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Research Article

Biofortification of Spring Barley Grain with Microelements through Sulfur Fertilization

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One means of enriching plants with microelements is agronomic biofortification, whereby the mineral composition of plants is stimulated through appropriate fertilization. A fertilizer component which has received much attention in recent years is sulphur. Due to the significant reduction in SO_2 emissions from industrial sources to the atmosphere, a progressive deficiency of this nutrient has been observed in soils in Poland and other parts of the world. Therefore, a study was undertaken to assess the effect of different application rates (20 and 40 $kg{\cdot}ha^{-1}$) and forms (elemental and ionic) of sulphur on the content of selected micronutrients (Mn, Fe, Zn, and Cu) and their proportions (Fe : Mn) in the grain of the Antek variety of spring barley. In a three-year single-factor field experiment setup on luvisols with low content of sulphur, the following fertilizers were tested: ammonium sulphate, potassium sulphate, and Wigor S (80% elemental sulphur and 20% bentonite). It was demonstrated that, in the fertilization of spring barley, supplementation of NPK with sulphur can be regarded as an agronobmic method of biofortification of grain with micronutrients because it beneficially affects the content of manganese, iron, zinc, and copper in the grain. An increase in the content of these micronutrients was found in the grain of plants fertilized with sulphur in comparison to plants that were not fertilized with this nutrient in each of the growing seasons. Ammonium sulphate, compared to the other fertilizers tested, had the greatest impact on the content and uptake of all micronutrients, with the exception of zinc. Marked differences in the effect of the application rates of 20 and 40 $kg{\cdot}S{\cdot}ha^{-1}$ were observed only for fertilizers containing the ionic form of sulphur. The beneficial effect of sulphur on the biofortification of microelements in spring barley grain indicates the need to include this nutrient in cultivation of this species.

1. Introduction

To maintain human health and well-being, at least 22 biogenic elements must be included in the diet [1], including zinc, manganese, copper, and iron [2, 3]. It is estimated that more than two billion people worldwide suffer from "hidden hunger" due to micronutrient deficiency [4]. A large portion of the human population does not take in enough of these elements with food because their diet is insufficiently varied and consists primarily of cereals. Among the widely available methods of supplementing micronutrient-deficit diets, we can distinguish supplementation of food products and feed and fortification of crops [1]. The HarvestPlus programme has been created to reduce hidden hunger by means of crop biofortification using genetic engineering methods [5]. The programme focuses on three critical nutrients recognized by the World Health Organization as the most limiting in diets: iron, zinc, and vitamin A. Another means of enriching plants with micronutrients is agronomic biofortification, involving stimulation of the mineral composition of plants through appropriate fertilization, which may resolve the problem of deficiencies in a safer and more economical manner. Wang et al. [3] suggest that the content of these elements in crops can be regulated by fertilization not only with micronutrients, but also with macronutrients, such as NPKMg and sulphur.

Due to its unique physiological role in plant metabolism, sulphur is considered one of the most important nutrients for plants. However, the literature data [6–9] clearly indicate that, at present, the soils of many regions of the world, including Poland [10], due to restrictions on emissions of industrial sulphur oxides to the atmosphere, contain too little available sulphur for correct plant growth. In Poland, monitoring of the nutrient content of arable soils showed that, in 2015, over 90% of soils had low sulphate content [11]. Symptoms of sulphur deficiency are observed not only in plant species with high requirements for this nutrient but also in those with relatively low sulphur requirements, which include spring barley. These conditions necessitate not only the inclusion of sulphur in the fertilization of crops but also research on the effects of such fertilization on the chemical composition of crops, including the content of micronutrients.

In view of the important role of sulphur in plant metabolism and the worsening sulphur deficiency in soils, a study was undertaken to assess the impact of varied sulphur application rates and forms on the content of selected micronutrients and their proportions in spring barley grain.

2. Materials and Methods

2.1. Field Experiment. The research was based on a field experiment conducted in 2010–2012 in Wierzchucinek at the Research Station of the University of Technology and Life Sciences in Bydgoszcz (53°26′N, 17°79′E). A field experiment was established on Luvisols [12]. The soil had average content of available forms of phosphorus, potassium, magnesium, manganese, and iron; low content of sulphur, zinc, and copper; and slightly acidic pH (Table 1).

