

## Research Article

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# Sulfur application alleviates chromium stress in maize and wheat

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**Abstract:** This study aimed to examine the influence of increasing doses of chromium (Cr) (26, 39, and 52 mg kg<sup>-1</sup> soil) and elemental sulfur (S) (60 mg kg<sup>-1</sup> soil) on growth, yield, and mineral nutrition in wheat and maize. Macro- and micronutrients and Cr concentrations were determined in the aboveground parts of plants. All examined doses of Cr caused a marked decrease in the fresh and dry weight of maize. Wheat was more tolerant than maize, and lower Cr doses caused a small but statistically significant increase in the total yield. Wheat accumulated more than twofold Cr than maize, and the concentrations increased with higher Cr concentrations in the soil. The application of S significantly improved the total biomass production and lowered the Cr content in both plants. Cr changed the mineral nutrition in both cereals, but the pattern of changes observed was not the same. Applying S alleviated some adverse effects caused by the Cr. Hence, it is concluded that the application of elemental S may be an effective strategy to reduce adverse effects in plants grown on soil contaminated by heavy metals, especially Cr.

**Keywords:** chromium(vi), elemental sulfur, macroelements, microelements, heavy metals, nutrients

## 1 Introduction

Throughout the world, heavy metals are serious environmental pollutants, and the resulting toxicity to all living organisms has become a growing problem. Some

heavy metals are important micronutrients, while others are nonessential toxic elements. One nonessential element that negatively affects plant growth and development is chromium (Cr), which has been found to have increased concentrations in the environment [1]. Cr is found in all environment spheres, including air, water, and soil, and the naturally occurring concentration in soil ranges from 10 to 50 mg kg<sup>-1</sup> [2]. In aquatic environments, Cr occurs most frequently in the state of trivalent [Cr(III)] and hexavalent [Cr(VI)]. In mammals, Cr (III) in trace amounts is essential for sugar, protein, and fat metabolism; however, Cr(VI) is a dangerous contaminant and a potential carcinogen [3,4]. Cr(VI) is usually linked with oxygen as chromate (CrO<sub>4</sub><sup>2-</sup>) or dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) and is considered to be the most toxic form of Cr [2]. To cope with highly toxic metals, plants have evolved complex mechanisms that allow them to regulate the concentration of metals in tissues and minimize potential damage. However, the presence of heavy metals in the environment can cause a range of disturbances in plants, from cell functioning to plant growth and yield. Different strategies can be adopted to help plants cope with heavy metal stress and reduced the risks associated with the introduction of heavy metals into the food chain. One strategy is to apply selected fertilizers, and sulfur (S) plays a very vital role under conditions involving heavy metals. S is not only an essential plant nutrient but is also involved in response and tolerance mechanisms to various biotic and abiotic stress conditions [5].

Alternatively, S is considered as a limiting nutrient in high-yielding agrosystems, especially in northern European countries [6,7]. Therefore, research concerning the interaction of S with different environmental stressors is needed. The average concentration of S in plant tissues ranges from 0.2 to 0.5% of dry matter [8]. Plants take S as SO<sub>4</sub><sup>2-</sup> ions; however, elemental S is also a good source of this element in the soil [9,10].

The main objective of this study was to examine the influence of Cr used at enhanced but naturally occurring and nonlethal doses and elemental S applied to the soil on the growth, yield, and mineral nutrition of wheat and maize.

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## 2 Methods

### 2.1 Materials and setup and procedure

Experiments were set up in four replicates in Wagner type pots of 5 kg of soil with the physical and chemical properties presented in Table 1.

Initially, the soil had an acidic pH, before liming of the soil was done, a medium level of phosphorus and low levels of potassium and magnesium. The amount of overall S and S-SO<sub>4</sub> in both soils was determined and classified as low fertility soil. The content of microelements was low for iron, medium for copper, and manganese, but high for zinc. The Cr content was determined to be within the naturally occurring range.

The studied agricultural plants were spring wheat (Tybalt variety) and maize (Mosso variety). The length of the vegetation period for the species of plants tested in the pot experiments was 115 days for wheat and 99 days for maize. Wheat was collected at full maturity stage, and maize was collected at the full bloom stage (BBCH 67).

Calcium was added to the soil (liming) before sowing. Calcium carbonate was applied at a dose calculated for 1 Hh (5 g CaCO<sub>3</sub>). The experimental design included eight groups used to study the interaction of applied elemental sulfur fertilization and Cr (Table 2).

Elemental S and Cr were applied before sowing the seeds. Elemental S was ground into an average grain size of less than 0.1 mm to increase the rate of S oxidation in the soil [11]. Cr(VI) was applied to the soil in the form of an aqueous solution of potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. A potassium chloride solution was used to compensate for the amount of K in pots when no potassium dichromate was added.

For both plants, the same dose of nitrogen was applied (1.6 g per pot; NH<sub>4</sub>NO<sub>3</sub> in an aqueous solution). Half of the dose was applied before sowing and a half during the top-dressing stage (spring wheat BBCH 30 and maize BBCH 19).

