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Residual effect of superphosphate on the sulphur status of soil and plants in a long-term NPK fertilisation experiment on a Chernozem in Hungary

Evelin Kármen Juhász, Rita Kremper, Áron Béni, Andrea Balláné Kovács*

Institute of Agricultural Chemistry and Soil Science, Faculty of Agricultural and Food Sciences and Environmental Management, University of Debrecen, Debrecen, Hungary
**Corresponding author: juhasz.evelin@agr.unideb.hu*

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Abstract: Recently, plant-available sulphur (S) in the soil is decreasing due to the limited use of S containing fertilisers and the reduction of atmospheric S deposition. The aim of this work was to evaluate the S status in a long-term fertilisation experiment on a Chernozem in Hungary, with control and 2 NPK rate treatments, considering that after 27 years of superphosphate (SP) use, SP was replaced by monoammonium phosphate in 2010. Plant and soil sampling were performed in 2017 at three different development stages of winter wheat. To assess the S status, the S balance was estimated (for 34 years), KCl soluble soil sulphate, S as well as nitrogen (N) concentration and some amino acids in wheat grain were measured. N/S ratios, S and N uptake of wheat were calculated. The residual effect of SP could be measured only in terms of KCl soluble SO_4^{2-}-S in soil. According to the wheat grain S concentration (0.08–0.10%) and N/S ratio (14.9–22.0), wheat was S deficient, despite the positive S balance in the fertilised plots. In this experiment, where S fertiliser was applied with 84 kg S/ha dose in 1983–2010, followed by a 7-year period without S fertilisation, S supply is necessary for achieving adequate wheat quality.

Keywords: *Triticum aestivum* L.; sulphur uptake; deficiency; methionine; cysteine

Sulphur (S) is an essential nutrient for plants. Proper S supply has a positive effect on vegetative growth, modifies protein content, and influences the amount and proportion of protein-forming amino acids (Aula et al. 2019). Sulphur is vital for the synthesis of cysteine and methionine; thus, it is an important factor affecting the bread-making quality of wheat as well (Tisdale et al. 1985).

The total S content of soil generally varies from 0.01% to 0.1% (Balík et al. 2009) and can be found in inorganic and organic forms. The different organic and inorganic S forms can be transformed in the process of mineralisation, immobilisation, oxidation and reduction (Siwik-Ziomek et al. 2013). Basically, these processes determine the short- and long-term S supplying capacity of the soil (Kovar and Grant 2011). Plant-available S can be divided into soluble inorganic sulphate, absorbed sulphate, and the fraction of soil organic S, which is mobilised during vegetation (Blair 2015).

In the past decades, the plant-available S in the soil is decreasing due to the limited use of superphosphate and sulphate-containing fertilisers and the enormous reduction of atmospheric S deposition, and these changes can cause S deficiency in plants (Schnug and Haneklaus 2005, Sutar et al. 2017). Since 2010, it has also become a common practice in Hungary to replace superphosphate fertiliser by monoammonium-dihydrogen-phosphate (MAP). Superphosphate is a mixture of monocalcium phos-

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phate [$Ca(H_2PO_4)_2$] and gypsum ($CaSO_4$). It was used as a source of phosphorus (17–18% P_2O_5), but it also contains 10–11% S (Scherer 2001). Superphosphate application over several years might build up soil S reserves. In this case, only a maintenance fertilisation rate should be required to compensate for the S losses from the soil-plant systems (Nguyen et al. 1989). Without effective S supply, plants can reach neither their maximum potential in terms of yield and quality nor can make efficient use of applied nitrogen (N) (Yu et al. 2018). Constant application of N fertiliser without any S supply may decrease the quality properties, especially the baking quality of wheat (De Ruiter and Martin 2001, Flaete et al. 2005).

Nowadays, climate change is making the implementation of irrigation increasingly important in intensive crop production systems. Irrigation not only provides water for the plant but also can influence soil properties. Adequate irrigation management can increase the moisture content of the soil, enhance biological activities as well as the accumulation of organic matter (OM) and increase the efficiency of organic and mineral fertilisers (Nikolskii et al. 2019). Under laboratory conditions, S mineralisation was positively correlated with soil moisture content. According to Yavitt et al. (1993), the rate of S mineralisation increased as soil moisture enhanced. However, the mineralisation of organic S to sulphate under wet conditions also promotes the leaching of the highly soluble sulphate form.