The field experiment was setup in three replications according to the random block method. The area of the plot was 20 m^2, and the area for harvest was 16 m^2. The Antek variety of spring barley was grown, with potato as a forecrop each year. The experimental factor was the type of the mineral fertilizer containing sulphur in elemental or ionic forms: two types of fertilizer containing this nutrient in sulphate form $S\text{-}SO_4^{2-}$ (ammonium sulphate with 24% S and potassium sulphate with 18% S) and one containing its elemental form $S\text{-}S^0$ (Wigor S–80% S and 20% bentonite). Therefore, two forms of sulphur were tested using three types of fertilizers. Each fertilizer was applied in amounts containing 20 and 40 $kg{\cdot}S{\cdot}ha^{-1}$. Agrotechnical procedures were carried out in accordance with the recommendations for spring barley. Uniform NPK fertilization was applied before sowing. Nitrogen was applied at a rate of 70 $kg{\cdot}N{\cdot}ha^{-1}$ in the form of ammonium nitrate (in the treatments with ammonium sulphate, the amount of ammonium nitrate was reduced accordingly); phosphorus (20 $kg{\cdot}P{\cdot}ha^{-1}$) in the form of triple superphosphate; and potassium (70 $kg{\cdot}K{\cdot}ha^{-1}$) as 50% potash, taking into account the amount introduced with potassium sulphate.

2.2. Weather Conditions. The area where the field experiment was conducted is characterized by significant variation in weather conditions from year to year and low precipitation—on average of about 460 mm per year (Table 2).

This is confirmed by the values of Selyaninov's hydrothermal coefficient:

$$K = \frac{P}{0.1 \sum t}, \qquad (1)$$

where P is the precipitation sum in the month in mm and t is the air temperature sum in the month >0°C.

The average K value was 1.61 in the 2010 growing season (fairly wet conditions), 1.30 in 2011 (optimal conditions), and 0.73 in 2012 (dry conditions). In comparison with the average from 1949–2012, precipitation in 2010 and 2011 was relatively high. In June and July 2010 and in May 2011, precipitation was much higher than the long-term average, as confirmed by the high Selyaninov's hydrothermal coefficient (K) for these months. The driest year was 2012, when in the entire growing season, i.e., from April to September inclusive with the exception of July, and rainfall was lower than the long-term average for those months. In all years of the study, air temperatures from May to August, except June 2010, were higher than the long-term average.

After harvest, the yield of spring barley grain was determined. In the dry matter of the grain, following mineralization in a mixture of concentrated hydrochloric acid and nitric acid, the content of micronutrients (Mn, Fe, Zn, and Cu) was determined by atomic absorption spectrometry (AAS).

2.3. Statistical Analysis. The results were analysed statistically by split-plot analysis of variance (ANOVA) according to a model consistent with the experimental design. Tukey's range test with a probability level of $p = 0.05$ was used to determine the significance of differences between means.

3. Results and Discussion

In Poland, spring barley grain is mainly used for fodder, both for on-farm preparation of compound concentrate feeds and in the feed industry. In the present study, the average content of Mn, Fe, Zn, and Cu in the spring barley grain was 11.1, 69.5, 66.5, and 4.7 $mg{\cdot}kg^{-1}$, respectively (Table 3).

Compared to optimal micronutrient concentrations in feeds, which are 40–70 $mg{\cdot}Mn{\cdot}kg^{-1}$, 40–80 $mg{\cdot}Fe{\cdot}kg^{-1}$, 50–100 $mg{\cdot}Zn{\cdot}kg^{-1}$, and 7.1–10.0 $mg{\cdot}Cu{\cdot}kg^{-1}$ [13], the Fe and Zn contents in the grain can be considered to be in the optimal range, while Mn and Cu levels were lower.

Significantly higher content of manganese, zinc, and copper was obtained in the barley grain grown in the first two growing seasons (2010 and 2011), which were wet, than in the very dry season of 2012. This is consistent with results reported by Gugała and Zarzecka [14], who showed that wet-growing conditions favour higher concentrations of tested micronutrients in crops.

