactive parts (seeds) contain more α-tocopherol, which effectively protects polyene fatty acids against oxidation (Hofius, Sonnewald 2003). Results of recent studies point to the antineoplastic effect of tocotrienols and their ability to decrease the cholesterol level (Aggarwal et al. 2010). Similarly to tocopherols, tocotrienols support fertility (Khanna et al. 2005) and provide antioxidant protection to living cells (Serbinova et al. 1991). When applied locally, they protect skin from damage caused by the UVB dose causing erythema (Pedrelli 2012). Tocotrienols have 40-60 times stronger antioxidant properties than tocopherols (Serbinova et al. 1991).

Wheat grain quality

Starch content in control grains reached 635 g kg^{-1} and was several percent higher than in the fertilized plants (Table 4). Sulfur fertilization increased the gluten content in grains, the highest amount of which (231 g kg^{-1}) was recorded after the application of a single dose of ammonium sulfate. However, increasing the dose of ammonium sulfate and elemental sulfur decreased the gluten content. Gluten index ranged from 93 to 100 and was the highest for grains of non-fertilized plants and plants fertilized with a double dose of elemental sulfur. The lowest activity of amylolytic enzymes was found in grains of plants fertilized with a double dose of elemental sulfur (falling number amounted to 380 s), and the highest one occurred in grains of plants fertilized with mineral fertilizers without sulfur and with a double dose of the mixture of ammonium nitrate and ammonium sulfate (249-250 s). Doubling the sulfate sulfur dose increased the activity of amylolytic enzymes.

Technological value of wheat grains depends primarily on genetic traits of a cultivar, but agricultural practice (including fertilization) is also important. In our study, the starch content in winter wheat grains was 590-635 g kg^{-1}. A similar starch content (601-648 g kg^{-1}) was recorded by Erekul et al. (2012), pointing to a negative relationship between the content of starch and protein in cereal grains.

In our study, the value of gluten content in wheat grains was lower than

Table 4

Qualitative parameters of wheat grain

Treatment	Starch content (g kg^{-1})	Gluten content (g kg^{-1})	Gluten index	Falling number (s)
No fertilization (control)	635	22	100	304
NPK	605	137	93	249
NPK + S1 (ammonium sulfate)	609	231	93	329
NPK + S1 (mixture of ammonium nitrate and ammonium sulfate)	593	177	96	316
NPK + S1 (elemental sulfur)	590	203	95	304
NPK + S2 (ammonium sulfate)	593	185	96	296
NPK + S2 (mixture of ammonium nitrate and ammonium sulfate)	601	191	94	250
NPK + S2 (elemental sulfur)	605	175	98	380

250 g kg^{-1}, which is the minimum gluten content in bread flour. We showed a beneficial effect of sulfur fertilization, especially at a lower dose, on the gluten content and gluten index value, which confirmed the observations of Jarvan et al. (2008) and Erekul et al. (2012). The optimal gluten index is 75-90%, highlighting the influence of environmental conditions on this value (Pompa et al. 2009). We obtained higher values of this parameter.

The falling number lower than 150 s points to very high amylolytic enzyme activity, and such grains should not be used for production of baking flour. It is best when the falling number equals 250-350 s. An excessively high value of this parameter (over 400 s) may have a negative effect on bread baking (bread would not be properly raised). We obtained values of the falling number (249-380 s) confirming good grain quality. Fertilization with sulfur, especially with a double dose, caused an increase in the falling number, which does not correspond with the results of Erekul et al. (2012).

CONCLUSIONS

1. Fertilized spring oilseed rape and winter wheat plants generally had a significantly higher primary yield than non-fertilized plants. Among the applied sulfur-containing fertilizers, elemental sulfur had the weakest yield-forming effect, and the mixture of ammonium nitrate and ammonium

sulfate produced the strongest effect. The amount of oilseed rape seed yield depended on the type of a fertilizer used (including the chemical form of sulfur), and not on the applied sulfur dose. An increase in a sulfur dose led to obtaining significantly higher yield of wheat grains only in the case of fertilization with the mixture of ammonium nitrate and ammonium sulfate.

2. Among the plants fertilized with sulfur, seeds of oilseed rape fertilized with a double dose of elemental sulfur and a single dose of the mixture of ammonium nitrate and ammonium sulfate had the highest fat content. Sulfur fertilization did not have a considerable effect on the fatty acids content in seeds, and led to an increase in the glucosinolate content (compared with the fertilization with mineral fertilizers without sulfur). The highest content of compounds that constitute vitamin E was shown in seeds of oilseed rape fertilized with a double dose of sulfur.

3. The starch content in grains of fertilized winter wheat was lower than in the control. Grains of plants fertilized with sulfur contained much more gluten than grains of non-fertilized wheat and of wheat fertilized with mineral fertilizers without sulfur (the highest gluten content was found in grains of wheat fertilized with a single dose of ammonium sulfate). The lowest activity of amylolytic enzymes was found after fertilization with a double dose of elemental sulfur, and the highest – after fertilization with mineral fertilizers without sulfur.

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