The size of the dose for the remaining macroelements depended on the soil properties. Doses were added to the 5 kg of soil per pot: 0.6 g phosphorus, 1.5 g potassium, and 0.3 g of magnesium. The fertilization of

**Table 2:** Treatment in the pot experiment

No	Groups	Elemental sulfur	Chromium
		mg kg <sup>-1</sup>	
1	Control – without So and Cr	—	—
2	S <sup>0</sup> -elemental sulfur	60	—
3	Cr 26	—	26
4	Cr 39	—	39
5	Cr 52	—	52
6	S <sup>0</sup> + Cr 26	60	26
7	S <sup>0</sup> + Cr 39	60	39
8	S <sup>0</sup> + Cr 52	60	52

microelements was applied in standard quantities for pot experiments in compounds that did not contain S. Macro- and microelements were applied before sowing (in an aqueous solution or solids) and mixed into the entire amount of soil in the pot. Soil moisture was maintained throughout the entire vegetation period of the cultivated plants at 60% field capacity.

### 2.2 Methods for chemical analysis

Before and after the vegetation experiments, representative soil and plant samples were collected for agricultural and chemical analysis. After taking preparations of the soil material, the following was determined: the soil pH of 1 mol dm<sup>-3</sup> KCl with the potentiometric method, the overall S content (S total) with the Butters–Chenery method [12], the content of S sulfates(VI) (S-SO<sub>4</sub>) with the Bardsley and Lancaster method [13], and the soluble form of Cr in soil were determined in 1 mol dm<sup>-3</sup> HCl by the Rinkis method [14].

In-plant material collected during the research, the following was determined: the overall level of nitrogen (N organic) with the Kjeldahl method, the overall level of S (S total) with the Butters–Chenery method. To determine other elements, the plant material was dry mineralized, then the ash was taken up with nitric acid and determined in solutions: phosphorus with the vanadic-molybdate method, potassium and calcium

**Table 1:** Physical–chemical soil properties

Agronomic category of soil	pH	C organic	S total	P	K	Mg	S-SO <sub>4</sub>	Cr	Zn	Mn	Fe	Cu
		g kg <sup>-1</sup> soil		mg kg <sup>-1</sup> soil soluble forms								
Medium	4.8	6.32	0.178	64	88	48	9.26	1.16	39	110	577	2.94

with flame photometry, magnesium with atomic absorption spectrophotometry (ASA), and Cr and microelements with the ASA method.

## 2.3 Statistical methods

The yield sizes and the results of the chemical analysis were subjected to a one-way variance analysis. An evaluation was made of the relevance of mean differences with the Tukey *post hoc* test with a significance level of  $p = 0.05$ . The statistical program Statistica v. 13 and R [15] were used to develop the test results.

**Ethical approval:** The conducted research is not related to either human or animal use.

## 3 Results

The effect of increasing doses of Cr (26, 39, and 52 mg kg<sup>-1</sup> soil) and elemental S (60 mg kg<sup>-1</sup> soil) was evaluated by examining plant growth in the yields of grain and straw of spring wheat and the fresh and dry matter of maize, and macro- and micronutrients and Cr concentrations in the aboveground parts of plants.

### 3.1 Plant growth and yield

All the examined doses of Cr caused a marked decrease in both the fresh and dry weight of maize and applying S significantly increased these parameters (Figure 1).

Under the highest Cr dose, maize growth parameters were more than 20% worse than in the control plants. Applying S significantly improved the maize biomass, and the accumulation of fresh and dry mass was 36% and 26% higher, respectively, than in plants not treated with S.

Wheat was more tolerant of Cr than maize, and both lower Cr doses caused a statistically significant increase in the weight of straw (Figure 2).

Cr used in the highest dose decreased the yield of straw and grain, and the grain yield was 20% lower than in the control plants. Applying S enhanced the grain yield by nearly 12% compared to plants treated with 52 mg Cr. In the remaining cases, S fertilization also caused statistically significant increases, and the yield of both grain and straw was higher than in the control plants.

## 3.2 Mineral nutrition

### 3.2.1 Macroelements

Concentrations of different macroelements in the wheat grain varied, but in most cases, the changes were less than 10% compared to the control plants. Calcium remained unaffected, and changes in the concentrations of nitrogen, phosphorus, magnesium, and potassium were relatively small (Tables 3 and 4).

As expected, the S content varied significantly. Applying S alone resulted in a 17% increase in the concentration of S in the grain compared with the control plants, while all the doses of Cr caused marked decreases (18% under the highest Cr dose). Supplementing with S had a very positive effect, and the S content was considerably higher than the level in the control plants (Table 3).

It is interesting to note that wheat grain grown in soil supplemented with the highest Cr dose and S had the biggest concentrations of nitrogen, magnesium, phosphorus, and potassium (Tables 3 and 4).

Cr did not negatively influence nitrogen or phosphorus concentrations in wheat straw but considerably reduced the level of the remaining macroelements. The greatest changes were observed for S and calcium, and these concentrations in straw ranged from 55% to 70% of the value in the control plants. Adding S to the soil resulted in a significant increase in the S content irrespective of the Cr dose, and it was approximately three higher than in plants grown without S and two times higher than in the control plants. In the case of Ca, supplementing with S had a positive effect only when Cr was applied in the lowest dose. The changes in potassium and magnesium were definitively smaller, and the content of these elements was unaffected by the application of S.