N and S are important protein components, and the right N/S ratio significantly contributes to grain quality as well as to the optimal yield of crop plants (Klikocka et al. 2018). Therefore besides the total S concentration, the N/S ratio of the wheat grain is a vital factor for the evaluation of the S supply of the plant. Other plant parameters can be used for identifying S status as well, i.e. SO_4^{2-} (Scaife and Burns 1986), the SO_4^{2-}/total S (Spencer and Freney 1980) or SNI (sulphur nutrition index) (Sedlář et al. 2019), but the most commonly used indicators to evaluate the S supply are the S concentration and the N/S ratio.

In our experiment, NPK containing fertilisers were supplied continuously for 34 years. S supplementation as superphosphate stopped from year 27 of the experiment and was not supplied thereafter until the time of sampling in 2017. The main goal of this work was to evaluate the S supply of winter wheat in a long-term NPK fertilisation experiment based on N and S balances, soil KCl soluble sulphate, N, S concentration and N/S ratios of wheat.

MATERIAL AND METHODS

A long-term field experiment. A multifactorial long-term field experiment was established on a typical Chernozem in 1983 at the Research Station of the University of Debrecen (47°33'N, 21°27'E) in Hungary. The long-term fertilisation experiment consists of a control and increasing NPK treatments with and without irrigation. The treatments were designed in a randomised block model with 4 replicates. The size of the experimental plots was 46 m^2. The main properties of the experimental soil (sampled in 1983) as the average for the field are pH_{KCl} = 6.46 (Metson 1961); C_{org} = 1.75% (Walinga et al. 1992); AL-P = 133.4 mg/kg; AL-K = 199.0 mg/kg; KCl-SO_4^{2-}-S = 9.13 mg/kg. Based on these parameters, the experimental soil was well supplied with N, medium with P and poorly with K.

The average total precipitation in 2017 in the growing season was 369 mm (30 years average: 411 mm), and the average annual mean temperature is 7.2 °C (30 years average: 6.9 °C). Winter wheat (*Triticum aestivum* L.) and maize (*Zea maize* L.) were cropped in a crop rotation (one crop/year). In the period from 1983 to 2010, the N, P and K nutrients were supplied as NH_4NO_3, superphosphate (with 10.9% S content) and KCl, respectively. Since 2010 superphosphate has been replaced by MAP, and S was not supplied anymore in the experimental area. 100% of the P and K doses were applied in the autumn, before sowing, while considering the environmental pollution risk, 50% of N was applied in autumn and the other 50% in spring for both crops.

In 2017, winter wheat (*Triticum aestivum* L.) was cropped in the experiment, and the following treatments were selected for our study: control, NPK1 (100 kg N/ha, 31 kg P/ha, 66 kg K/ha) and NPK2 (200 kg N/ha, 62 kg P/ha, 132 kg K/ha) in irrigated and non-irrigated treatments. In the sampling year, irrigation was supplied two times in the irrigated plots. The first irrigation (2 × 20 mm) was on 27–28 May, 5 days before the second soil and plant sampling date, and the second irrigation (2 × 20 mm) was on 1–2 June, one month before the third sampling date.

Calculation of nutrient balances. The cumulative N and S balances were calculated from the differences of input (applied mineral fertilisers) and output (as nutrient uptake by plants) of N and S for 1983–2016. The cumulative nutrient balances in different treatments for maize and wheat, respectively, were calculated based on the yearly nutrient balances. Based on our calculations, a significant negative S balance (–619.65 kg S/ha) and negative N balance (–5 248.8 kg N/ha) were observed in control. The S balance turned to positive in the fertilised treatments (NPK1: 226.3 kg S/ha; NPK2: 1 373.0 kg S/ha), while the N balance remained negative even at the highest fertiliser dose (–1 073.6 kg N/ha).

Plant sampling and analysis. Plant samples were collected in 2017 in three different growth stages of winter wheat according to the BBCH scale: at BBCH 30–32 stage – stem elongation (leaves) on 24th April, at BBCH 61–65 stage – flowering (leaves) on 31st May and at BBCH 89 stage – ripening (grain and straw) on 5th July. The total N and S concentration of winter wheat was measured by elemental analysis (Elementar Vario EL, Hanau, Germany). N/S ratios of wheat were calculated. The S containing amino acids in grain samples were measured by ion-exchange chromatography (MSZ EN ISO 13903, 2005, Csapó et al. 2005). The nutrient uptake by grain and straw was calculated from the yield of wheat and the N and S concentration of plant samples.

Soil sampling and analysis. Soil sampling was performed three times in 2017 (at the same time as plant sampling) from the topsoil 0–25 cm of experimental plots for all treatments. Soil samples were air-dried, ground and passed through a 2 mm sieve. The sulphate fraction of soil was measured in 1 mol/L KCl extractant. 10 g soil was shaken with 25 mL extractant. Extracts were filtered, and sulphate was measured by the turbidimetric method. This method is based on the forming of $BaSO_4$ precipitate in a slightly acid medium when excess $BaCl_2 \cdot 2\ H_2O$ is added to the solution containing sulphate-S (Zhao and McGrath 1994).