The fertilizers significantly affected the content of all elements, generally increasing their content compared to the grain of plants not fertilized with sulphur. In the case of Mn, Fe, and Cu, the highest concentrations were obtained as a result of application of ammonium sulphate; the differences

Table 1: Content of available forms of micro- and macronutrients of soil (0–30 cm) prior to the plot experiment (mg·kg^{-1}).

	Macronutrients				Micronutrients				
	P-P_2O_5	K-K_2O	Mg-MgO	S-SO_4	Mn	Cu	Zn	Fe	B
	47.5 (40.3–54.6)	64.6 (53.1–76.0)	29.1 (26.3–32.2)	11.3 (8.3–14.2)	66 (45–86)	1.5 (0.9–2.0)	1.3 (0.9–1.5)	1117 (823–1410)	1.1 (0.55–0.78)
Wealth	Average	Low	Average	Low	Average	Low	Low	Average	Low

Table 2: Temperature and precipitation distribution throughout the field experiment.

Years	Months IV	V	VI	VII	VIII	IX	
Air temperature (°C)							Mean
2010	7.0	13.1	14.3	19.3	18.6	11.7	14.0
2011	7.5	15.7	16.3	18.9	19.9	12.9	15.2
2012	6.4	14.4	17.6	19.2	18.4	13.6	14.9
1949–2012	8.0	13.0	16.3	18.5	17.8	13.4	14.5
Monthly precipitation (mm)							Sum
2010	42.4	34.9	80.5	146.1	49.7	57.8	414.4
2011	17.7	111.5	31.3	77.9	58.0	70.5	366.9
2012	18.5	18.1	30.4	110.6	17.7	16.7	207.6
1949–2012	27.2	43.9	54.4	72.9	55.8	40.8	295.0
Selyaninov's hydrothermal coefficient							Mean
2010	2.01	0.86	1.87	2.43	0.85	1.64	1.61
2011	0.79	2.28	0.63	1.32	0.94	1.81	1.30
2012	0.95	0.42	0.57	1.77	0.30	0.40	0.73
1949–2012	1.21	1.00	1.14	1.25	0.96	0.97	1.08

with respect to the control were 19.2%, 19.5%, and 6.5%, respectively. The fact that ammonium sulphate, a physiologically acidic fertilizer, had the greatest effect on the content of all elements tested in the spring barley grain was probably due to the acidifying effect of this fertilizer on the soil, which is confirmed by changes in pH and hydrolytic acidity (Table 4). According to Islam [15], Kozłowska-Strawska [16], and Klikocka [17], the supply of available forms of micronutrients in the soil depends mainly on the soil reaction.

As soil pH increases, strong adsorption of Cu^{2+} and Zn^{2+} ions by soil colloids results in a decrease in the content of copper [4, 18] and zinc [19]. The application of sulphur may have led to acidification of the soil environment, which is conducive to a greater supply of available forms of copper, and in consequence, as demonstrated by our research, an increase in the content of microelements in the spring barley grain.

For Mn, Fe and Zn, the effect of Wigor S was less beneficial than that of the fertilizers containing ionic forms of sulphur. This fertilizer contains elemental sulphur, which is considered more difficult to assimilate than the ionic form, as it must undergo microbiological transformation to the sulphate form in the soil, involving bacteria of the genus *Thiobacillus*. The differences between the effect of fertilizers containing sulphur in ionic and elemental forms were smaller in the 2010 and 2011 growing seasons, when precipitation was higher (Table 2), than in the dry year of 2012. The high moisture level may have been conducive to high biological activity in the soil and the transformation of sulphur from Wigor S to forms available for plants.

The process of oxidation of elemental sulphur to sulphate depends on the physicochemical properties of the soil. Studies by He et al. [20] carried out on four soils and by Degryse et al. [21] on twenty soils have confirmed the substantial effect of soil temperature, moisture, aeration, and pH on sulphur transformation. In an incubation study, He et al. [20] used first-order kinetics to demonstrate that the half-life $t_{1/2}$ of elemental sulphur ranged from 12 to 176 days, depending on the type of soil. Yang et al. [22] found a significant correlation between the concentration of sulphates formed as a result of oxidation of elemental sulphur and the population size of not only *Thiobacillus* bacteria but also aerobic heterotrophic sulphur-oxidizing bacteria. In addition to environmental factors, the degree of pulverization of elemental sulphur may also play a role [23].