In many cases, maize reacted differently to the growing conditions than wheat. Cr, particularly when used in higher doses, resulted in increased concentrations of nitrogen, magnesium, potassium, and calcium in maize shoots, and the presence of S decreased the content. S content was unaffected by Cr, and the combined action of Cr and S caused a 1.5-fold increase in the concentration of this element. Phosphorus concentrations were lower under the higher Cr doses and applying S increased this parameter above the values observed in the control plants.

### 3.2.2 Cr

All Cr doses caused a significant increase in Cr concentration in the straw of wheat and maize (Table 5).

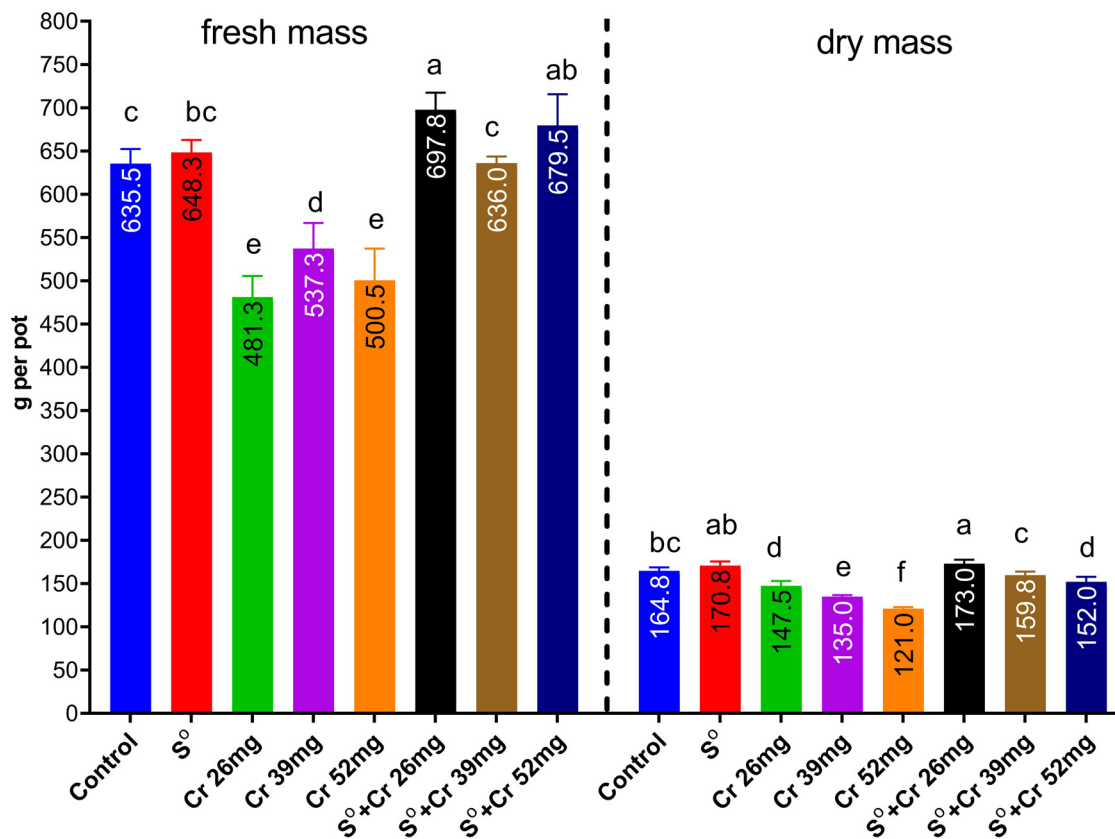


Figure 1: Yield of maize.

Wheat accumulated twofold more Cr than maize, and the concentration increased with higher Cr concentrations in the soil (from 170% to 238% of the control for the lowest and highest Cr dose, respectively). Wheat fertilized with S contained significantly less Cr than nonfertilized plants. Similar relationships were observed in maize. The lowest doses of Cr did not affect Cr concentrations in wheat grain. However, the highest dose resulted in an 18% increase when compared with the control plants. Supplementing with S considerably reduced this value.

### 3.2.3 Microelements

Cr did not affect the content of manganese in wheat straw, but it did lead to an increased level in the grain (Table 6).

In all cases, the applying S increased the manganese concentrations above that of the value in the control plants.

In both the grain and straw of plants grown under the highest Cr dose and S, the Mn concentration was

nearly 40% greater than in the control plants. In the case of corn, the observed increases in manganese concentrations (from 14–30% more than the value in the control plants) were mainly due to the presence of Cr in the soil.

Differences in iron concentrations in the examined plants were small and, in almost all cases, did not differ significantly from the control plants.

Under all examined conditions, the copper concentrations in maize were the same level, and in wheat, the levels fluctuated. In wheat grain, the highest concentration (175% of the control) was observed under the highest dose of Cr and S, while in straw, there was a small but statistically significant decrease.

Zinc concentrations in wheat grain were the same with the exception of plants grown in soil with Cr (the highest dose) alone or in combination with S, when the zinc concentration increased by 11% when compared with the control. Alternatively, in wheat straw, the highest zinc concentration occurred in plants grown under the lowest Cr dose alone or in combination with S. In maize, the presence of Cr in the soil led to a significant increase in zinc concentrations, ranging from 40% to 70% more than the values in the control plants.