Statistical analysis. For statistical analysis of measured plant and soil data, Microsoft Excel 2016 (Redmond, USA) and IBM SPSS Statistics 22 programs (Chicago, USA) were used. The results were statistically analysed by using two factors (fertilisation, irrigation) analysis of variance (significance level of $P < 0.05$) with post hoc comparisons using the Tukey test. The relationship between sulphate fraction of soil and plant parameters were determined by Pearson's correlation.

RESULTS AND DISCUSSION

KCl soluble sulphate concentration in soil. In order to follow the residual effect of superphosphate applications, 7 years after the use of S containing fertiliser, the KCl soluble sulphate fraction of soil was measured (Table 1).

The SO_4^{2-}-S in KCl solution ranged between 2.26 and 5.23 mg/kg and was the lowest in spring, at the stage of stem elongation of wheat and increased in time. Förster et al. (2012) and Reich et al. (2016) also measured lower SO_4^{2-}-S levels in soil in spring and explained this by leaching of sulphate and low mineralisation rates of S. There were no differences between KCl soluble SO_4^{2-}-S values of the control and NPK1 treatment, where 42.4 kg S/ha/year has been supplied for 23 years. Significantly higher SO_4^{2-}-S values were measured in the NPK2 treatment compared to control, where 84.8 kg S/ha/year had been supplied for 23 years. This could be due to the much more positive S balance resulted by superphosphate which was applied between 1983 and 2010. However, according to Brook (1979), 10 mg/kg KCl extractable sulphate is reported as a critical level for plant-available S in soil. Blair et al. (1991) compared different kinds of extractants in their studies and also found that the critical level of KCl soluble SO_4^{2-}-S was 6.5 mg/kg. Based on these critical values, it can be concluded that the KCl soluble SO_4^{2-}-S values of our experiment in 2017

Table 1. Long-term effect of fertilisation and irrigation on the KCl soluble SO_4^{2-}-S (mg/kg) content of soil during the growing stages of winter wheat

Treatment	Irrigated	Non-irrigated	Mean
Stem elongation (BBCH 30–32)			
Control	2.39	2.89	2.64^{a}
NPK1	2.58	3.14	2.86^{ab}
NPK2	2.86	3.64	3.25^{b}
Mean	2.61^{A}	3.22^{B}	2.92
Flowering (BBCH 61–65)			
Control	5.04	2.26	3.65^{a}
NPK1	4.59	3.00	3.79^{a}
NPK2	5.23	3.06	4.15^{a}
Mean	4.95^{B}	2.77^{A}	3.86
Ripening (BBCH 89)			
Control	4.79	2.67	3.73^{a}
NPK1	4.88	3.82	4.35^{ab}
NPK2	5.13	4.54	4.84^{b}
Mean	4.93^{B}	3.68^{A}	4.31

The results were analysed separately for each sampling date. Different small letters indicate significant differences between the fertilisation treatments within a column; different capital letters indicate significant differences between irrigation treatments within a line ($P < 0.05$)

was not sufficient for the wheat development even in the NPK2 treatment. However, it is important to highlight that sulphate in soil changes continuously depending on plant uptake, fertilisation, mineralisation, immobilisation and reflects only the current state of the soil.

The KCl soluble SO_4^{2-}-S of irrigated plots at BBCH 61–65 and 89 of wheat were higher than the non-irrigated plots. The increase can be explained by the changes in solubility conditions and mineralisation processes due to irrigation.

The yield of winter wheat. The grain yield of winter wheat ranged between 2.29 and 9.19 t/ha and significantly increased as a result of increasing doses of NPK fertilisers compared to the control (Figure 1). The yield increment in NPK1 and NPK2 treatments were 4.09 and 6.31 t/ha compared to the control, respectively. According to Wang et al. (2014), irrigation can improve the availability of soil nutrients, promoting the absorption of soil nutrients by crops and increasing yield. In our experiment, a significant yield increase was observed due to irrigation.