The application of 40 kg·S·ha^{-1} in the form of ammonium sulphate generally resulted in significantly higher content of all tested micronutrients in the barley grain as compared to the application of 20 kg·S·ha^{-1}. In the case of zinc, similar variation in the effect of the application rates was also noted for the use of potassium sulphate. These application rates of Wigor S generally did not cause marked differences in the content of microelements.

The results of our study, as well as studies by many authors on various cereal species, e.g., Barczak et al. [24] on oat, Kaczor and Brodowska [25] and Singh-Shivay et al. [26] on wheat, and Kulczycki [23] on maize, indicate that sulphur fertilization of crops cultivated in conditions of soil deficiency of this nutrient positively affects the content of micronutrients in the grain. This has also been confirmed in research on other species of crop plants: potato [27–29]. The literature also contains studies that do not confirm this relationship [16]. It seems, therefore, that sulphur fertilization may be helpful in the biofortification of cereal grain with micronutrients. The positive effect of sulphur on the content of zinc and iron, which is insufficient in the diet of a large portion of the human population, is particularly important. It is estimated that over 17% of the world's population is at risk of zinc deficiency (25% in sub-Saharan Africa and 29% in South Asia) [4]. No such data are available for iron, but iron deficiency is considered to be the main cause of anaemia, which on a global scale affects 800 million women and children [5].

Zinc is a component of about 200 enzyme systems and is essential for normal human growth and development, as it participates in metabolism of carbohydrates, proteins, and phosphates. Iron deficiency during childhood and adolescence impairs mental development and learning ability. In adults, it reduces the ability to do physical work.

Assessment of the supply of iron and manganese to crop plants includes consideration of their proportions. Optimal

Table 3: The content of microelements by spring barley grain ($mg{\cdot}kg^{-1}$).

Year	Control	Type of fertilizer						Mean
		$(NH_4)_2SO_4$		K_2SO_4		Wigor S		
		Dose of sulphur ($kg{\cdot}ha^{-1}$)						
		20	40	20	40	20	40	
Content of Mn								
2010	8.7^{a}	9.7^{bc}	10.5^{d}	10.1^{cd}	10.8^{d}	9.1^{ab}	9.7^{bc}	9.8
2011	10.4^{a}	11.4^{bc}	11.9^{c}	11.3^{bc}	11.0^{ab}	11.5^{bc}	11.9^{c}	11.3
2012	10.8^{a}	12.9^{c}	14.2^{c}	11.7^{b}	12.6^{cd}	11.9^{bc}	11.2^{ab}	12.2
Mean	9.9^{a}	11.3^{b}	12.2^{c}	11.0^{b}	11.5^{bc}	10.8^{b}	10.9^{b}	11.1
		11.8		11.3		10.9		
Content of Fe								
2010	68.5^{a}	74.5^{ab}	84.3^{c}	76.2^{b}	74.0^{ab}	78.1^{bc}	74.5^{ab}	75.7
2011	63.5^{a}	65.7^{a}	83.5^{c}	74.2^{b}	82.8^{c}	64.0^{a}	69.9^{ab}	71.9
2012	57.7^{ab}	69.6^{c}	75.1^{c}	51.9^{a}	59.8^{b}	54.4^{ab}	57.8^{ab}	60.9
Mean	63.2^{a}	69.9^{ab}	81.0^{c}	67.4^{ab}	72.2^{b}	65.5^{ab}	67.4^{ab}	69.5
Content of Zn								
2010	60.4^{c}	62.9^{d}	54.6^{b}	45.3^{a}	69.0^{e}	57.8^{bc}	63.6^{d}	59.1
2011	71.0^{ab}	67.6^{a}	78.1^{d}	71.1^{b}	76.1^{cd}	73.8^{bc}	79.5^{d}	73.9
2012	65.8^{c}	61.2^{b}	71.2^{d}	73.3^{d}	81.4^{e}	60.0^{b}	53.4^{a}	66.6
Mean	65.7^{a}	63.9^{a}	68.0^{b}	63.3^{a}	75.5^{c}	63.9^{a}	65.5^{a}	66.5
Content of Cu								
2010	3.1	2.5	3.1	2.9	2.9	3.1	3.0	2.9
2011	5.7	5.7	5.9	5.8	5.7	6.3	5.9	5.9
2012	5.1	5.7	6.8	4.6	5.0	5.0	5.2	4.8
Mean	4.6	4.6	5.2	4.4	4.6	4.8	4.7	4.7
		4.9		4.5		4.8		

Note. Cu: $LSD_{0.05}$ = n.s.