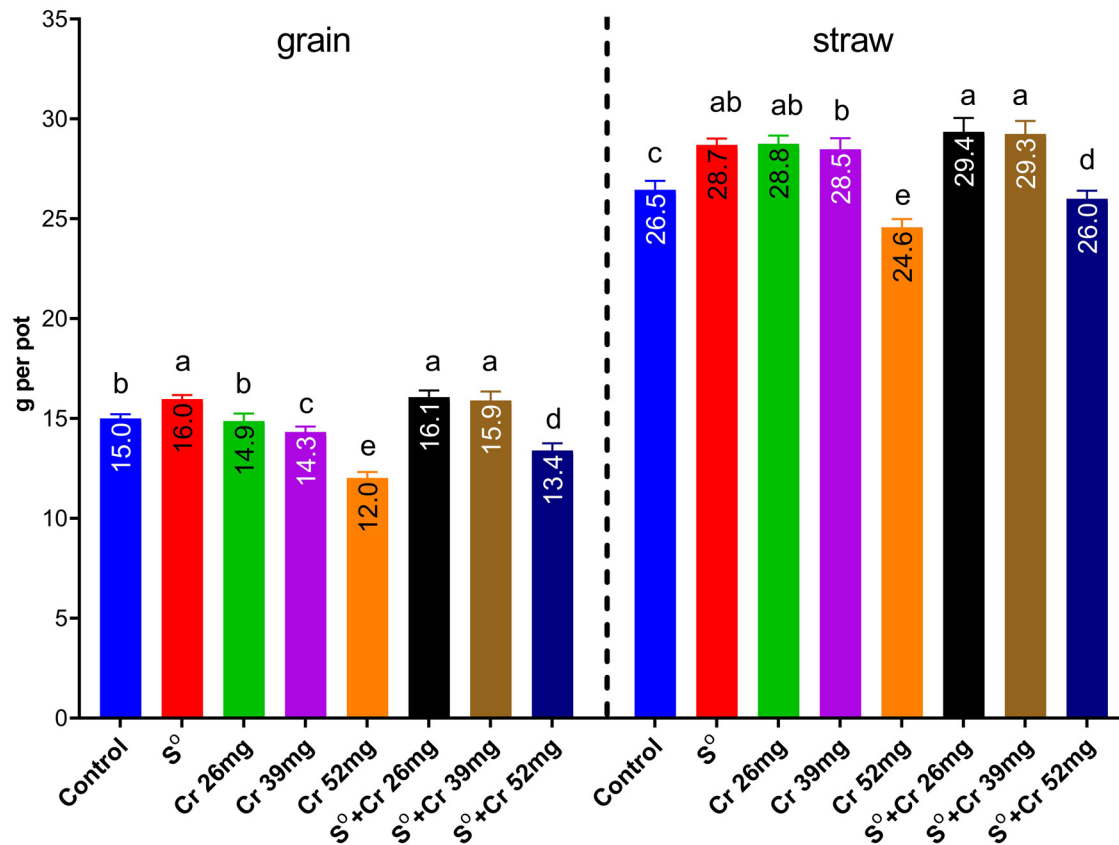


Figure 2: Yield of spring wheat.

Table 3: Nitrogen and sulfur content and uptake in cultivated plants

Groups	Spring wheat						Maize			
	Grain		Straw		(Grain + straw)		Content		Uptake	
	Content g kg <sup>-1</sup> d.m.				Uptake mg pot <sup>-1</sup>		g kg <sup>-1</sup> d.m.		mg pot <sup>-1</sup>	
Nitrogen										
Control	21.2	b	6.65	bcd	494	bc	8.99	c	1,482	a
S <sup>o</sup>	21.9	a	6.28	d	530	d	8.80	c	1,502	a
Cr 26 mg	21.0	b	6.65	bcd	504	c	9.97	a	1,471	a
Cr 39 mg	21.2	b	6.88	bc	499	c	9.63	b	1,300	bc
Cr 52 mg	21.2	b	7.50	a	439	a	10.16	a	1,229	c
S <sup>o</sup> + Cr 26 mg	21.8	a	6.45	cd	540	d	8.41	d	1,454	a
S <sup>o</sup> + Cr 39 mg	21.2	b	6.55	cd	528	d	8.47	d	1,352	b
S <sup>o</sup> + Cr 52 mg	21.9	a	7.05	ab	476	b	8.91	c	1,354	b
Sulphur										
Control	1.64	b	1.44	c	62.5	d	0.32	d	52.4	b
S <sup>o</sup>	1.92	a	2.41	b	99.7	f	0.45	bc	76.0	a
Cr 26 mg	1.39	c	0.94	d	47.6	c	0.31	d	45.7	c
Cr 39 mg	1.35	c	0.84	de	43.1	b	0.32	d	42.8	c
Cr 52 mg	1.34	c	0.80	e	35.9	a	0.31	d	37.8	d
S <sup>o</sup> + Cr 26 mg	1.90	a	2.61	a	107.0	g	0.44	c	75.3	a
S <sup>o</sup> + Cr 39 mg	1.71	b	2.61	a	103.4	fg	0.47	ab	74.7	a
S <sup>o</sup> + Cr 52 mg	1.82	a	2.68	a	94.0	e	0.49	a	73.8	a

