



Article

Application of Urea and Ammonium Nitrate Solution with Potassium Thiosulfate as a Factor Determining Macroelement Contents in Plants

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Abstract: The following research hypotheses were established in this study: the applied urea and ammonium nitrate solution with potassium thiosulfate (UAN-KTS) has a positive effect on the chemical composition of spring wheat, spring rape and maize; fertilization with nitrogen, potassium and sulfur increases their contents in the usable parts of plants; the forms of applied fertilizers reduce the antagonistic effect of nitrogen and potassium on the content of other elements in plants. Two doses of nitrogen (N 1—optimal dose of nitrogen for a plant species; N 2—25% lower dose of nitrogen) and different ratios of N:K:S elements (N:K:S—without K and S; N:K₁:S₁—a narrowed ratio; N:K₂:S₂—the optimal ratio; N:K₃:S₃—an expanded ratio) were applied. The experiment was carried out on two soils of different quality. The improved soil quality resulted in a significant increase in the calcium (as opposed to magnesium) content of the three crops, in the nitrogen and sulfate–sulfur (VI) content of spring wheat grain and spring rapeseed, and in the phosphorus content of spring rapeseed and maize aerial parts. Reducing the dose (N 2) had a negative effect on the nitrogen content of spring wheat and on the sulfate–sulfur (VI) content of spring rape, maize and especially spring wheat. Increasing the N:K:S ratio had a small but usually antagonistic effect on the nitrogen content of all plant species, but a synergistic one on the potassium content of spring wheat, maize and partly of spring rape, and especially on the content of sulfate–sulfur (VI) in the crops. The effect of type of soil and fertilizers with different N:K:S ratios on the content of other macronutrients was related to plant species. The new fertilizer with the N:K₂:S₂ ratio had the greatest effect on the content of the tested macronutrients in spring wheat, spring rape and maize. In order to confirm the obtained relationships, it seems justified to carry out field experiments and studies with other plant species.



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1. Introduction

One of the requirements for obtaining high and good quality crop yields is to supply the crop with appropriate amount of nutrients, including macroelements. The quality of crops is modified by a number of factors, including the environmental pollution, fertilization, crop species, soil type and subtype, soil acidity and nutrient richness, antagonism and synergism between nutrients, counts of soil microorganisms, and soil enzymatic activity [1–4]. Nutrient deficiency can distort the normal course of physiological processes in plants. Deficiency of any macro- or micronutrient can be a triggering factor for plant diseases, resulting in reduced yields [5]. Environmental pollution and intensive agriculture often disrupt the ionic balance in plants, where the relationships between the following elements are extremely important: calcium to phosphorus, potassium to calcium and to

magnesium, calcium to magnesium; equally important are the relationships between certain microelements. Analysis of the content of macroelements in plants shows that today's crops are poorer in magnesium but richer in potassium, phosphorus and nitrate (V) than a century ago [6].

Fertilization, especially nitrogen and potassium fertilization, has a particularly strong influence on the ionic relationships between elements. This occurs most often between nitrogen (especially ammonium) and potassium, calcium and magnesium, and between potassium and magnesium, calcium and sometimes nitrogen. Nitrogen fertilizers account for about 56% of total world consumption, phosphorus fertilizers for 24% and potassium fertilizers for 20% [7]. Nitrogen and potassium fertilizers can cause significant changes in the chemical composition of plants [8]. The natural concentration of microelements in soil is usually sufficient to cover the nutritional needs of crops. Some amounts of macroelements and microelements are removed with harvested crops, but they are replenished in the soil by mineral, natural and organic fertilizers [9]. However, intensive and unbalanced mineral fertilization, especially with nitrogen fertilizers, can lead to decreased concentrations of some macroelements in the arable horizon of the soil, which is not indifferent to the growth and development of crops [10]. A relatively small amount of fertilizer components are used by plants. According to Duhan et al. [11], 40 to 70% of N, 80 to 90% of P and 50 to 70% of K from fertilizers are not used by plants because they are lost and migrate into the environment.

Macroelements, especially nitrogen and potassium, are important determinants of soil fertility and crop yield [12,13]. Potassium and nitrogen are among the basic macroelements that determine a plant's yield and quality. Potassium plays a special role in plants, where it is involved in numerous biochemical and physiological processes, such as photosynthesis, energy conversion, protein synthesis or the uptake of water, macroelements and trace elements [14,15]. Poor-quality sandy soils, which are deficient in the nutrients necessary for plant growth and development, are prevalent in many countries around the world. In addition, some nutrients, such as potassium and nitrogen, are leached from the soil by water deposited by atmospheric precipitation [16]. Therefore, regular application of mineral fertilizers is essential to ensure adequate conditions for the proper growth and development of crops. Fertilizers must be applied in doses that both meet the nutritional needs of the crop and allow for the crop to absorb nutrients in optimal amounts [17].

Under field conditions, the utilization of nitrogen from mineral fertilizers does not exceed 60% and decreases with increasing nitrogen fertilizer doses [18]. The remaining and sometimes substantial amount of nitrogen from fertilizers enriches soils to a limited extent in forms available to plants. The content of these forms of nitrogen (and of other elements) in the soil depend on several factors, including the amount of fertilizer applied, the type of a cropping system, losses by gaseous and leaching pathways, the amount of organic matter in the soil, the pH of the soil environment, or climatic conditions [19,20]. Plants absorb nutrients from liquid fertilizers more quickly than from solid fertilizers. Liquid fertilizers consist of a solution of urea and ammonium nitrate (UAN)—which is mainly used by large-scale agricultural producers—and have a major impact on plants in dry years with periods of drought during the growing season [21]. It should be added that losses of nitrogen after an application of UAN are lower than after application of other nitrogen fertilizers [20,22,23]. Nitrogen uptake by plants is usually limited to monovalent ions: NH_4^+ cations and NO_3^- anions [8]. Nitrogen uptake by plants depends on the reaction of the soil. NO_3^- ions are taken more quickly by plants in acidic soils, and NH_4^+ ions in less acidic environments. The NH_4^+ ion can also be transformed to NO_2^- and then to NO_3^- as a result of the nitrification process [24]. Nitrates (V) are the compounds that are only loosely bound to the solid phase of the soil and therefore can migrate with water, which favors the leaching of some of their pool. This is most often observed in light soils. Leaching mainly affects the nitrate form, which explains why nitrification of ammonium to the nitrate form plays a major role in exacerbating nitrogen losses [25]. Excessive doses of nitrogen can contribute to higher losses of nitrate (V) through leaching [8]. Potassium is

mainly taken up by plants mostly as K^+ ions. Among the major macrolelements, potassium is another example of an element that is quite easily leached from the surface to deeper soil layers by precipitation [8]. This explains why the doses of fertilizers, especially nitrogen and potassium ones, must be adapted to the nutritional needs of the crops and to the elemental abundance of the soil [10]. Adequate sulfur content in plants, due to the fact that it is a component of amino acids in plant proteins, is necessary for the proper growth and development of plants. In addition, it can determine the taste and smell of plants [21]. It is equally important to produce fertilizers that can meet the needs of plants during the critical phases of their growth and development.

The above factors have led to the need to, in the form of fertilizers, provide plants with components necessary for their growth and development, with nutrients (especially nitrogen and potassium) that are easily accessible and at the same time are not released from the soil very intensively. The growing problem of potassium and sulfur deficiency in crop production is forcing the search for new fertilizer products that are sources of these elements. When introducing new fertilizers, components should be selected to minimize antagonistic (negative) interactions between components while maximizing their synergistic effects. This will ensure optimal nutrient use efficiency and increased crop yield [26]. Recently, more and more attention has been paid to the production and use of liquid nitrogen fertilizers containing sulfur and especially potassium. We decided to create a new fertilizer by combining a fast-acting UAN with potassium thiosulfate (KTS) to provide the plants with nutrients in the right proportions. The thiosulfate component was added to extend the duration of the fertilizer's effect because the thiosulfate molecule delays nitrification [27]. In soil, the thiosulfate part of the molecule ($S_2O_3^{2-}$) oxidizes to form sulfate (SO_4^{2-}). While in the case of UAN, there are many references [20–23] discussing its influence on plants, in the case of KTS, there are few and they do not apply to typical plants grown in agriculture [27,28]. Therefore, there is a need to conduct research on the influence of KTS on these plants. The main advantage of using liquid fertilizers is that they spread very evenly over the field surface, which is not fully possible when using solid fertilizers [29], e.g., urea, ammonium sulfate, potassium salt or potassium sulfate. Thiosulfates applied topically decompose to release sulfate–sulfur, which is directly bioavailable to plants, and elemental sulfur, which is oxidized to an available form. Therefore, thiosulfates are an excellent source of readily available sulfur and reserve sulfur for later use by plants [30]. In conclusion, both nitrogen and potassium fertilization, as well as sulfur and other elements, are essential for high yields of crops of the right quality. The use of UAN-KTS in the correct proportions between fertilizer components has a very positive effect on the yield of corn, spring wheat and especially spring oilseed rape [31]. However, there is a paucity of research on the effects of UAN in combination with KTS on plants.

In view of the above considerations, the following research hypotheses were established in this study: the applied urea and ammonium nitrate solution with potassium thiosulfate (UAN-KTS) has a positive effect on the chemical composition of plants; fertilization with nitrogen, potassium and sulfur increases them in the usable parts of plants; the forms of applied fertilizers reduce the antagonistic effect of nitrogen and potassium on the content of other elements in plants. The experiment was carried out on two soils of different quality. To determine the effect of UAN-KTS on plants, total nitrogen, phosphorus, potassium, calcium, magnesium and sulfate–sulfur were analyzed. Species that are widely grown and of great economic importance were selected as test crops. These are wheat (*Triticum aestivum* L.), maize (*Zea mays* L.) and spring rape (*Brassica napus* L. var. *napus*). Wheat and maize are the second and third most important cereal crops in the world, respectively, and spring rape is one of the most important crops in central Europe [32]. Maize is a crop used for animal feed, human consumption and industrial purposes [33]. Their cultivation, especially maize and spring rape, requires the use of high doses of fertilizers [34,35]. The main objective of this study was to determine the effect of a new fertilizer—urea and ammonium nitrate solution with potassium thiosulfate (UAN-KTS)—on the chemical composition of crops (spring wheat, spring rape and maize)

grown on two soils of different quality, as well as to determine the appropriate proportions of fertilizer components for these plant species.