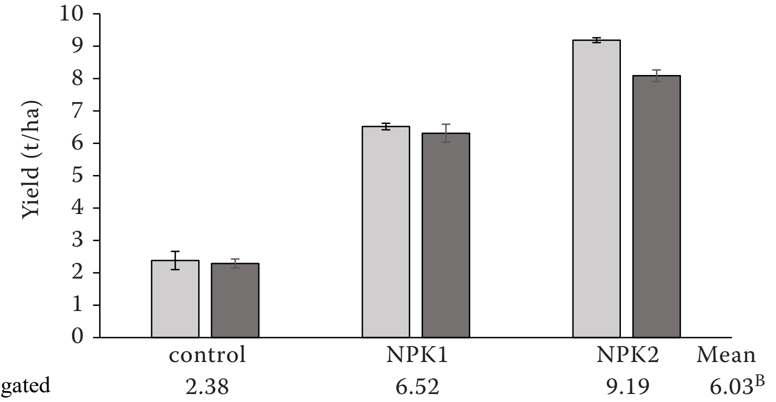
The N, S concentration and N/S ratio of winter wheat. The lowest N concentration was observed in the control plots in all development stages (Table 2). As it was expected, the increasing NPK doses caused significantly higher N concentration in the plant material compared to the control. The highest N concentration was found in NPK2 treatment. There were no significant changes between the plant N concentration in the irrigated and the non-irrigated plots.

The critical N concentration in above-ground biomass is described as the lowest N concentration required to achieve the maximum yield at any moment during the development (Plénet and Lemaire 1999). As stated by Reuter et al. (1997), the critical N concentration of wheat at the stage of BBCH 30–32 is 2.6%. Our N concentration of wheat in all treatments were higher than this critical N concentration. The critical N concentration of wheat leaves at BBCH 61–65 is 2.1% (Chapman 1967, Reuter et al. 1997). Comparing this critical concentration with our results, it can be concluded that wheat N concentration at the flowering stage was low.

The N concentration of wheat grain varied from 1.35% to 2.28%. The lowest value was observed in the control, while the highest one was found in the NPK2 treatment, where the N concentration was 30–50% higher than in the control. Goos et al. (1982) determined 2% as the critical N concentration for wheat grain. In our experiment, the N concentration of grain was higher than this critical value only in NPK2 treatment.

At BBCH 30–32, the S concentration of leaves varied between 0.23% and 0.30%. The S concentration did not change significantly as a result of increasing NPK doses. At BBCH 61–65, the S values of above-ground biomass became lower and ranged from 0.11% to 0.15%. This is in agreement with the founding of Robson et al. (1995), who observed a decrease in S concentration with increasing plant age. There were no differences between the S concentration of control and fertilised plants. From stem elongation to flowering, the irrigation did not affect the S concentration of the plant.

The S concentration of wheat grain ranged between 0.08% and 0.10%. Sager (2012) found in their similar



	control	NPK1	NPK2	Mean
□ Irrigated	2.38	6.52	9.19	6.03^B
■ Non irrigated	2.29	6.31	8.09	5.56^A
Mean	**2.34^a**	**6.42^b**	**8.64^c**	5.80

Figure 1. The average grain yield of winter wheat. Different small letters indicate significant differences between the fertilisation treatments within a line; different capital letters indicate significant differences between irrigation treatments within a column ($P < 0.05$)

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Table 2. Long-term effect of fertilisation and irrigation on changes of nitrogen (N) and sulphur (S) concentration as well as the N/S ratio of winter wheat during the growing season

Treatment	N (%)			S (%)			N/S		
	irrigated	non-irrigated	mean	irrigated	non-irrigated	mean	irrigated	non-irrigated	mean
Stem elongation – BBCH 30–32 (leaves)									
Control	2.95	3.28	3.11^{a}	0.26	0.23	0.24^{a}	11.56	14.34	12.95^{a}
NPK1	4.12	4.36	4.24^{b}	0.28	0.24	0.26^{a}	14.53	18.35	16.44^{b}
NPK2	4.72	4.85	4.78^{c}	0.30	0.25	0.27^{a}	15.87	19.38	17.63^{b}
Mean	3.93^{A}	4.16^{A}	4.04	0.28^{A}	0.24^{A}	0.26	13.99^{A}	17.36^{B}	15.67
Flowering – BBCH 61–65 (leaves)									
Control	1.09	0.99	1.04^{a}	0.11	0.11	0.11^{a}	9.85	9.10	9.47^{a}
NPK1	1.58	1.39	1.48^{b}	0.13	0.10	0.11^{a}	12.60	13.52	13.06^{ab}
NPK2	1.86	1.81	1.83^{c}	0.15	0.13	0.14^{a}	12.73	14.12	13.42^{b}
Mean	1.51^{A}	1.40^{A}	1.45	0.13^{A}	0.11^{A}	0.12	11.73^{A}	12.25^{A}	11.99
Ripening – BBCH 89 (wheat grain)									
Control	1.35	1.41	1.38^{a}	0.09	0.08	0.09^{a}	14.88	17.16	16.02^{a}
NPK1	1.86	1.72	1.79^{b}	0.09	0.09	0.09^{a}	21.45	19.38	20.41^{ab}
NPK2	2.28	2.04	2.16^{c}	0.10	0.10	0.10^{a}	21.97	21.07	21.52^{b}
Mean	1.83^{A}	1.72^{A}	1.78	0.09^{A}	0.09^{A}	0.09	19.43^{A}	19.20^{A}	19.32