**Table 4:** Macroelements (P, K, Mg, and Ca) content and uptake in cultivated plants

Groups	Spring wheat						Maize			
	Grain		Straw		(Grain + straw)		Content		Uptake	
	Content g kg <sup>-1</sup> d.m.				Uptake mg pot <sup>-1</sup>		g kg <sup>-1</sup> d.m.		mg pot <sup>-1</sup>	
Phosphorus										
Control	2.56	Bc	1.14	d	64.5	a	8.41	b	1,386	b
S <sup>0</sup>	2.61	b	1.25	c	68.4	b	8.30	b	1,417	ab
Cr 26 mg	2.45	cd	1.34	b	71.2	b	8.51	b	1,256	c
Cr 39 mg	2.31	d	1.34	b	74.6	c	7.21	c	974	d
Cr 52 mg	2.51	bc	1.40	ab	74.8	c	7.08	c	856	e
S <sup>0</sup> + Cr 26 mg	2.61	b	1.17	d	75.6	c	8.55	ab	1,479	a
S <sup>0</sup> + Cr 39 mg	2.49	bc	1.23	c	76.1	c	8.85	a	1,414	ab
S <sup>0</sup> + Cr 52 mg	2.83	a	1.42	a	77.7	c	8.60	ab	1,307	c
Potassium										
Control	3.84	bcd	12.00	a	375	c	50.3	c	8,284	a
S <sup>0</sup>	4.04	ab	10.85	cd	376	c	49.5	cd	8,462	a
Cr 26 mg	3.54	ef	11.53	abc	384	c	47.5	cd	7,004	b
Cr 39 mg	3.43	f	10.50	d	348	b	54.4	b	7,341	b
Cr 52 mg	3.79	cd	11.30	bc	324	a	61.8	a	7,481	b
S <sup>0</sup> + Cr 26 mg	3.95	abc	11.98	ab	414	d	40.9	e	7,079	b
S <sup>0</sup> + Cr 39 mg	3.67	de	10.90	cd	377	c	46.3	d	7,393	b
S <sup>0</sup> + Cr 52 mg	4.11	a	11.08	cd	343	ab	48.2	cd	7,317	b
Magnesium										
Control	0.83	b	1.10	b	41.4	c	4.43	f	729	e
S <sup>0</sup>	0.84	b	1.20	a	47.7	d	4.40	f	752	de
Cr 26 mg	0.81	b	1.00	c	40.7	c	5.85	c	862	a
Cr 39 mg	0.74	c	0.84	e	34.3	a	6.21	b	838	ab
Cr 52 mg	0.91	a	0.91	d	33.2	a	6.48	a	784	cd
S <sup>0</sup> + Cr 26 mg	0.83	b	0.98	c	42.1	c	4.82	e	834	abc
S <sup>0</sup> + Cr 39 mg	0.75	c	0.90	de	38.1	b	5.04	de	805	bc
S <sup>0</sup> + Cr 52 mg	0.91	a	0.87	de	34.8	a	5.19	d	789	bcd
Calcium										
Control	0.183	a	3.38	b	91.7	d	3.69	bc	608	a
S <sup>0</sup>	0.188	a	3.73	a	110.0	e	3.52	cd	601	a
Cr 26 mg	0.158	a	2.38	d	70.3	b	3.33	de	490	c
Cr 39 mg	0.145	a	1.92	e	56.1	a	3.91	b	528	bc
Cr 52 mg	0.178	a	1.94	e	50.1	a	4.19	a	507	bc
S <sup>0</sup> + Cr 26 mg	0.163	a	2.73	c	82.6	c	3.40	de	587	a
S <sup>0</sup> + Cr 39 mg	0.148	a	2.12	de	64.4	b	3.35	de	535	b
S <sup>0</sup> + Cr 52 mg	0.173	a	1.81	e	49.3	a	3.23	e	491	c

### 3.2.4 Total mineral uptake

In wheat (Tables 3 and 4), all Cr doses considerably lowered the uptake of calcium (the maximum reduction came out at 45% compared with the control plants) and S (a maximum of a 43% decrease compared with the control). The highest dose of Cr lowered the uptake of phosphorus, potassium, and magnesium, and in the case of magnesium, there was a 20% decrease in total uptake by wheat. Applying S significantly improved the uptake of S at all Cr doses and calcium at the lowest Cr dose in wheat (Table 4). The total uptake of Cr was similar to the

two higher Cr doses and supplementing with S considerably lowered this parameter (Table 5). Among the microelements, the largest changes (a 20% difference in comparison to the control plants) were found for copper in wheat grown under the highest Cr dose and applied S improved this parameter (Table 6).