2. Materials and Methods

2.1. Methodology

The research was based on three-pot experiments conducted in a greenhouse at the University of Warmia and Mazury in Olsztyn (northeastern Poland). It was carried out on two soils of different quality. The soils had the following characteristics: Soil 1: granulometric composition—sand (sand > 0.05 mm 91.9%, silt 0.002–0.05 mm 7.4%, clay < 0.002 mm 0.7%); pH in 1 M KCl dm^{−3}—6.17; total organic carbon (TOC)—3.95 g kg^{−1} dry matter (DM); total nitrogen—0.67 g kg^{−1} DM; available phosphorus—14.83 mg P kg^{−1} DM; available potassium—102.0 mg K kg^{−1} DM; available magnesium—29.57 mg Mg kg^{−1} DM; sulfur—18.97 mg S-SO₄ kg^{−1} DM. Soil 2: granulometric composition—loamy sand (sand > 0.05 mm 77.6%, silt 0.002–0.05 mm 19.9%, clay < 0.002 mm 2.5%); pH in 1 M KCl dm^{−3}—5.73; TOC—5.64 g kg^{−1} DM; total nitrogen—1.12 g kg^{−1} DM; available phosphorus—22.16 mg P kg^{−1} DM; available potassium—145.0 mg K kg^{−1} DM; available magnesium—36.18 mg Mg kg^{−1} DM; sulfur—15.92 mg S-SO₄ kg^{−1} DM. The granulometric composition of the soil corresponds to the classification of the World Reference Base for Soil Resources [36].

There were three-factorial experiments. The first-order factor was the soil kind: Soil 1—of lower quality; Soil 2—of higher quality. The second factor was 2 doses of nitrogen: N 1—optimal nitrogen dose for a given crop species; N 2—a nitrogen dose 25% lower than the first one. The third-order factor consisted of different ratios of N:K:S elements, such as N:K:S—without potassium and sulfur fertilization; N:K₁:S₁—a narrowed ratio; N:K₂:S₂—an optimal ratio; N:K₃:S₃—an extended ratio. The fertilizers were tested on three crops: spring wheat (*Triticum aestivum* L.) of the cultivar Harenda, spring rape (*Brassica napus* L. var. *napus*) of the cultivar Lumen, and maize (*Zea mays* L.) of the cultivar Kadryl. The N:K:S, N:K₁:S₁, N:K₂:S₂ and N:K₃:S₃ ratios were 1:0:0, 1:0.5:0.3, 1:0.7:0.5 and 1:0.9:0.6, respectively, in the spring wheat and spring rape experiments, and 1:0:0, 1:0.8:0.5, 1:1.1:0.7 and 1:1.4:1 in maize pots. The doses of fertilizers were adjusted to meet the nutrient requirements of the plants. Nitrogen doses were as follows: 140 mg N kg^{−1} of soil under spring wheat and 160 mg N kg^{−1} of soil under spring rape and maize in the N 1 series, and 105 mg N kg^{−1} of soil under spring wheat and 120 mg N kg^{−1} of soil under spring rape and maize in the N 2 series. Other fertilizer rates are listed in Table 1.

Table 1. Doses of fertilizers (mg kg^{−1} of soil).

Varieties	Spring Wheat (<i>Triticum aestivum</i> L.)				Spring Rape (<i>Brassica napus</i> L. var. <i>napus</i>)				Maize (<i>Zea mays</i> L.)			
N:K:S	N:K:S	N:K ₁ :S ₁	N:K ₂ :S ₂	N:K ₃ :S ₃	N:K:S	N:K ₁ :S ₁	N:K ₂ :S ₂	N:K ₃ :S ₃	N:K:S	N:K ₁ :S ₁	N:K ₂ :S ₂	N:K ₃ :S ₃
N:K:S ratio	1:0:0	1:0.5:0.3	1:0.7:0.5	1:0.9:0.6	1:0:0	1:0.5:0.3	1:0.7:0.5	1:0.9:0.6	1:0:0	1:0.8:0.5	1:1.1:0.7	1:1.4:1
N 1 series												
N	140	140	140	140	160	160	160	160	160	160	160	160
P ₂ O ₅	60	60	60	60	80	80	80	80	80	80	80	80
K ₂ O	0	70	98	126	0	80	112	144	0	128	176	224
S	0	42	70	84	0	54	80	108	0	80	112	160
N 2 series												
N	105	105	105	105	120	120	120	120	120	120	120	120
P ₂ O ₅	60	60	60	60	80	80	80	80	80	80	80	80
K ₂ O	0	53	74	95	0	60	84	108	0	96	132	168
S	0	31.5	52.5	63	0	36	60	72	0	60	84	120

A new liquid fertilizer containing nitrogen, potassium and sulfur was used. This fertilizer is composed of classical commercial urea and ammonium nitrate solution (Grupa Azoty Zakłady Azotowe “Puławy” S.A., Puławy, Poland) and new, innovative potassium thiosulfate (UAN-KTS). KTS is obtained from the desulfurization of flue gases from the

sulfuric acid plant. UAN-KTS contains 32% N, 25% K₂O and 17% S. UAN-KTS was applied to each test site in appropriate N:K:S ratios according to the test scheme and dosages shown in Table 1. Phosphorus was applied separately as Super FosDar 40 (41.2% P₂O₅). In addition, microelements were added to all experimental sites in the same doses: Zn 5 mg (ZnSO₄ · 7H₂O), Cu 5 mg (CuSO₄ · 5H₂O), B–0.33 (H₃BO₃), Mo 5 mg ((NH₄)₆Mo₇O₂₄ · 4H₂O) and Mn 5 mg (MnSO₄ · H₂O). The innovation of the fertilizer used in the experiment, based on a solution of urea and ammonium nitrate solution with potassium thiosulfate (UAN-KTS), is related to its production process. The potassium thiosulfate solution used was produced by an innovative technology using waste gases from the sulfuric acid plant. First, potassium sulfate (IV) was produced by absorbing sulfur dioxide from the sulfuric acid plant, reducing its emissions and nitrogen oxide emissions to the atmosphere by approximately 90%. Next, 50% potassium thiosulfate solution was obtained from potassium sulfate (IV) and sulfur from the desulfurization process. A product of very high purity and high UV stability was obtained. The produced potassium thiosulfate solution and UAN were used as raw materials for the production of liquid UAN-KTS. This innovative production method makes it possible to reduce the negative impact of greenhouse gas emissions on the environment during the production of granular fertilizers, as well as to manage waste (wastewater, solutions and exhaust gases from fertilizer production, and sludge from wastewater treatment), which is very important from the point of view of environmental protection and meeting the requirements of pro-environmental programs, such as the closed-loop economy.

The UAN-KTS was applied at two times: before sowing the crops and during the vegetative development of the crops: 60% before sowing and 40% at the tillering stage in spring wheat—BBCH 23; 50% before sowing and 50% before the leaves formed a rosette in spring rape—BBCH 15; and 50% before sowing and 50% at the 4–6 leaf stage of maize—BBCH 15. The fertilizers were diluted with distilled water before application to soil. Phosphorus fertilizers and microelements were applied before sowing. The UAN-KTS, phosphorus fertilizer (Super FosDar 40) and microelements were applied before sowing. The fertilizers were thoroughly mixed with soil and transferred to pots with 9 kg capacity (top diameter—24 cm; bottom diameter—19 cm; height—25 cm). The experimental design for each of the three test plants included 48 pots, i.e., 16 objects (combinations) in 3 replicates, for a total of 144 pots.

After filling the pots with soil containing the applied fertilizers, the test plants were sown on April 12. The number of plants per pot was 15 plants for spring wheat, 8 plants for spring rape and 8 plants for maize. The soil moisture content in all the pots was maintained at a stable level equal to 60% of the maximum water capacity throughout the whole experiment. The weather data during the test were typical: the length of the day was from 9 h 2 min to 16 h 26 min; the average air temperature was 13.8 °C; the average humidity was 64.3%. The crops were harvested at the following growth stages: spring wheat at full maturity—BBCH 89 (20 July); spring rape at technological maturity—BBCH 85 (18 July); maize at the tasseling stage—BBCH 59 (21 June). The plant species grown in the pot experiments are shown in Figure 1. The plants (spring wheat—15 plants; spring rape—8 plants; maize—8 plants) were cut at ground level. Samples of all plants were taken from each pot for laboratory analysis (grain from spring wheat—average 44 g; seed from spring rape—average 36 g; aerial parts from maize—average 890 g).