The results were analysed separately for each sampling date. Different small letters indicate significant differences between the fertilisation treatments within a column; different capital letters indicate significant differences between irrigation treatments within a line ($P < 0.05$)

research values in winter wheat (average 0.083% S). Győri (2005) obtained a higher S concentration of wheat grain in a long-term field experiment (average 0.15% S). According to Reussi et al. (2012), the critical S concentration of wheat grain is 0.12%. In our experiment, the S concentration did not exceed this value, even in the NPK2 treatment. The increasing NPK fertiliser doses and irrigation did not have any significant influence on the S concentration of wheat grain. However, Lerner et al. (2006) observed an increase in grain S as a result of N fertilisation. These results confirm what was determined by Randall et al. (1981), who concluded that S concentration in grain depends not only on S availability but also on N availability.

In all studied development stages, the smallest N/S ratio was found in the control treatment and the values enhanced due to the increasing NPK doses. The leaves N/S ratio was influenced by irrigation only at stem elongation, where these values were higher in the non-irrigated plots compared to the values of the irrigated plots.

As stated by Randall et al. (1981) and Naeem and Macritchie (2003), a grain N/S ratio below 17:1 seems to be adequate for optimum quality and quantity of wheat. In our experiment, only the N/S ratio of wheat grain in the irrigated control treatment was lower than this critical N/S ratio because of the low plant N concentration. As a result of increasing N doses, the N/S ratio significantly increased and ranged from 19.4 to 22.0 and thus exceeded the critical N/S value. However, Kalocsai et al. (2006) found that the N/S = 20–21:1 ratio of wheat grain does not necessarily mean S deficiency. Moreover, they detected the best baking quality at this ratio.

Reussi et al. (2012) suggested that wheat S supply should be assessed by taking both S concentration (0.12%) and N/S ratio (17:1) of grain into account. According to our data (S concentration: 0.08–0.10%; N/S: 14.9–22.0), it can be stated that wheat was S deficient because the N/S ratios were above 17:1 and the S concentration was below 0.12% in most cases.

The N and S uptake by wheat. The amount of N uptake by grain ranged between 28.6 and 208.5 kg/ha, while the N uptake by straw was much lower and varied from 3.3 to 28.6 kg/ha (Table 3). The significantly higher N uptake by grain was due to the higher N concentration of grain (Assefa et al. 2021). The lowest N uptake was detected in control, and this value was increased by N fertiliser doses. Irrigation further increased the N uptake by wheat compared to values of non-irrigated plots.

The S uptake varied from 1.83 to 9.50 and 2.03–10.76 kg/ha by grain and straw, respectively. The lowest S uptake of grain and straw was found in control, while the maximum S uptake was detected in the NPK2 treatment. In the case of grain, there were no differences in S uptake in the control and NPK1 treatments; only the highest fertiliser dose caused significantly higher grain S uptake compared to the control. In the case of straw, both NPK doses enhanced the S uptake.

The total plant S uptake (grain + straw) varied from 3.93 to 18.75 kg S/ha and significantly enhanced in NPK1 and further increased in NPK2 treatments, which might have been caused by the positive S balance. Irrigation had no effect on total S uptake.

Overall, grain N uptake was substantially higher than straw N uptake, while S uptake was higher in the case of straw. Fertilisation increased both N and S uptake by wheat (grain + straw), but N uptake was about ten times higher than S uptake. In our experiment, only the N uptake was affected by irrigation.

Amino acid concentration of winter wheat grain. The S containing amino acids were measured only in control and the NPK2 treatment (Table 4). Cysteine concentration of grain varied between 0.7 and 1.2 mg/g, and the methionine concentration ranged from 0.6 to 1.4 mg/g. Järvan et al. (2008) measured higher cysteine (1.5–3.1 mg/g) and methionine concentration (1.1–2.1 mg/g) in winter wheat grain in a long-term field experiment with S and N fertilisation. The NPK2 fertilisation enhanced the amount of S containing amino acids, but irrigation had a different effect on these parameters because cysteine concentration was higher in the irrigated plots, while higher methionine concentration was measured in the non-irrigated plots. Zhang et al. (2017) also measured higher methionine concentration in the non-irrigated treatment.