Generally, in maize, Cr lowered the uptake of nitrogen, S, phosphorus, potassium, and calcium, and increased the total uptake of magnesium. Applying S ameliorated the uptake of nitrogen, phosphorus, and S and did not change the uptake of potassium. Regardless of the Cr concentration or the presence of sulfur, the



Table 5: Chromium content and uptake in cultivated plants

Groups	Spring wheat						Maize			
	Cr content			Cr uptake			Cr content		Cr uptake	
	g kg <sup>-1</sup> d.m.			μg pot <sup>-1</sup>			g kg <sup>-1</sup> d.m.		μg pot <sup>-1</sup>	
	Grain	Straw		(Grain + straw)						
Control	0.77	cd	2.68	e	82.6	a	1.12	g	185	c
S <sup>0</sup>	0.76	de	2.92	e	96.1	b	1.14	g	195	c
Cr 26 mg	0.80	bc	4.56	c	142.9	d	1.97	c	291	a
Cr 39 mg	0.80	bc	5.09	b	156.4	e	2.11	b	285	ab
Cr 52 mg	0.91	a	6.38	a	167.9	e	2.38	a	288	ab
S <sup>0</sup> + Cr 26 mg	0.72	e	3.45	d	112.6	c	1.56	f	271	b
S <sup>0</sup> + Cr 39 mg	0.74	de	3.55	d	115.7	c	1.70	e	272	b
S <sup>0</sup> + Cr 52 mg	0.83	b	4.15	c	119.1	c	1.85	d	281	ab

uptake of Cr remained at similar levels. The total uptake of copper and iron was remarkably reduced by Cr, and supplementing with S led to a better uptake of these elements. Cr caused an increase in the accumulation of zinc in maize, and additional S promoted this process.

### 3.2.5 Soil parameters after cultivation

The soil reaction (pH) after the cultivation of wheat significantly decreased when compared with the control object after applying elemental S, while after the application of Cr, there was a significant increase (Table 7).

Similar trends in soil pH changes were observed in the soil after cultivating maize. Applying S to the soil significantly increased the content of total S and sulfates (VI) in the soil after growing both wheat and corn. For groups where elemental S was used in the soil after wheat cultivation, a higher content of sulfates was found when compared with the soil after maize cultivation. The addition of Cr to the soil significantly increased the content of this element when compared with groups where this metal was not added into the soil.

## 4 Discussion

Cr is the second most common metal contaminant in groundwater, soil, and sediments, and its toxicity to biota is an increasing problem on a global scale [1]. For plants, Cr is a non-essential element, and at high concentrations, it is highly toxic for microorganisms,

plants, and animals [2,16]. Cr contamination of the soil may inhibit seed germination, root growth, seedling growth, and development and reduce the biomass and grain yield of crop plants. The amount of Cr in the soils ranges widely between 5 and 1,000 mg kg<sup>-1</sup> depending on the soil type. Among various valence states, Cr(III) and Cr(VI) are the most stable forms and may interconvert in soil [17–19], with Cr(VI) being the most toxic for plants. This form is relatively stable and mobile in soils that are sandy or contain low concentrations of organic matter [19]. Hexavalent Cr in concentrations as low as 0.5 ppm in nutrient solutions and 5 ppm in soil has been reported to reduce plant growth [20].

### 4.1 The influence of Cr

In the present study, we found that relatively low doses of Cr reduced crop productivity and changed the mineral status and applying elemental S to the soil may alleviate these negative influences. The studied data on crop growth showed that maize was more sensitive to Cr than wheat, and with increasing levels of Cr, the dry mass of maize decreased. There are many reports that plants exposed Cr have inhibited growth [21–24]. However, there are also reports indicating that Cr applied at low doses can have hormetic effects, namely low amounts of a contaminant have positive effects on an organism [25]. Our results showed that the lowest Cr dose (26 mg kg<sup>-1</sup> soil) stimulated the growth of wheat shoots.

The mechanisms that build plant tolerance to heavy metals are connected with processes that reduce the