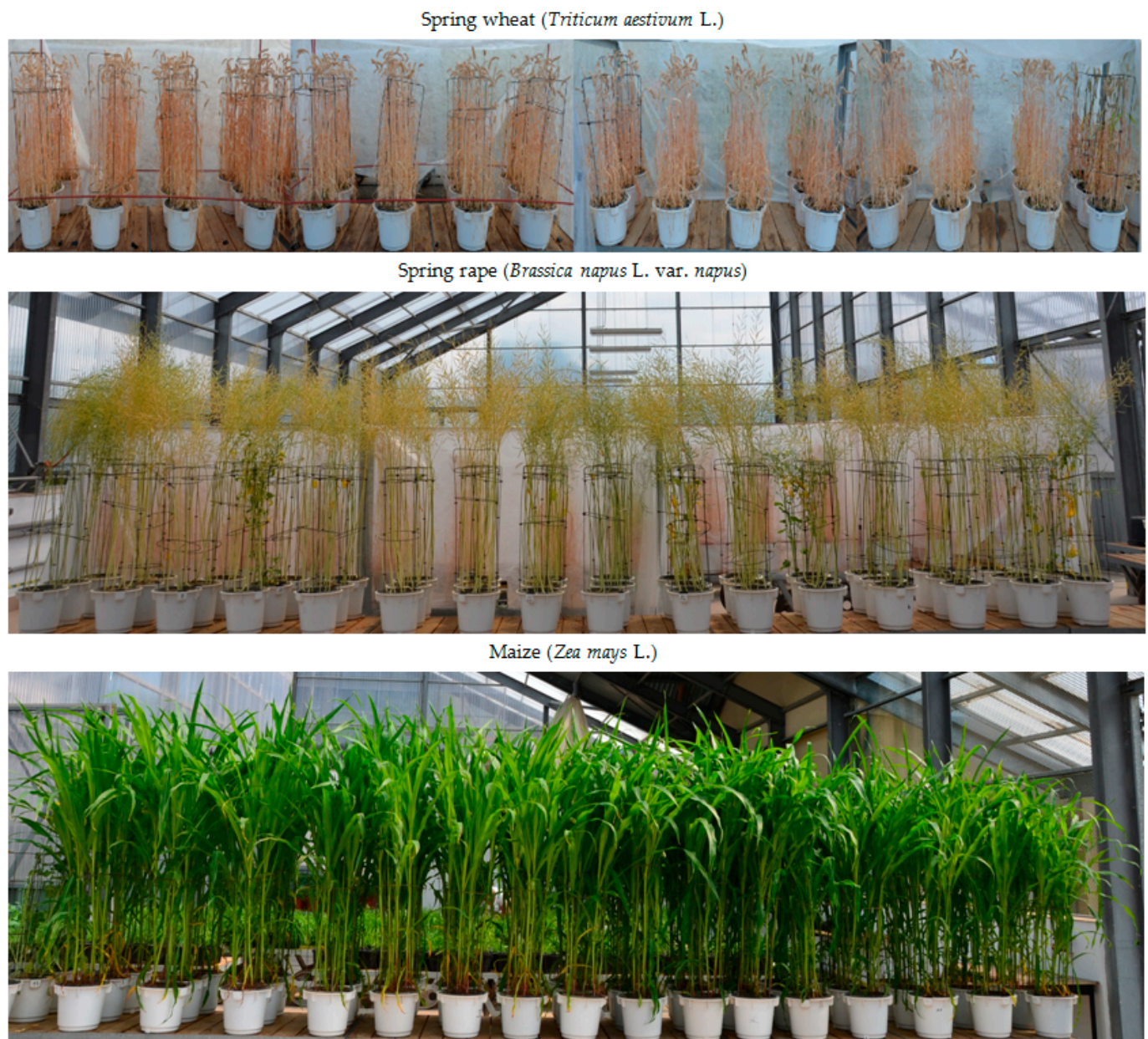


Figure 1. Plant species grown in the pot experiments.

2.2. Laboratory and Statistical Analysis Methods

Samples of the crops were taken at harvest. Next, they were cut, dried at 60 °C and ground. They were then wet-digested in concentrated 95% sulfuric acid (H₂SO₄ analytical grade, Avantor Performance Materials Poland S.A., Gliwice, Poland) in a Speed-Digester K-439 (BÜCHI Labortechnik AG, Flawil, Switzerland). The following determinations were then carried out: content of total nitrogen using the Kjeldahl method on a KjelFlex K-355 Kjeldahl distiller (Büchi Labortechnik AG, Flawil, Szwajcaria) [37,38]; phosphorus using the colorimetric method [38]; potassium, calcium and magnesium using the atomic absorption spectrometric (AAS) method on a SpectrAA 240FS spectrophotometer (Varian Inc., Mulgrave, VIC, Australia) [38]; sulfate–sulfur (VI) using the nephelometric method with 2% CH₃COOH and activated carbon (analytical grade, Avantor Performance Materials Poland S.A., Gliwice, Poland) [38,39]. Prior to the actual experiment, the basic soil properties were determined, such as the granulometric composition using the laser method on the Mastersizer 3000 analyzer (Malvern Instruments Ltd., Worcestershire, UK) [40], pH_{1M KCl}

with the potentiometric method [41], total nitrogen content with the Kjeldahl method on a KjelFlex K-355 Kjeldahl distiller (Büchi Labortechnik AG, Flawil, Schwajcaria) [37,42], the soil content of available forms of phosphorus and potassium with the Egner–Riehm method [43,44], and sulfur by nephelometry, according to the protocol by Bardsley and Lancaster [45]. The research results were statistically processed in a Statistica 13 package [46], by performing a three-factorial analysis of variance (ANOVA), in addition to which the percentage of observed variation was calculated according to ANOVA with the coefficient η^2 . For variable systems, ANOVA was used to calculate one-dimensional results for each variable tested. The unidimensional results were then multiplied by 100 and divided by the sum of all variables.

3. Results

3.1. Chemical Composition of the Crops

The content of micronutrients and total protein in the crops depended on both on the kind of soil and on the fertilization with potassium, nitrogen and sulfur.

3.1.1. Nitrogen

An increase in the soil quality caused a significant increase in the nitrogen content, reaching an average of 21% in spring wheat grain and 10% in spring rapeseed compared to its content in the same plant species grown in the poorer soil. However, this factor had no significant effect on the nitrogen content in the aerial organs of maize (Table 2, Figure 2).

Table 2. Nitrogen content in plants (g kg^{−1} D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	18.95	17.36	18.16	22.31	21.00	21.66
N:K ₁ :S ₁	18.39	16.71	17.55	20.91	19.13	20.02
N:K ₂ :S ₂	18.11	17.27	17.69	21.93	19.32	20.63
N:K ₃ :S ₃	17.55	15.87	16.71	21.65	22.96	22.31
Average	18.25	16.80	17.53	21.70	20.60	21.15
LSD _{0.01}	A—0.59; B—0.59; C—0.83; A × B—n.s.; A × C—0.83; B × C—n.s.; A × B × C—1.66					
Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed						
N:K:S	33.41	32.06	32.74	36.49	31.83	34.16
N:K ₁ :S ₁	28.75	28.19	28.47	32.20	30.80	31.50
N:K ₂ :S ₂	26.97	26.79	26.88	30.43	31.36	30.90
N:K ₃ :S ₃	28.70	30.61	29.66	33.60	32.06	32.83
Average	29.46	29.41	29.44	33.18	31.51	32.35
LSD _{0.01}	A—0.89; B—0.89; C—1.26; A × B—n.s.; A × C—n.s.; B × C—1.78; A × B × C—n.s.					
Maize (<i>Zea mays</i> L.) aerial parts						
N:K:S	7.19	8.59	7.89	9.33	8.59	8.96
N:K ₁ :S ₁	7.28	7.56	7.42	7.93	7.37	7.65
N:K ₂ :S ₂	7.19	7.56	7.38	8.87	6.07	7.47
N:K ₃ :S ₃	8.49	8.87	8.68	8.12	5.88	7.00
Average	7.54	8.15	7.84	8.56	6.98	7.77
LSD _{0.01}	A—n.s.; B—n.s.; C—1.26; A × B—n.s.; A × C—n.s.; B × C—1.78; A × B × C—n.s.					

n.s.—non-significant.

Changes in the nitrogen content in spring wheat grain and in spring rapeseed after the application of the lower N dose were relatively small. The lower N dose resulted in a significant decrease in the total nitrogen content in spring wheat grain by an average of 5% in the higher-quality soil and by 8% in the lower-quality soil compared to the higher

N dose. The effect of N dose on the nitrogen content in spring rapeseed and in the aerial organs of maize was different in two soils and insignificant. The broader N:K:S ratio had a rather antagonistic effect on the nitrogen content in the grain of spring wheat, in the seed of spring rape and in the aerial parts of maize, but these changes were small, in the order of a few percent.