The increased amount of cysteine and methionine concentration in NPK2 treatment may be due to the positive S balance and the yearly application of high N fertiliser dose.

Correlation between the plant and soil parameters. Pearson's correlation was used to evaluate the relationship between S uptake of wheat and KCl soluble sulphate in soil. The relationships between plant and soil parameters were examined at three development stages of wheat.

The weakest relationship between plant S uptake and KCl soluble SO_4^{2-}-S in soil was observed at the flowering stage of wheat (r = 0.15). Tighter, however, still not significant correlation (r = 0.59 and 0.60) were found between plant S uptake and KCl soluble SO_4^{2-}-S fraction of soil at stem elongation and ripening of wheat, respectively.

The lack of a strong correlation between soil sulphate concentration and plant sulphur uptake might

Table 3. Long-term effect of fertilisation and irrigation on sulphur (S) and nitrogen (N) uptake by grain, straw and the total biomass

		N uptake (kg/ha)			S uptake (kg/ha)		
		irrigated	non-irrigated	mean	irrigated	non-irrigated	mean
Grain	control	28.6	31.5	30.1^a	1.90	1.83	1.87^a
	NPK1	120.3	105.4	112.9^b	5.64	5.49	5.57^{ab}
	NPK2	208.5	168.1	188.3^c	9.50	7.99	8.75^b
	mean	119.1^B	101.7^A	110.4	5.68^A	5.10^A	5.39
Straw	control	3.5	3.3	3.4^a	2.03	3.21	2.62^a
	NPK1	14.3	11.7	13.0^b	6.28	8.54	7.41^b
	NPK2	28.6	19.5	24.0^c	8.34	10.76	9.65^c
	mean	15.4^B	11.5^A	13.5	5.55^A	7.50^B	6.53
Total uptake	control	32.1	34.8	33.4^a	3.93	5.04	4.59^a
	NPK1	134.6	117.1	125.9^b	11.92	14.03	12.98^b
	NPK2	237.0	187.6	212.3^c	17.84	18.75	18.29^c
	mean	134.6^B	113.2^A	123.9	11.23^A	12.61^A	11.92

The results were analysed separately for each sampling date. Different small letters indicate significant differences between the fertilisation treatments within a column; different capital letters indicate significant differences between irrigation treatments within a line ($P < 0.05$)

Table 4. Effect of fertilisation and irrigation on cysteine and methionine concentration of wheat grain

Treatment	Cysteine (mg/g)			Methionine (mg/g)		
	irrigated	non-irrigated	mean	irrigated	non-irrigated	mean
Control	1.0	0.7	0.9^a	0.6	1.0	0.8^a
NPK2	1.2	1.0	1.1^b	1.3	1.4	1.4^b
Mean	1.1^B	0.9^A	1.0	1.0^A	1.2^B	1.1

Different small letters indicate significant differences between the fertilisation treatments within a column; different capital letters indicate significant differences between irrigation treatments within a line ($P < 0.05$)

be due to the high variability of sulphate concentration in soil solution.

In our experiment, the effect of S application supplied as superphosphate for 27 years until 2010 can still be measured in 2017 (despite the continuous crop production and presumable leaching) in terms of increased KCl soluble sulphate fraction of soil. However, even in the NPK2 treatment, S deficiency of wheat was observed based on S concentration and N/S ratios. N deficiency was also detected in the control and NPK1 treatments. The N supply of wheat was adequate for wheat growth and yield formation in NPK2 treatment despite of the negative cumulative N balance, which can be attributed to the good N supplying capacity of the Chernozem soil (Izsáki 2010). Irrigation can lead to better soil moisture resulting in enhanced mineralisation of the organic S fraction; thus, significantly higher KCl soluble sulphate was measured in the irrigated plots. Plant N and S concentrations were not affected by irrigation. Our results show that under the conditions of our long-term field experiment on soil with high soil organic matter (Chernozem), where continuous S application with a dose of 84 kg S/ha was applied between 1983 and 2010, followed by 7 years without S fertilisation, S supply has to be recommended despite of the positive cumulative S balance (+1 373 kg S/ha) related to the period of 1983–2016.

REFERENCES

Assefa S., Haile W., Tena W. (2021): Effects of phosphorus and sulphur on yield and nutrient uptake of wheat (*Triticum aestivum* L.) on Vertisols, North Central, Ethiopia. Heliyon, 7: e06614.

Aula L., Dhillon J.S., Omara P., Wehmeyer G.B., Freeman K.W., Raun W.R. (2019): World sulphur use efficiency for cereal crops. Agronomy Journal, 111: 2485–2492.