Table 4: Hydrolytic and exchangeable acidity of soil in a field experiment.

Year	Control	Type of fertilizer						Mean
		$(NH_4)_2SO_4$		K_2SO_4		Wigor S		
		Dose of sulphur ($kg{\cdot}ha^{-1}$)						
		20	40	20	40	20	40	
Hydrolytic acidity mmol $(+){\cdot}kg^{-1}$								
2010	1.94^{bc}	1.84^{ab}	2.01^{c}	1.91^{bc}	2.01^{c}	1.75^{a}	1.70^{a}	1.88
2011	2.01^{cd}	1.92^{bc}	2.10^{d}	1.75^{a}	1.84^{ab}	1.75^{a}	1.76^{a}	1.87
2012	2.11^{bc}	2.19^{cd}	2.28^{d}	1.84^{a}	1.84^{a}	2.10^{b}	1.85^{a}	2.03
Mean	2.02^{cd}	1.98^{bc}	2.13^{d}	1.83^{a}	1.90^{abc}	1.87^{ab}	1.77^{a}	1.93
		2.06		1.87		1.82		
pH_{KCl}								
2010	5.5	4.9	4.5	4.8	4.9	5.2	5.0	
2011	5.2	4.7	4.4	4.9	5.0	5.4	4.9	
2012	5.4	5.0	4.9	5.2	4.9	5.3	5.3	
Mean	5.4	4.9	4.6	4.9	4.9	5.3	5.0	5.0
		4.8		4.9		5.2		

mineral composition guarantees the appropriate quantitative ratios between elements, which are a measure of the value of feed obtained from crops grown for fodder purposes and the nutritional value of crops intended for human consumption [30, 31]. The state of ion balance in the plant is one of the important factors determining the quality of animal feed and human food [32]. During iron deficiency, symptoms of manganese toxicity can be observed in plants, whereas manganese deficiency can result from excess iron in the soil [33]. This is why the right balance between these elements is important. The correct Fe : Mn ratio in cereal grain is in the range from 1.5 : 1 to 2.5 : 1 [34]. In the present study, the average value of this ratio in the spring barley grain was 6.35 : 1 (Table 5), which may indicate an iron surplus with a simultaneous deficiency of manganese [29]. The use of sulphur did not significantly affect the value of the Fe : Mn ratio.

The uptake of the microelements tested in the spring barley grain is a resultant of their content and the grain yield.

Table 5: Quantitative ratio Fe : Mn in barley grain.

Year	Control	$(NH_4)_2SO_4$		K_2SO_4		Wigor S		Mean
		Type of fertilizer; Dose of sulphur (kg·ha^{-1})						
		20	40	20	40	20	40	
2010	7.87	7.68	8.03	7.54	6.85	8.58	7.68	7.73
2011	6.11	5.76	7.02	6.57	7.53	5.57	5.87	6.39
2012	5.34	5.40	5.29	4.44	4.75	4.57	5.16	4.94
Mean	6.38	6.28	6.78	6.18	6.38	6.24	6.24	6.35

Table 6: Micronutrient uptake of barley grain (g·ha^{-1}).