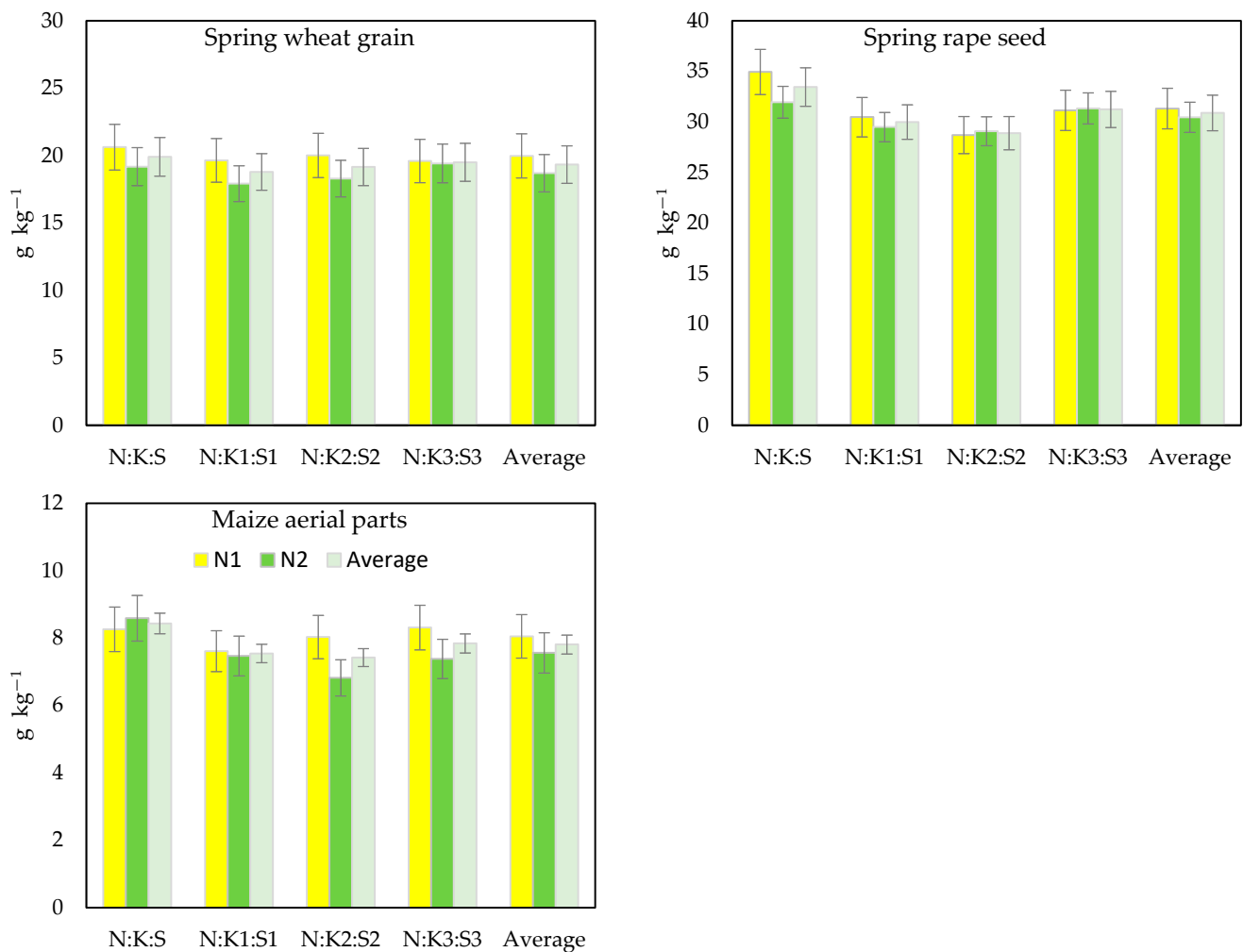


Figure 2. Effect of N:K:S ratio and N dose on nitrogen content of plants (averages from all series).

3.1.2. Phosphorus

The increased soil quality resulted in a relatively small increase in the phosphorus content accumulated in the seed of spring rape and aerial parts of maize compared to the phosphorus content of the crops grown in the low-quality soil (Table 3, Figure 3). The lower N dose caused an 17% average increase of in phosphorus content in spring wheat grain, and an 8% average increase in spring rapeseed harvested from pots with the richer soil compared to the higher N dose. The differences were not statistically significant for spring rape and in maize. No significant trends were observed in the changes in phosphorus content of spring wheat grain, spring rapeseed or aerial parts of maize after application of N:K:S fertilization.

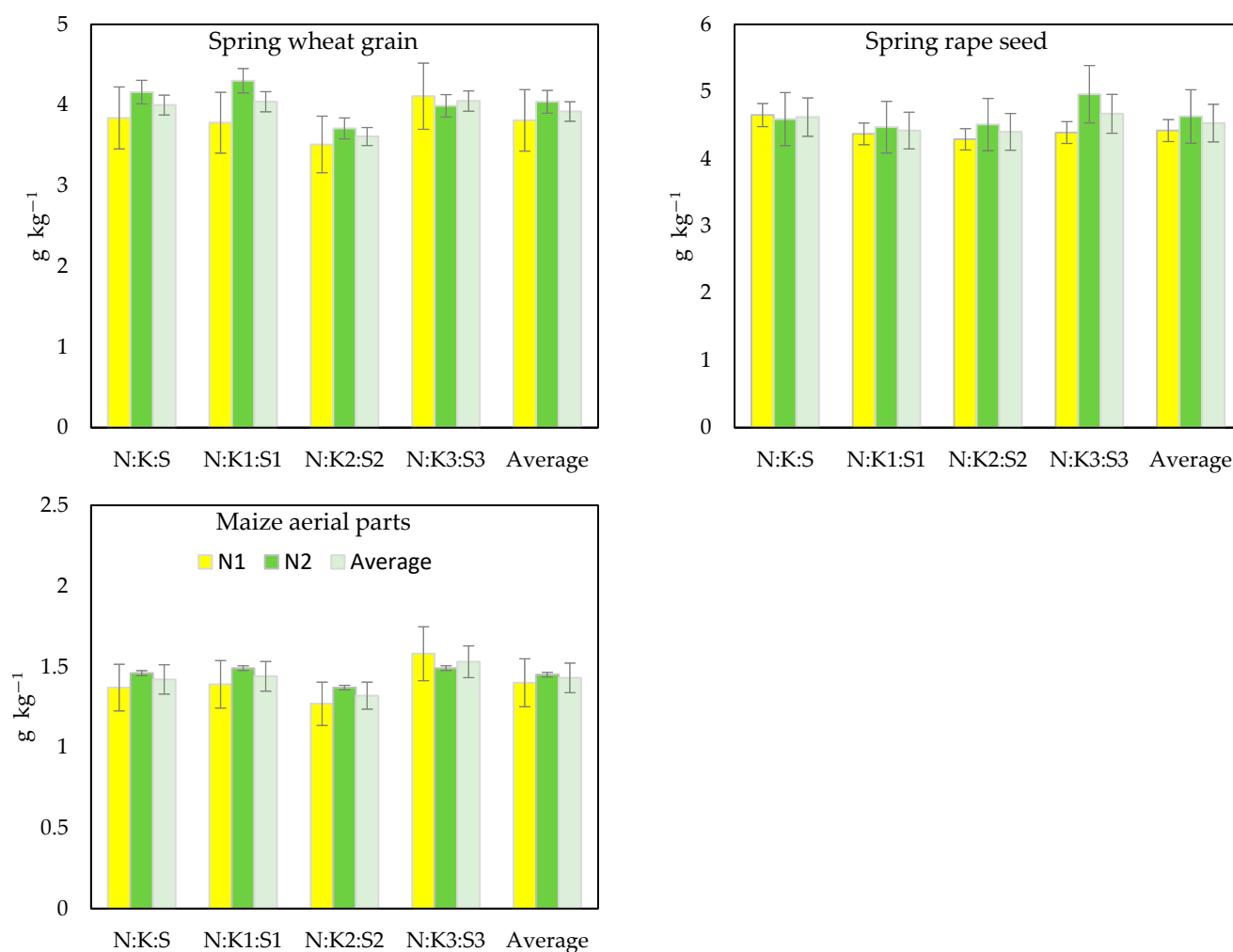


Figure 3. Effect of N:K:S ratio and N dose on phosphorus content of plants (averages from all series).

Table 3. Phosphorus content in plants (g kg⁻¹ D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	3.76	4.10	3.93	3.92	4.22	4.07
N:K ₁ :S ₁	4.12	3.93	4.03	3.44	4.66	4.05
N:K ₂ :S ₂	3.82	3.86	3.84	3.20	3.56	3.38
N:K ₃ :S ₃	4.62	3.85	4.24	3.60	4.12	3.86
Average	4.08	3.94	4.01	3.54	4.14	3.84
LSD _{0.01}	A—n.s.; B—n.s.; C—n.s.; A × B—n.s.; A × C—n.s.; B × C—n.s.; A × B × C—n.s.					
Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed						
N:K:S	4.55	4.34	4.45	4.75	4.84	4.80
N:K ₁ :S ₁	4.13	4.16	4.15	4.61	4.78	4.70
N:K ₂ :S ₂	4.21	4.26	4.24	4.36	4.76	4.56
N:K ₃ :S ₃	4.34	4.64	4.49	4.44	5.27	4.86
Average	4.31	4.35	4.33	4.54	4.91	4.73
LSD _{0.01}	A—0.22; B—n.s.; C—n.s.; A × B—n.s.; A × C—n.s.; B × C—n.s.; A × B × C—n.s.					

Table 3. Cont.

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Maize (<i>Zea mays</i> L.) aerial parts						
N:K:S	1.28	1.27	1.28	1.46	1.65	1.56
N:K ₁ :S ₁	1.23	1.41	1.32	1.55	1.57	1.56
N:K ₂ :S ₂	1.18	1.55	1.37	1.35	1.18	1.27
N:K ₃ :S ₃	1.45	1.54	1.50	1.71	1.43	1.57
Average	1.29	1.44	1.36	1.52	1.46	1.49
LSD _{0.01}	A—0.22; B—n.s.; C—n.s.; A × B—n.s.; A × C—n.s.; B × C—n.s.; A × B × C—n.s.					

n.s.—non-significant.

3.1.3. Potassium

The richer soil showed a small but positive effect on the content of this element in the spring wheat grain and maize aerial parts (Table 4, Figure 4). The influence of N dose on the content of potassium in the seed of spring rape and aerial organs of maize depended on the soil kind. A decrease in the N dose resulted in a 10% decrease in potassium content in spring rapeseed harvested from pots filled with the poorer soil but increased its accumulation by 14% in spring rapeseed grown in the richer soil. For maize, inverse relationships were observed. The lower N dose caused a significant increase (by 14%) in the potassium content of the aerial parts of maize grown in poor quality soil but limited the accumulation of this element by 10% on the richer soil, so that the cumulative effect of nitrogen on the potassium content of the maize aerial parts was negligible.