Balík J., Kulhánek M., Černý J., Száková J., Pavlíková D., Čermák P. (2009): Differences in soil sulphur fractions due to limitation of atmospheric deposition. Plant, Soil and Environment, 55: 344–352.

Blair G.J., Chinoim N., Lefroy R.D.B., Anderson G.C., Crocker G.J. (1991): A soil sulphur test for pastures and crops. Australian Journal of Soil Research, 29: 619–626.

Blair G.J. (2015): Development of a soil sulphur test and sulphur enhanced fertilisers from the soil up. In: Proceedings of the 17th ASA Conference, Hobart, 20. 09.–24. 09.

Brook R.H. (1979): Sulphur in agricultural. Abstracts on Tropical Agricultural, 5: 9–20.

Chapman H.D. (1967): Plant analysis values suggestive of nutrient status of selected crops. In: Hardy G.W. (ed): Soil Testing and Plant Analysis. Part II: Plant Analysis. Madison, Wisconsin Soil Science Society of America Special Publication, 2: 77–92.

Csapó J., Lóki K., Csapó-Kiss Z., Albert C. (2005): Separation and determination of the amino acids by ion exchange column chromatography applying post-column derivatization. Acta Agraria Kaposváriensis, 9: 33–51.

De Ruiter J.M., Martin R.J. (2001): Management of nitrogen and sulphur fertilizer for improved bread wheat (*Triticum aestivum*) quality. New Zealand Journal of Crop and Horticultural Science, 29: 287–299.

Flaete N.E.S., Hollung K., Ruud L., Sogn T., Faergestad E.M., Skarpeid H.J., Magnus E.M., Uhlen A.K. (2005): Combined nitrogen and sulphur fertilisation and its effect on wheat quality and protein composition measured by SE-FPLC and proteomics. Journal of Cereal Science, 41: 357–369.

Förster S., Welp G., Scherer H.W. (2012): Sulfur specification in bulk soil as influenced by long-term application of mineral and organic fertilizers. Plant, Soil and Environment, 58: 316–321.

Goos R.J., Westfall D.G., Ludwick A.E., Goris J.E. (1982): Grain protein content as an indicator of N sufficiency for winter wheat. Agronomy Journal, 74: 130–133.

Győri Z. (2005): Sulphur content of winter wheat grain in long term field experiments. Communications in Soil Science and Plant Analysis, 36: 373–382.

Izsáki Z. (2010): Nitrogen turnover of chernozem meadow soil in a long-term mineral fertilisation trial. Acta Agronomica Hungarica, 58: 57–62.

Järvan M., Edesi L., Adamson A., Lukme L., Akk A. (2008): The effect of sulphur fertilization on yield, quality of protein and baking properties of winter wheat. Agronomy Research, 6: 459–469.

Kalocsai R., Giczi Zs., Schmidt R., Szakál P., Barkóczy M. (2006): Effect of sulphate fertilization on the quality of winter wheat. Cereal Research Communications, 34: 529–532.

Klikocka H., Marks M., Barczak B., Szostak B., Podleśna A., Podleśny J. (2018): Response of spring wheat to NPK and S fertilization. The content and uptake of macronutrients and the value of ionic ratios. Open Chemistry, 16: 1059–1065.

Kovar J.L., Grant C.A. (2011): Nutrient cycling in soils: sulphur. In: Hatfield J.L., Sauer J.T. (eds.): Soil Management: Building a Stable Base for Agriculture. Madison, Soil Science Society of America, 103–115. ISBN: 978-0-891-18853-7

Lerner S.E., Seghezzo M.L., Molfese E.R., Ponzio N.R., Cogliatti M., Rogers W.J. (2006): N-and S-fertilizer effects on grain composition, industrial quality and end-use in durum wheat. Journal of Cereal Science, 44: 2–11.

Metson A.J. (1961): Methods of Chemical Analysis for Soil Survey Samples – Soil Bureau, Bulletin 12. Wellington, New Zealand Department of Scientific and Industrial Research, 208.

Naeem H.A., Macritchie F. (2003): Effect of sulphur nutrition on agronomic and quality attributes of wheat. In: Abrol Y.P., Ahmed A. (eds.): Sulphur in Plants. Dordrecht, Springer. 305–322. ISBN: 978-94-017-0289-8

Nguyen M.L., Rickard S.D., McBride S.D. (1989): Pasture production and changes in phosphorus and sulphur status in irrigated pastures receiving long-term applications of superphosphate fertiliser. New Zealand Journal of Agricultural Research, 32: 245–262.

Nikolskii Y.N., Aidarov I.P., Landeros-Sanchez C., Pchyolkin V.V. (2019): Impact of long-term freshwater irrigation on soil fertility. Irrigation and Drainage, 68: 993–1001.