**Table 6:** Microelements (Mn, Fe, Cu, and Zn) content and uptake in cultivated plants

Groups	Spring wheat						Maize			
	Grain		Straw		(Grain + straw)		Content		Uptake	
	Content g kg <sup>-1</sup> d.m.				Uptake mg pot <sup>-1</sup>		g kg <sup>-1</sup> d.m.		mg pot <sup>-1</sup>	
Manganese										
Control	36.1	e	92.3	d	2,983	a	43.1	d	7,105	cd
S <sup>0</sup>	46.4	bc	118.0	b	4,129	de	40.4	e	6,900	cd
Cr 26 mg	44.4	cd	90.0	d	3,248	b	48.9	c	7,207	c
Cr 39 mg	44.1	cd	90.8	d	3,216	b	52.1	b	7,028	cd
Cr 52 mg	51.3	a	94.8	d	2,946	a	54.8	a	6,631	d
S <sup>0</sup> + Cr 26 mg	43.2	cd	103.8	c	3,739	c	52.1	b	9,016	a
S <sup>0</sup> + Cr 39 mg	41.9	d	121.8	ab	4,228	e	56.3	a	8,982	a
S <sup>0</sup> + Cr 52 mg	49.7	ab	127.3	a	3,974	d	54.8	a	8,325	b
Iron										
Control	51.4	bc	85.3	ab	3,024	bc	69.8	abc	11,502	ab
S <sup>0</sup>	53.3	ab	89.3	a	3,411	de	68.3	bc	11,656	a
Cr 26 mg	47.6	cd	83.8	ab	3,118	bcd	70.5	abc	10,392	cd
Cr 39 mg	49.9	bcd	80.3	ab	3,002	bc	72.2	ab	9,738	de
Cr 52 mg	55.5	a	78.8	b	2,603	a	73.0	a	8,834	f
S <sup>0</sup> + Cr 26 mg	52.8	ab	88.8	ab	3,451	e	67.9	c	11,734	a
S <sup>0</sup> + Cr 39 mg	46.9	d	86.0	ab	3,258	cde	67.6	c	10,798	bc
S <sup>0</sup> + Cr 52 mg	53.5	ab	81.8	ab	2,844	ab	61.3	d	9,306	ef
Copper										
Control	3.42	bc	6.09	a	212	c	3.21	a	529	ab
S <sup>0</sup>	3.52	bc	5.76	b	221	cd	3.35	a	572	a
Cr 26 mg	3.37	bc	5.12	d	197	b	3.29	a	486	b
Cr 39 mg	3.25	c	5.13	d	193	b	3.18	a	429	c
Cr 52 mg	3.33	bc	5.28	d	170	a	3.07	a	371	d
S <sup>0</sup> + Cr 26 mg	3.72	ab	5.79	b	230	d	3.37	a	582	a
S <sup>0</sup> + Cr 39 mg	3.53	bc	5.55	c	218	c	3.32	a	530	ab
S <sup>0</sup> + Cr 52 mg	3.99	a	5.67	bc	200	b	3.27	a	496	b
Zinc										
Control	43.7	b	27.3	c	1,379	b	7.0	c	1,158	e
S <sup>0</sup>	43.8	b	24.9	e	1,414	bc	7.5	c	1,281	de
Cr 26 mg	44.3	b	29.4	ab	1,505	d	11.6	a	1,707	ab
Cr 39 mg	42.9	b	25.6	de	1,345	b	11.6	a	1,571	bc
Cr 52 mg	48.7	a	27.0	cd	1,250	a	11.9	a	1,437	cd
S <sup>0</sup> + Cr 26 mg	44.6	b	30.7	a	1,617	e	9.8	b	1,691	ab
S <sup>0</sup> + Cr 39 mg	42.8	b	27.9	bc	1,495	cd	11.4	a	1,818	a
S <sup>0</sup> + Cr 52 mg	48.6	a	29.5	a	1,419	bcd	11.6	a	1,772	a

uptake and transport of metals and with detoxification inside the cells [26]. The toxicity of Cr to plants depends on the concentration of the metal, its oxidation state, soil type, and the plant itself.

Interestingly, the shoots of both cereals grown under the highest dose of Cr contained 13% more nitrogen than the control plants. This may indicate that the N uptake and transport within the plant were not disrupted by Cr, and it is possible that both cereals activate a similar defense process in response to Cr. Many compounds containing nitrogen play an important role in the cellular detoxification of heavy metals. In the present study, we

did not examine these metabolites, but the increased N levels confirm that statement [27–30].

On the other hand, S concentrations in the shoots of the studied cereals varied when exposed to Cr. Cr treatment did not change the S concentrations in maize, but significantly lowered it in wheat. However, even the lower level of S in wheat straw was approximately three times higher than in maize. The greater tolerance of wheat to Cr may be associated with the high S concentration in this plant. Generally, plants differ greatly in their uptake and requirements for S, and S concentrations in plant tissues can vary over wide



**Table 7:** Soil pH and the content of S total, sulfates( $\text{SO}_4$ ), and Cr in the soil

Groups	pH		S total		S-SO <sub>4</sub>		S-SO <sub>4</sub> in S total		Cr	
	KCl 1 M dm <sup>-3</sup>		mg kg <sup>-1</sup>		mg kg <sup>-1</sup>		%		mg kg <sup>-1</sup>	
Spring wheat										
Control	6.54	c	150	E	10.6	c	7.06	d	1.18	e
S <sup>0</sup>	6.35	d	176	A	48.5	a	27.5	bc	1.11	e
Cr 26 mg	6.78	b	161	d	10.2	c	6.35	d	13.4	cd
Cr 39 mg	6.81	ab	164	cd	11.3	c	6.92	d	15.6	ab
Cr 52 mg	6.90	a	161	d	9.30	c	5.76	d	16.8	a
S <sup>0</sup> + Cr 26 mg	6.58	c	171	ab	44.2	b	25.9	c	13.1	d
S <sup>0</sup> + Cr 39 mg	6.64	c	170	abc	51.2	a	30.2	a	15.0	bc
S <sup>0</sup> + Cr 52 mg	6.80	b	169	bc	47.7	a	28.3	ab	15.6	ab
Maize										
Control	5.47	c	124	d	5.81	c	4.70	c	1.05	e
S <sup>0</sup>	5.34	c	172	ab	10.0	b	5.82	b	1.00	e
Cr 26 mg	6.46	a	139	c	6.09	c	4.38	c	11.7	c
Cr 39 mg	6.41	a	134	c	6.13	c	4.59	c	13.2	bc
Cr 52 mg	6.41	a	133	c	6.06	c	4.57	c	14.6	ab
S <sup>0</sup> + Cr 26 mg	6.02	b	165	b	11.5	a	7.00	a	9.85	d
S <sup>0</sup> + Cr 39 mg	6.09	b	175	a	12.4	a	7.12	a	14.5	ab
S <sup>0</sup> + Cr 52 mg	6.39	a	175	a	11.8	a	6.76	a	15.0	a

ranges. Small grains and maize usually contain the least amounts [31]. S is necessary for the proper growth and development of plants, however, like nitrogen, it also plays regulatory and defense functions in a plant's response to environmental stress and participates in the biosynthesis of some defense metabolites. A S-containing amino acid, cysteine, plays a central role in the detoxification of heavy metals. Cysteine is a primary metabolite for the synthesis of glutathione, phytochelatins, and metallothioneins. A higher S concentration in wheat straw likely allows this plant to accumulate considerably more Cr than maize without visible growth inhibition. Zayed and Terry [32] state that a critical Cr concentration in most plants is between 1 and 10  $\text{mg kg}^{-1}$  dry mass. Our results showed that the determined Cr content in the wheat straw and maize shoots fell within this range.