Table 4. Potassium content in plants (g kg^{−1} D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	5.50	5.55	5.53	5.88	5.76	5.82
N:K ₁ :S ₁	5.55	5.81	5.68	5.91	5.71	5.81
N:K ₂ :S ₂	5.76	5.92	5.84	5.81	6.38	6.10
N:K ₃ :S ₃	5.66	5.93	5.80	6.00	6.21	6.11
Average	5.62	5.80	5.71	5.90	6.02	5.96
LSD _{0.01}	A—0.22; B—n.s.; C—n.s.; A × B—n.s.; A × C—n.s.; B × C—n.s.; A × B × C—n.s.					
Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed						
N:K:S	10.39	8.17	9.28	6.29	6.17	6.23
N:K ₁ :S ₁	6.63	6.53	6.58	7.31	6.85	7.08
N:K ₂ :S ₂	6.68	6.52	6.60	5.07	7.00	6.04
N:K ₃ :S ₃	7.00	6.50	6.75	5.01	7.01	6.01
Average	7.68	6.93	7.30	5.92	6.76	6.34
LSD _{0.01}	A—0.38; B—n.s.; C—0.53; A × B—0.53; A × C—0.75; B × C—0.75; A × B × C—1.06					
Maize (<i>Zea mays</i> L.) aerial parts						
N:K:S	7.47	8.79	8.13	9.09	10.79	9.94
N:K ₁ :S ₁	10.89	12.77	11.83	14.42	13.84	14.13
N:K ₂ :S ₂	12.76	14.29	13.53	17.27	12.91	15.09
N:K ₃ :S ₃	16.12	18.41	17.27	17.45	14.67	16.06
Average	11.81	13.57	12.69	14.56	13.05	13.81
LSD _{0.01}	A—0.27; B—n.s.; C—0.38; A × B—0.38; A × C—0.53; B × C—0.53; A × B × C—0.75					

n.s.—non-significant.

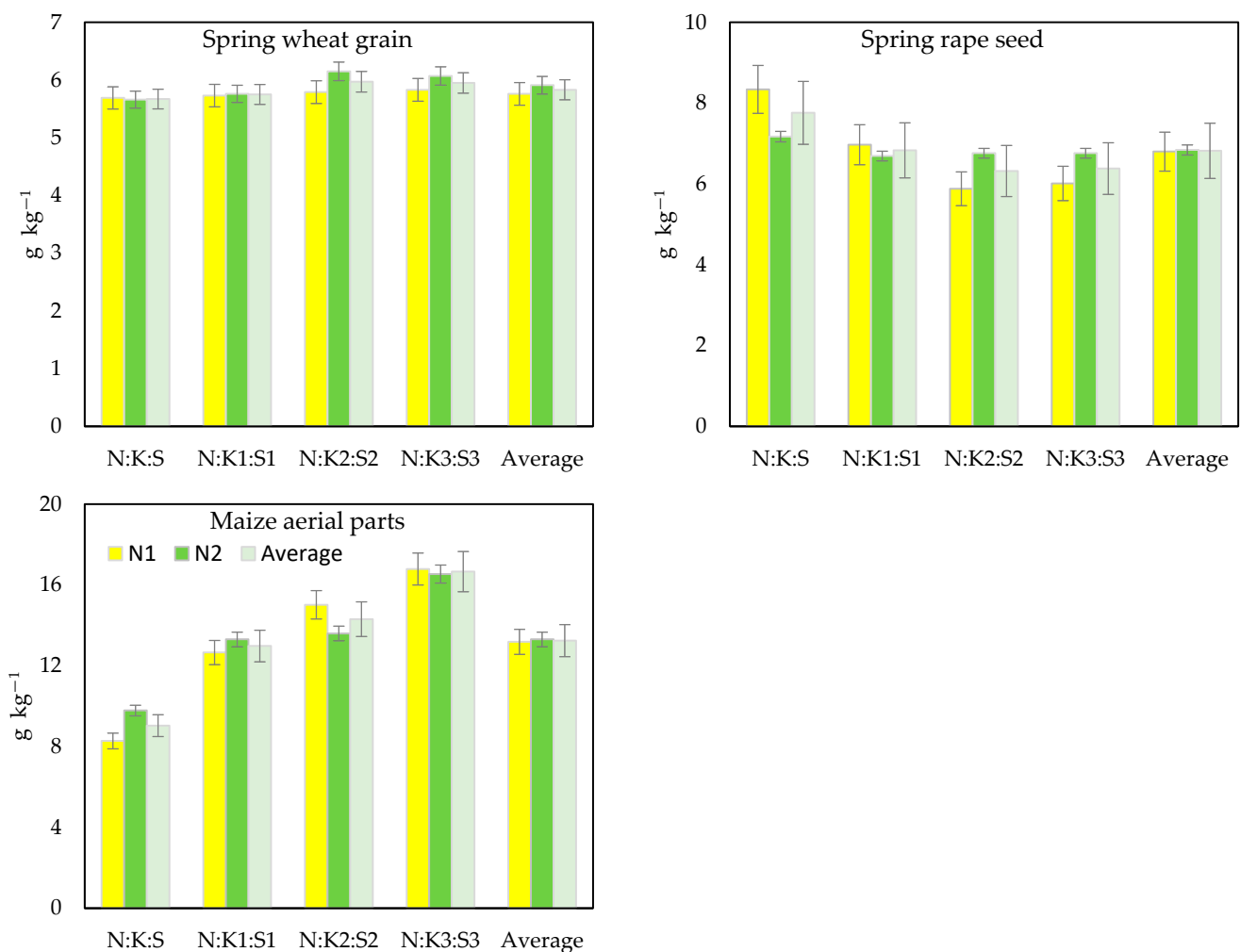


Figure 4. Effect of N:K:S ratio and N dose on potassium content of plants (averages from all series).

The application of potassium fertilizers generally had a positive effect on the content of this element in the crops, with the greatest, significant increase in its accumulated amount being observed in maize and the smallest, insignificant one in spring wheat. Soil application of fertilizers with expanded N:K:S ratios contributed to a considerable and significant increase in the potassium content in maize aerial organs. This increase in maize was particularly high, more than doubled, when the fertilizer with the N:K₃:S₃ ratio was added to the low-quality soil (in both series with UAN). With regard to the soil of higher quality, the application of this fertilizer produced a weaker effect on the potassium content in maize aerial organs, from an increase of 92% in the series with the higher N dose to 36% in the treatments with the lower N dose compared to the control. The widening of the N:K:S ratio in the fertilizers had a positive effect on the content of potassium in spring rapeseed, but only in the higher-quality soil. When the fertilizer with the N:K₁:S₁ ratio was applied to the soil of higher quality, a significant increase (16%) in the content of potassium in spring rapeseed was observed in the series with N 1, while the application of the fertilizers with the N:K₂:S₂ and N:K₃:S₃ ratios in the series with N 2 resulted in an increase of 14% in relation to the control. In contrast, the application of the same fertilizers on the poorer soil caused negative relationships in spring rapeseed.

3.1.4. Magnesium

None of the tested factors were found to have a significant and clear effect on the content of magnesium of spring wheat grain (Table 5, Figure 5).

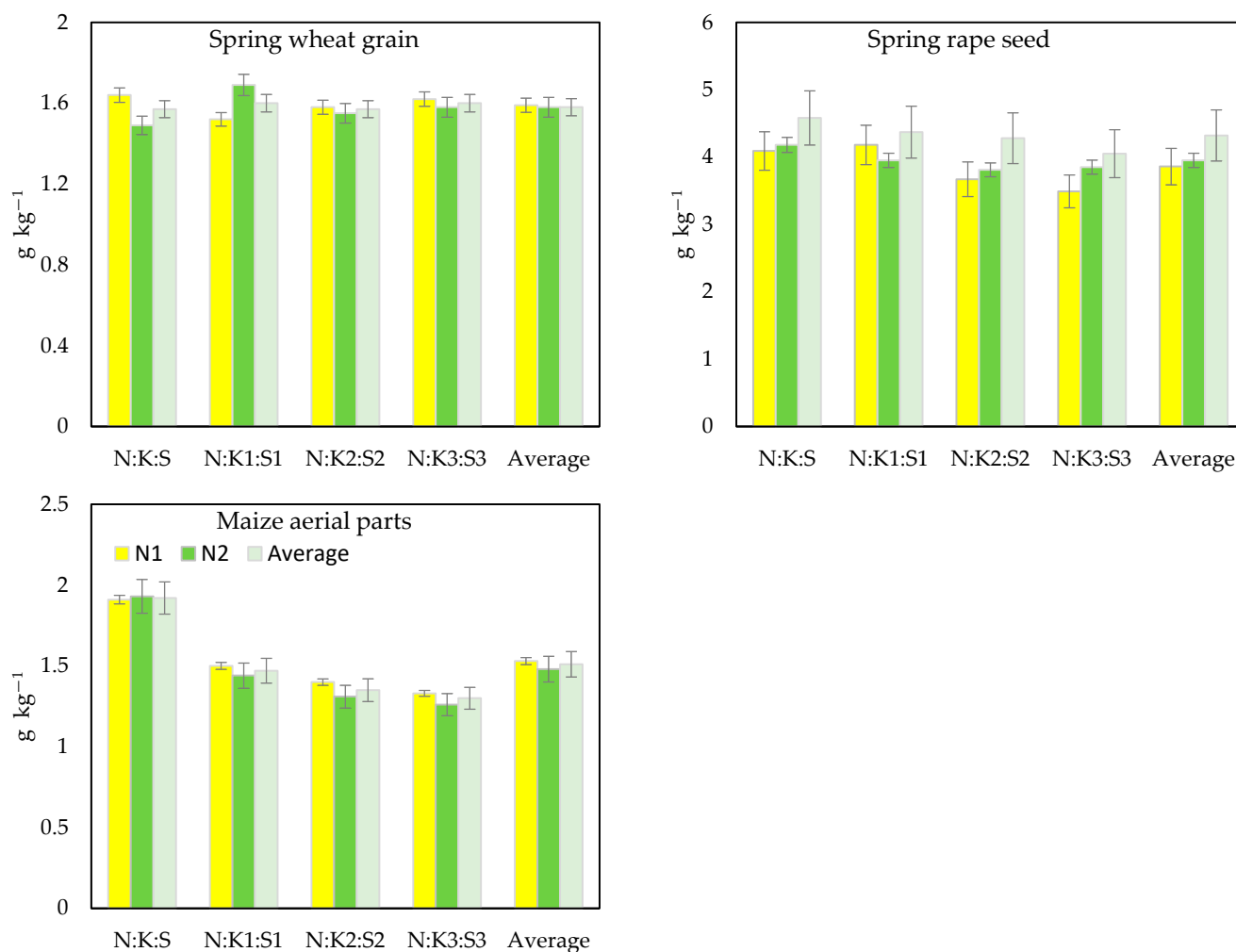


Figure 5. Effect of N:K:S ratio and N dose on magnesium content of plants (averages from all series).