Plénet D., Lemaire G. (1999): Relationships between dynamics of nitrogen uptake and dry matter accumulation in maize crops. Determination of critical N concentration. Plant and Soil, 216: 65–82.

Randall P.J., Spencer K., Freney J.R. (1981): Sulphur and nitrogen fertilizer effects on wheat. I. Concentrations of sulphur and nitrogen and the nitrogen to sulphur ratio in grain in relation to the yield response. Australian Journal of Agricultural Research, 32: 203–212.

Reich M., Shahbaz M., Prajapathi D.H., Parmar S., Hawkesford M.J., de Kok L.J. (2016): Interactions of sulphate with other nutrients as revealed by H_2S fumigation of Chinese cabbage. Frontiers in Plant Science, 7: 541–548.

Reussi N., Echeverría H.E., Rozas H.S. (2012): Stability of foliar nitrogen/sulfur ratio in spring red wheat and sulphur dilution curve. Journal of Plant Nutrition, 35: 990–1003.

Reuter D.J., Robinson J.B., Dutkiewicz C. (1997): Plant Analysis: An Interpretation Manual. 2nd Edition. Melbourne, CSIRO Publishing, 349–882. ISBN: 9780643101265 0643101268

Robson A.D., Osborne L.D., Snowball K., Simmons W.J. (1995): Assessing sulfur status in lupins and wheat. Australian Journal of Experimental Agriculture, 35: 79–86.

Sager M. (2012): Levels of sulphur as an essential nutrient element in the soil-crop-food system in Austria. Agriculture, 2: 1–11.

Scaife A., Burns I.G. (1986): The sulphate-S/total S ratio in plants as an index of their sulphur status. Plant and Soil, 91: 61–71.

Scherer H.W. (2001): Sulphur in crop production – invited paper. European Journal of Agronomy, 14: 81–111.

Schnug E., Haneklaus S. (2005): The role of sulphur in sustainable agriculture. In: Proceedings of the 1st Sino-German Workshop on Aspects of Sulphur Nutrition of Plants, Shenyang, 23–27 May 2004, 283: 131–135.

Sedlář O., Balík J., Kulhánek M., Černý J., Suran P. (2019): Sulphur nutrition index in relation to nitrogen uptake and quality of winter wheat grain. Chilean Journal of Agricultural Research, 79: 486–492.

Siwik-Ziomek A., Lemanowicz J., Koper J. (2013): Arylsulphatase activity and the content of total sulphur and its forms under the influence of fertilisation with nitrogen and other macroelements. Journal of Elementology, 18: 437–447.

Spencer K., Freney J.R. (1980): Assessing the sulphur status of field-grown wheat by plant analysis. Agronomy Journal, 72: 469–472.

Sutar R.K., Pujar A.M., Kumar B.N.A., Hebsur N.S. (2017): Sulphur nutrition in maize – a critical review. International Journal of Pure and Applied Bioscience, 5: 1582–1596.

Tisdale S.L., Nelson W.L., Beaton J.D. (eds.) (1985): Soil Fertility and Fertilizers. 4th Edition. New York, Macmillan Publishing Company. ISBN: 0024208302

Walinga I., Kithome M., Novozamsky I., Houba V.J.G., van der Lee J.J. (1992): Spectrophotometric determination of organic carbon in soil. Communications in Soil Science and Plant Analysis, 23: 1935–1944.

Wang C.Y., Liu W.X., Li Q.X., Ma D.Y., Lu H.F., Feng W., Xie Y.X., Zhu Y.J., Guo T. (2014): Effects of different irrigation and nitrogen regimes on root growth and its correlation with above-ground plant parts in high-yielding wheat under field conditions. Field Crops Research, 165: 138–149.

Yavitt J.B., Wieder R.K., Wright S.J. (1993): Soil nutrient dynamics in response to irrigation of a Panamanian tropical moist forest. Biogeochemistry, 19: 1–25.

Yu Z.T., Juhasz A., Islam S., Diepeveen D., Zhang J.J., Wang P.H., Ma W.J. (2018): Impact of mid-season sulphur deficiency on wheat nitrogen metabolism and biosynthesis of grain protein. Scientific Reports, 8: 2499.

Zhang P., Ma G., Wang C., Lu H., Li S., Xie Y., Ma D., Zhu Y., Guo T. (2017): Effect of irrigation and nitrogen application on grain amino acid composition and protein quality in winter wheat. PLoS One, 12: e0178494.

Zhao F.J., McGrath S.P. (1994): Extractable sulphate and organic sulphur in soils and their availability to plants. Plant and Soil, 164: 243–250.

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