Year	Control	$(NH_4)_2SO_4$		K_2SO_4		Wigor S		Mean
		Type of fertilizer; Dose of sulphur (kg·ha^{-1})						
		20	40	20	40	20	40	
Uptake of Mn								
2010	37.1^{a}	44.3^{b}	50.0^{cd}	46.9^{b}	51.7^{d}	44.6^{b}	43.5^{b}	45.4
2011	39.2^{a}	44.9^{bc}	48.6^{d}	45.4^{bcd}	44.6^{b}	44.4^{b}	48.4^{cd}	45.1
2012	43.0^{a}	53.4^{c}	60.9^{e}	51.0^{bc}	55.3^{d}	50.2^{bc}	45.6^{a}	51.3
Mean	39.6^{a}	47.5^{bc}	53.2^{d}	47.8^{d}	50.5^{cd}	46.4^{b}	45.8^{b}	47.3
		50.4		49.2		46.1		
Uptake of Fe								
2010	291.8^{a}	340.5^{b}	401.3^{d}	353.6^{bc}	354.5^{bc}	382.7^{cd}	333.8^{b}	350.5
2011	239.4^{a}	258.9^{ab}	340.7^{e}	298.3^{c}	335.4^{de}	247.0^{a}	284.5^{bc}	285.4
2012	229.6^{a}	288.1^{c}	322.2^{d}	226.3^{a}	262.5^{bc}	229.6^{a}	235.2^{ab}	256.2
Mean	252.6^{a}	295.8^{bc}	354.7^{d}	292.7^{bc}	317.5^{c}	286.4^{bc}	284.5^{ab}	297.9
		325.3		305.1		285.5		
Uptake of Zn								
2010	257.3^{b}	287.5^{b}	259.9^{b}	210.2^{a}	330.5^{c}	283.2^{b}	284.9^{b}	273.4
2011	267.7^{a}	266.3^{a}	318.6^{cd}	285.8^{abcd}	308.2^{bcd}	284.9^{abc}	323.6^{d}	293.6
2012	261.9^{a}	253.4^{a}	305.4^{b}	319.6^{bc}	357.3^{cd}	379.8^{d}	339.4^{bc}	316.7
Mean	262.3^{a}	269.1^{a}	294.6^{ab}	271.9^{a}	332.0^{c}	316.1^{bc}	316.0^{bc}	294.5
		281.9		302.0		316.1		
Uptake of Cu								
2010	13.0^{abc}	11.3^{a}	14.5^{c}	13.3^{abc}	14.1^{bc}	15.1^{c}	13.5^{abc}	13.5
2011	21.6^{a}	22.4^{ab}	24.1^{b}	23.4^{ab}	23.2^{ab}	24.2^{b}	23.9^{b}	23.3
2012	20.3^{a}	23.6^{b}	29.0^{c}	20.1^{a}	22.0^{ab}	21.1^{a}	21.2^{a}	22.5
Mean	18.3^{a}	19.1^{a}	22.5^{b}	18.9^{a}	19.8^{a}	20.1^{a}	19.5^{a}	19.8
		20.8		19.4		19.8		

The accumulation of micronutrients in the spring barley grain was greatest for iron (on average 297.9 kg·ha^{-1}) and zinc (294.5 kg·ha^{-1}) and much lower for manganese (47.3 kg·ha^{-1}) and copper (19.8 kg·ha^{-1}) (Table 6).

Substantial variation in the accumulation of these nutrients in the grain was noted between growing seasons, due to the significant differences in grain yield in the years of the research.

The fertilizers tested had a positive effect on the uptake of all microelements, but the differences between their uptake with the grain of fertilized and nonfertilized plants were statistically confirmed mainly for manganese, iron, and zinc. For all these nutrients, except zinc, ammonium sulphate proved the most conducive to their uptake, but the differences between the effects of fertilizers were generally not significant. The application of 40 kg·S·ha^{-1} in ionic form (ammonium and potassium sulphates) increased the uptake of microelements by spring barley grain as compared to the 20 kg·S·ha^{-1} application rate, which could be due to the positive effect of sulphur on the yield as well as the typically higher content of micronutrients following the application of greater amount of sulphur (Table 3).

4. Conclusions

The research conducted on soils with low sulphur content has shown that the inclusion of sulphur in fertilization of spring barley can be regarded as an agronomic method of biofortification of grain with micronutrients, as it positively affects the content of manganese, iron, zinc, and copper in the grain. In each year of the study, an increase in the content of these micronutrients was observed in the grain of plants fertilized with sulphur in comparison to plants that were not fertilized with this nutrient. Among the tested fertilizers, ammonium sulphate had the greatest impact on the content and uptake of all micronutrients, except for zinc. Marked differences in the effect of the 20 and 40 $kg \cdot S \cdot ha^{-1}$ application rates were noted only for fertilizers containing the ionic form of sulphur. The positive effect of sulphur on the biofortification of spring barley grain with microelements indicates the need to include this nutrient in cultivation of this species.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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