Table 5. Magnesium content in plants (g kg⁻¹ D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	1.68	1.49	1.59	1.60	1.49	1.55
N:K ₁ :S ₁	1.55	1.84	1.70	1.48	1.53	1.51
N:K ₂ :S ₂	1.70	1.63	1.67	1.46	1.47	1.47
N:K ₃ :S ₃	1.52	1.49	1.51	1.71	1.67	1.69
Average	1.61	1.61	1.61	1.56	1.54	1.55
LSD _{0.01}	A—n.s.; B—n.s.; C—n.s.; A × B—n.s.; A × C—0.17; B × C—0.17; A × B × C—n.s.					
Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed						
N:K:S	4.58	4.38	4.48	3.60	3.98	3.79
N:K ₁ :S ₁	4.37	3.99	4.18	3.99	3.90	3.95
N:K ₂ :S ₂	4.28	3.79	4.04	3.05	3.82	3.44
N:K ₃ :S ₃	4.05	3.93	3.99	2.92	3.77	3.35
Average	4.32	4.02	4.17	3.39	3.87	3.63
LSD _{0.01}	A–0.14, B–n.s., C–0.20, A × B–0.20, A × C–n.s., B × C–0.28, A × B × C–0.40					

Table 5. Cont.

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Maize (<i>Zea mays</i> L.) aerial parts						
N:K:S	1.99	2.00	2.00	1.83	1.85	1.84
N:K ₁ :S ₁	1.40	1.56	1.48	1.59	1.31	1.45
N:K ₂ :S ₂	1.34	1.46	1.40	1.46	1.15	1.31
N:K ₃ :S ₃	1.33	1.43	1.38	1.33	1.09	1.21
Average	1.52	1.61	1.56	1.55	1.35	1.45
LSD _{0.01}	A–0.06, B–n.s., C–0.09, A × B–0.09, A × C–n.s., B × C–n.s., A × B × C–0.18					

n.s.—non-significant.

In the soil of higher quality, the content of magnesium in the seed of spring rape and in the aerial parts of maize was lower than in the soil of lower quality. The latter element was 13% and 7% lower, respectively, in the crops grown on the low-quality soil. The impact of N dose on the content of magnesium in spring rapeseed and in maize was analogous to that found for potassium. The influence of N dose on the magnesium content in maize aerial parts was insignificant. Also, an antagonistic effect of potassium on the content of magnesium in spring rapeseed and the maize aerial parts was observed with increasing fertilizer doses and increasing N:K:S ratios. The fertilizer with the N:K₃:S₃ ratio caused a decrease in the magnesium content in the seed of spring rape by 12% (N 1) and 10% (N 2) in the poorer soil and by 19% (N 1) and 5% (N 2) in the richer soil, and in the aerial parts of maize by 33% (N 1) and 29% (N 2) on the soil of low quality and by 27% (N 1) and 41% (N 2) on the soil of higher quality, in comparison with the control objects.

3.1.5. Calcium

By improving the soil quality, a significant increase in the content of calcium was achieved: 27% more in spring wheat grain and 46% more in spring rapeseed. The content of calcium in maize also increased significantly (Table 6, Figure 6). The lower N dose was associated with a 7% increase in the calcium content in spring wheat grain. However, this relationship was only observed in the plants grown on the low quality soil.

There was no clear effect of N fertilization on the calcium content in the seed of spring rape and in the aerial parts of maize. On the soil of lower quality, the application of the lower N dose resulted in a lower calcium concentration (27% less) in the seed of spring rape, and a higher calcium content (16% more) in the aerial parts of maize. On the contrary, in the higher quality soil, the same N dose caused an increase in the calcium content in the seed of spring rape and a decrease in the aerial parts of maize.

Increasing of the N:K:S ratio in fertilizers caused an increase in the calcium content in the spring wheat grain on richer soil and in the maize aerial parts on the poorer soil and fertilized with the higher N dose. There was also a decrease in the content of calcium in wheat grain on the poorer soil and in maize on the richer soil fertilized with the lower N dose. On the richer soil, the increase in the calcium content of spring wheat grain reached 53% in the series with the higher N dose and 41% when the lower N dose was applied. On the low quality soil and fertilized with the higher N dose, the increase of the N:K:S ratio resulted in a decrease of the calcium content in the spring wheat grain. On the other hand, the content of calcium in the spring wheat grain did not show such clear changes when the lower N dose was applied. In both soils supplied with the higher N dose, a wider N:K:S ratio correlated with a decreased calcium content in the spring rapeseed. The highest decrease in the content of this element, more than 50%, occurred in the spring rapeseed harvested from the series with the higher N dose on the soil of low quality. The seed of spring rape grown on higher quality soil and fertilized with N 2 contained a higher amount

of calcium in response to the N:K:S ratio increased to N:K₁:S₁. An analogous effect was observed in the seed of spring rape in the N 2 series on the poorer soil.

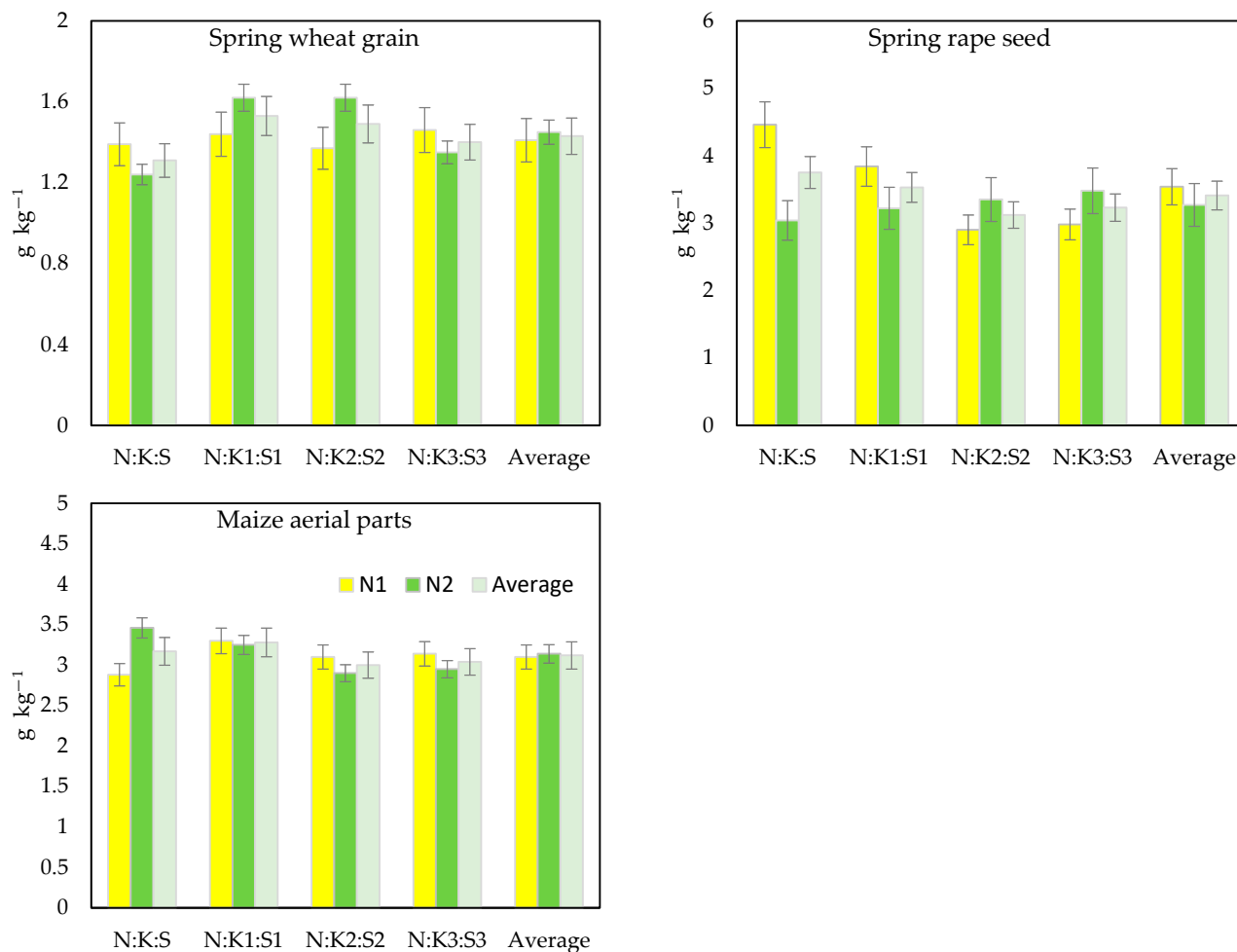


Figure 6. Effect of N:K:S ratio and N dose on calcium content of plants (averages from all series).

Table 6. Calcium content in plants (g kg⁻¹ D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	1.58	1.19	1.39	1.20	1.28	1.24
N:K ₁ :S ₁	1.13	1.60	1.37	1.74	1.64	1.69
N:K ₂ :S ₂	1.09	1.56	1.33	1.64	1.67	1.66
N:K ₃ :S ₃	1.08	0.89	0.99	1.84	1.80	1.82
Average	1.22	1.31	1.27	1.61	1.60	1.60
LSD _{0,01}	A–0.12, B–n.s., C–0.16, A × B–n.s., A × C–0.23, B × C–0.23, A × B × C–0.33					
Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed						
N:K:S	4.49	2.19	3.34	4.42	3.89	4.16
N:K ₁ :S ₁	3.82	2.07	2.95	3.85	4.36	4.11
N:K ₂ :S ₂	2.53	2.13	2.33	3.27	4.56	3.92
N:K ₃ :S ₃	1.96	2.96	2.46	3.99	4.00	4.00
Average	3.20	2.34	2.77	3.88	4.20	4.04
LSD _{0,01}	A–0.21, B–0.21, C–0.30, A × B–0.30, A × C–0.42, B × C–0.42, A × B × C–0.57					

Table 6. Cont.