The nutritional state connected with the remaining macronutrients (P, K, Ca, Mg) was different in wheat and maize. Maize contained significantly more of all of these elements than wheat, and in some cases, the exposure of plants to Cr led to a higher concentration of K, Mg, and Ca but a decreased P content. Cr can interfere with the uptake and transport of some essential ions, such as iron, sulfate, and phosphate. There is evidence that carriers involved in their uptake are also engaged in the uptake of Cr by plants [33,34]. Our results showed that Cr did not affect phosphorus uptake negatively in wheat, although it did disrupt this process in maize.

The used doses of Cr were relatively low, and the observed disturbances in the levels of microelements were not critical to plant growth and development. The increase in Zn and Mn concentrations in maize may be considered as a positive effect because these metals are important for cell protection against reactive oxygen species generated under heavy metal stress. Zn, Mn, and Cu are essential components of superoxide dismutase that is a key element in cellular antioxidative mechanisms. The studied wheat straw contained considerably more Zn, Mn, and also Cu than maize, and this may have been due to a greater tolerance of wheat to Cr. We found that grain quality was negatively affected by the highest Cr dose; the Cr content was 18% higher than in the control plants, and the S content was 18% lower. However, as expected, the Cr content in the grain was a few times lower than in the straw. In the aerial parts of plants, the leaves usually contain more Cr than other parts like the seeds. In general, Cr concentrations in the shoots of plants are very low and large amounts of the metal remain in the plant roots [35,36].

Concentrations of the microelements Mn, Fe, and Zn increased by 42%, 10%, and 11%, respectively, when compared with the control plants. Our results showed that Cr simultaneously affected the content of many minerals, which could lead to a mineral imbalance in plants. Several studies have demonstrated that Cr could induce changes in the mineral nutrition of plants [37–40]. However, it is not possible to make a clear

generalization, because ultimately a plant's response is dependent on many factors, such as the Cr concentration, metal speciation, the availability of other nutrients, the presence of some soil additives and the plant genotype.

## 4.2 Cr and supplementary S fertilization

Adequate mineral fertilization is very important under all stress conditions. As mentioned earlier, under heavy metal stress S is particularly important because of its role in the cellular detoxification of metals. The presented results showed that applying elemental S improved the mineral-nutrient status in plants and ultimately plant growth and grain quality. Under the highest Cr dose, the S supply improved both the dry weight of wheat straw and grain yield when compared with plants grown with Cr alone. As expected, applying S increased the S concentration in both cereals and significantly lowered the Cr concentration.

Wheat simultaneously exposed to Cr and S accumulated significantly less Cr and considerably more S than plants grown without this macroelement. Sulfate originating from elemental S may inhibit the penetration of Cr into the cells and the translocation within the plant. The absorption of Cr involves the use of S transporters and carriers; hence, a sulfate deficiency promotes Cr uptake [1]. Likewise, maize reacted very positively to the presence of elemental S in the soil. Thus, S fertilization provides an effective strategy for reducing the adverse effect of Cr, and the applying S may be particularly recommended in sites contaminated with this metal.

From an agricultural point of view, the total amount of minerals accumulated by plants cultivated in particular pots is very important. Obviously, this parameter depends on the total plant biomass. The total biomass production of maize was approximately four-fold greater than wheat; hence, the levels of the accumulated minerals were several times higher than in wheat. The greatest differences were observed in the case of phosphorus, potassium, calcium, and magnesium, and the smallest, only 20%, for zinc. Wheat was characterized by a high concentration of S in the examined parts of plants and this resulted in a higher total uptake of this element when compared with maize. In our opinion, this property is responsible for greater wheat tolerance to Cr than maize.

Changes in the soil pH of fertilized soil can be impacted by the dose of S or the form applied. Elemental

S oxidation is a biological process that depends on many factors [41]. The rate of this process depends on the size, composition, and activity of the microbial population [42]. An increase in the share of sulfates(VI) in the total S in the soil after applying elemental S to the soil may indicate a high oxidation rate of elemental S [9,43]. In soils to which only Cr(VI) was added, a significant increase in soil pH in relation to the control group was found [40].

## 5 Conclusion

Cr changed the status of essential elements in both cereals, but the observed patterns were not the same. The disruption in mineral nutrition and the accumulation of Cr in the aboveground parts of plants resulted in decreased total dry matter production. Applying elemental S considerably decreased the Cr concentration in plants, increased the S concentration, and ultimately improved the yield. Thus, elemental S fertilization may be an effective strategy for reducing the adverse effects of Cr in plants.

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