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Maize (<i>Zea mays</i> L.) aerial parts						
N:K:S	2.25	3.25	2.75	3.51	3.67	3.59
N:K ₁ :S ₁	2.92	3.37	3.15	3.68	3.13	3.41
N:K ₂ :S ₂	2.98	3.07	3.03	3.21	2.73	2.97
N:K ₃ :S ₃	2.97	3.19	3.08	3.30	2.71	3.01
Average	2.78	3.22	3.00	3.43	3.06	3.24
LSD _{0.01}	A–0.17, B–n.s., C–0.25, A × B–0.25, A × C–0.34, B × C–0.34, A × B × C–0.48					

n.s.—non-significant.

3.1.6. Sulfate–Sulfur (VI)

The increase in the soil quality was conducive to the accumulation of sulfate–sulfur (VI) in seed of spring rape and grain of spring wheat (Table 7, Figure 7). The content of this compound in plants grown on the low quality soil more than doubled in spring wheat grain and increased by 15% in spring rape. The higher soil quality contributed to a significant reduction of the content of sulfate–sulfur (VI) in the maize aerial parts by 7%.

The lower dose of nitrogen (N 2) caused a 31% decrease in the content of sulfate–sulfur (VI) in the spring wheat grain (but only on the richer soil), a 3–10% in the spring rapeseed, and a 3–13% decrease in the aerial maize parts, compared to the higher dose.

When the N:K:S ratio was increased, there was an increase in the content of sulfate–sulfur (VI) in the spring wheat grain (compared to the objects without potassium), smaller on the poorer soil and higher on the richer soil. The highest increase in the content of sulfate–sulfur (VI) in the spring wheat grain on the soil with higher quality was recorded under the effect of the fertilizer in which the ratio of the three elements was N:K₃:S₃. In this case, the mentioned increase was 2.5-fold in the spring wheat grain in the series with the N 2 dose and more than three-fold in the series with the N 1 dose. On the poorer soil, the changes in the content of sulfate–sulfur (VI) in spring wheat grain were smaller, reaching 40% at the most in the series with N 1, but larger than in the objects with N 2. The highest increase occurred in seed of spring rape, where it reached the maximum of 86% (N 1) and 93% (N 2) on the poorer soil and 80% (N 1) and 78% (N 2) on the richer soil. The fertilizer with the N:K₃:S₃ ratio caused a very high increase in the content of sulfate–sulfur (VI) in maize aerial organs: by 4-fold (N 1) and more than 3.5-fold (N 2) on the poorer soil, and more than 5-fold (N 1) and 3-fold (N 2) on the richer soil.

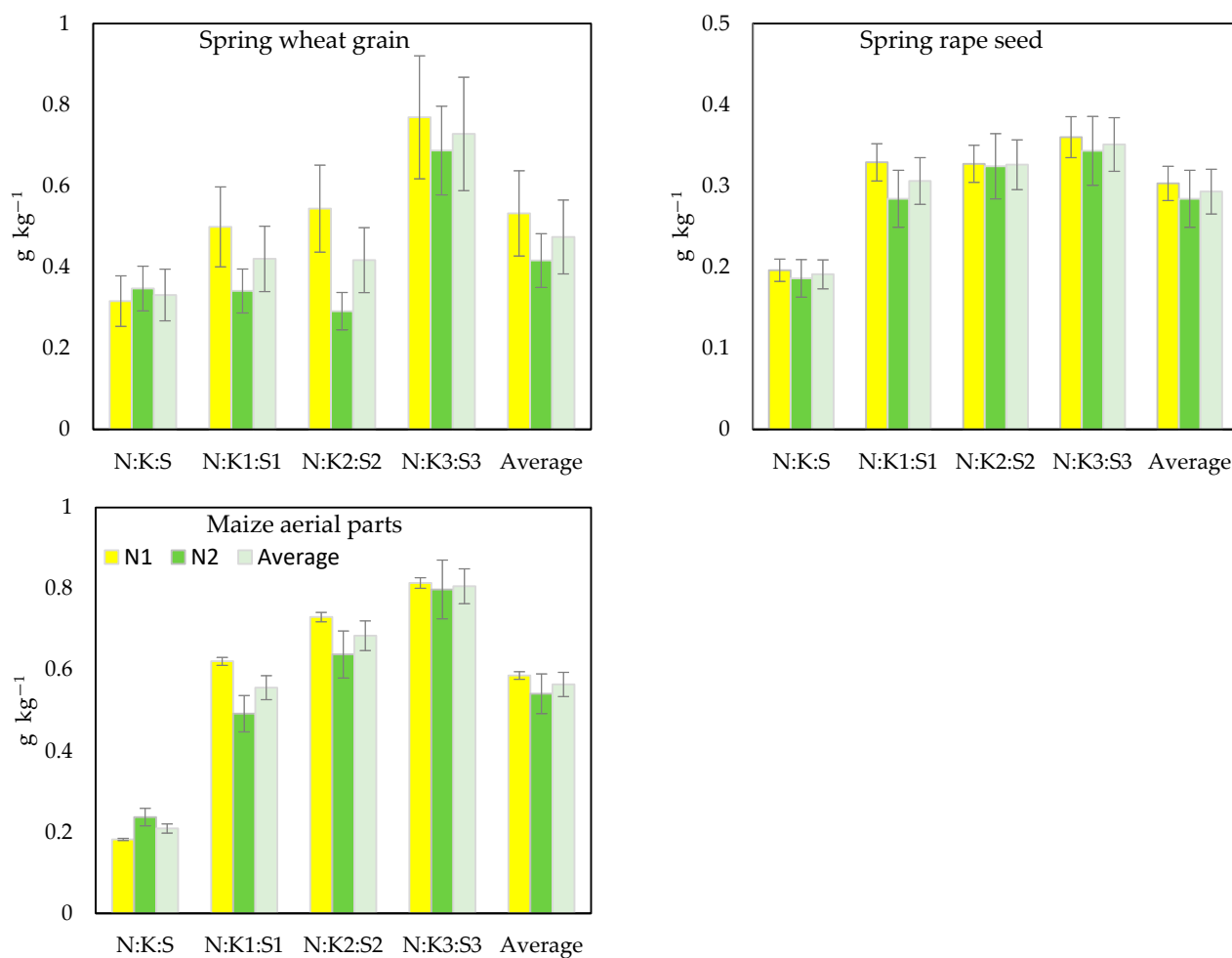
Table 7. Sulfate–sulfur (VI) content in plants (g kg^{−1} D.M.).

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
Spring wheat (<i>Triticum aestivum</i> L.) grain						
N:K:S	0.243	0.281	0.262	0.388	0.413	0.401
N:K ₁ :S ₁	0.328	0.353	0.341	0.669	0.328	0.499
N:K ₂ :S ₂	0.339	0.289	0.314	0.748	0.293	0.521
N:K ₃ :S ₃	0.318	0.320	0.319	1.220	1.054	1.137
Average	0.307	0.311	0.309	0.756	0.522	0.639
LSD _{0.01}	A—0.020; B—0.020; C—0.028; A × B—0.028; A × C—0.040; B × C—0.040; A × B × C—0.057					

Table 7. Cont.

N:K:S (C)	Soil Kind (A)					
	Soil 1			Soil 2		
	Nitrogen Dose (B)					
	N 1	N 2	Average	N 1	N 2	Average
	Spring rape (<i>Brassica napus</i> L. var. <i>napus</i>) seed					
N:K:S	0.205	0.173	0.189	0.187	0.198	0.193
N:K ₁ :S ₁	0.253	0.260	0.257	0.405	0.307	0.356
N:K ₂ :S ₂	0.311	0.270	0.291	0.343	0.378	0.361
N:K ₃ :S ₃	0.382	0.334	0.358	0.337	0.352	0.345
Average	0.288	0.259	0.274	0.318	0.309	0.313
LSD _{0.01}	A—0.020; B—0.020; C—0.028; A × B—n.s.; A × C—0.039; B × C—n.s.; A × B × C—0.056					
	Maize (<i>Zea mays</i> L.) aerial parts					
N:K:S	0.202	0.251	0.227	0.161	0.223	0.192
N:K ₁ :S ₁	0.592	0.459	0.526	0.649	0.524	0.587
N:K ₂ :S ₂	0.778	0.675	0.727	0.681	0.600	0.641
N:K ₃ :S ₃	0.801	0.920	0.861	0.827	0.676	0.752
Average	0.593	0.576	0.585	0.580	0.506	0.543
LSD _{0.01}	A—0.023; B—0.023; C—0.032; A × B—0.032; A × C—0.046; B × C—0.046; A × B × C—0.064					

n.s.—non-significant.

**Figure 7.** Effect of N:K:S ratio and N dose on sulfate-sulfur (VI) content of plants (averages from all series).

3.2. Analysis of the Cumulative Effect of the Experimental Factors

The analysis of the cumulative effect of the tested factors, expressed as percentages of the observed variation determined with the ANOVA method, shows the presence of significant correlations between the analyzed plant parameters (content of nitrogen, phosphorus, potassium, magnesium, calcium and sulfate–sulfur(VI) in plants) formed under the influence of the soil and the applied N doses as well as fertilizers with different N:K:S ratios (Figures 8–10).

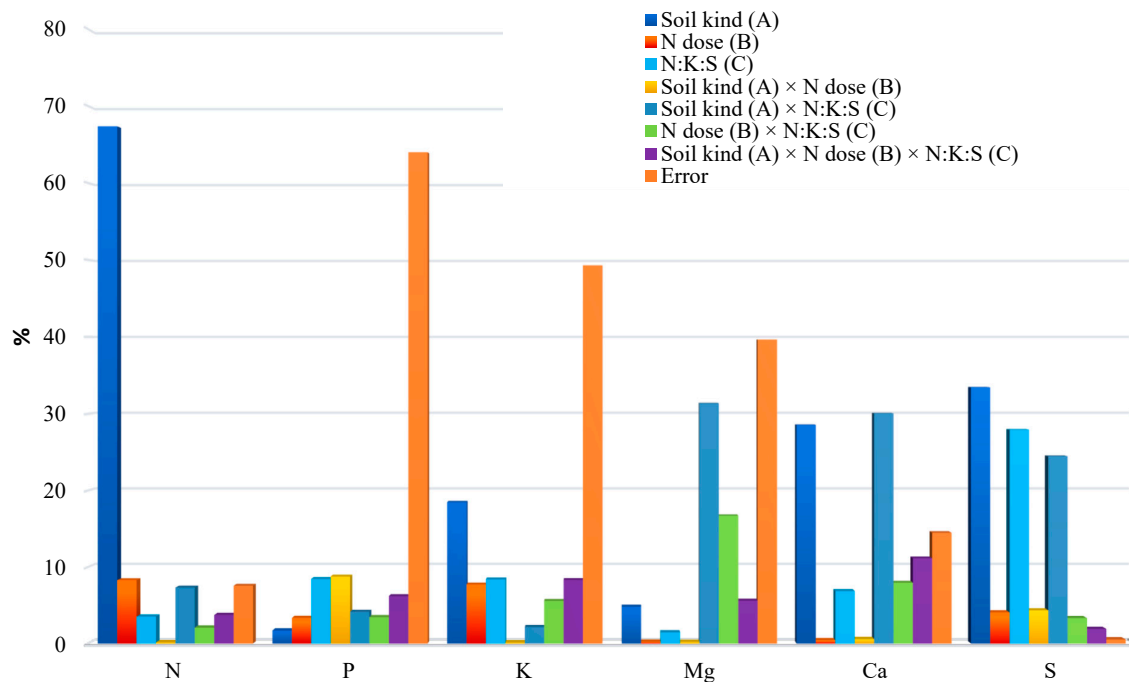


Figure 8. Relative effect of factors on chemical composition of spring wheat—*Triticum aestivum* L. (in percent).

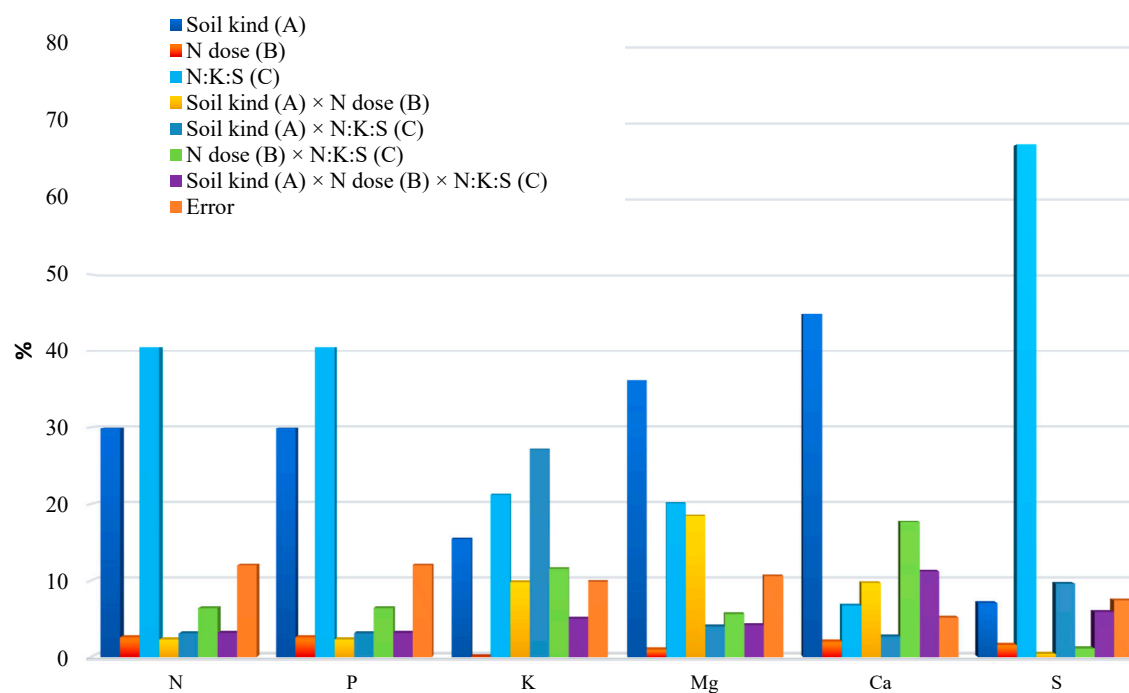


Figure 9. Relative effect of factors on chemical composition of spring rape—*Brassica napus* L. var. *napus* (in percent).

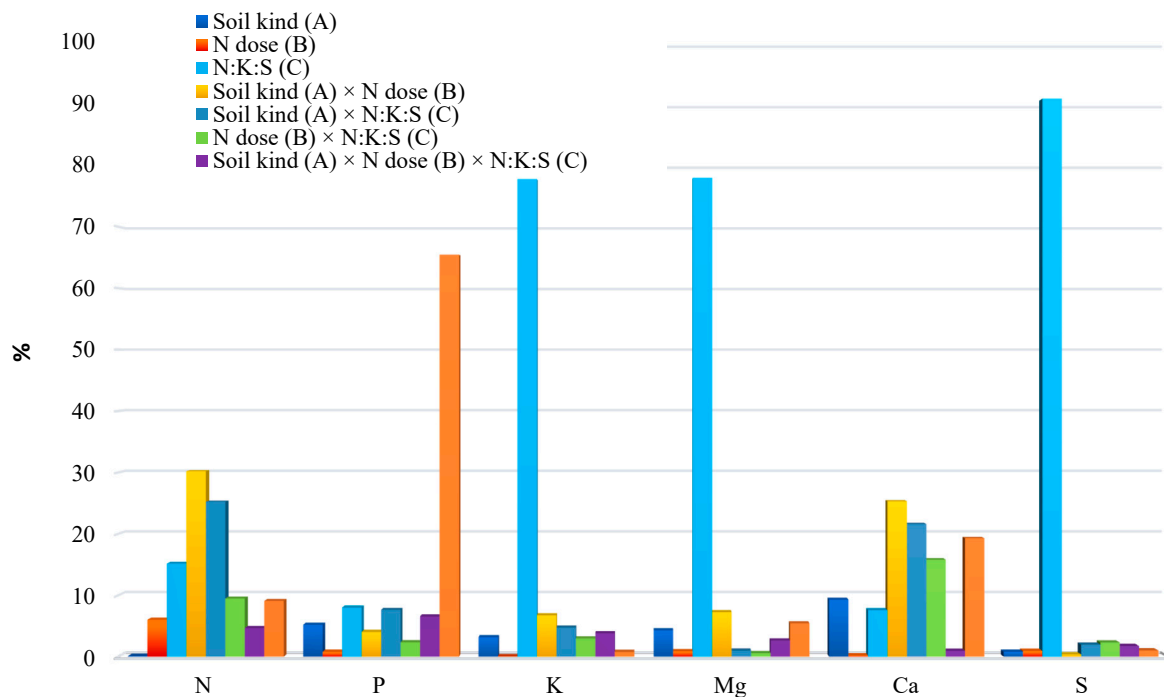


Figure 10. Relative effect of factors on chemical composition of maize—*Zea mays* L. (in percent).

3.2.1. Spring Wheat

The soil kind had the strongest effect on the content of the following elements in the spring wheat grain: nitrogen (67.4%), potassium (18.5%), calcium (28.5%) and sulfate–sulfur (VI) (33.4%) (Figure 8).

Appropriate N:K:S ratios in the fertilizers had a strong effect only on the sulfate–sulfur (VI) content (27.9%). The N dose had the weakest influence on the chemical composition of spring wheat grain, as its contribution to the cumulative impact on the content of elements in spring wheat grain never exceeded 8%.

3.2.2. Spring Rape

After calculating the percentage of the observed variation, thus statistically expressing the cumulative effect of the analyzed factors on spring rape, it was found that the soil kind had a strong influence on the chemical composition of spring rapeseed, including the content of nitrogen and phosphorus (29.9%), potassium (15.4%), magnesium (36.1%), calcium (44.9%) and sulfate–sulfur (VI) (33.4%) (Figure 9). The optimal proportions of N:K:S in the fertilizers mainly affected the content of nitrogen and phosphorus (40.6%), potassium (21.2%), magnesium (20.1%) and sulfate–sulfur (VI) (66.9%). The N doses had the least influence on the chemical composition of spring rape.

3.2.3. Maize

The soil kind and N doses had a weak effect on the chemical composition of maize aerial parts (Figure 10). The optimal proportions of N:K:S in the fertilizers had the strongest effect on the content of nitrogen (15.2%), phosphorus (8.0%), potassium (77.7%), magnesium (78.0%) and sulfate–sulfur (VI) (90.8%).

4. Discussion

When studying the effects of fertilizers on plants, interactions, mainly antagonistic but sometimes synergistic ones, between some elements must be taken into account. Interactions play an important role in the uptake and content of elements in plants. According to Rietra et al. [26], 117 interactions between nutrients (macro- and micronutrients) and plant yield were found: 17 antagonistic and as many as 43 synergistic. No interactions were

found in 35 cases. Fertilization with nitrogen, potassium and sulfur increases the content of these elements in plants, but at the same time affects the uptake of other macronutrients, which is mainly associated with antagonism between some elements. However, it depends on the plant species, soil properties and the form of fertilizers used [26]. Under favorable conditions, nitrogen can have an antagonistic effect on the uptake of potassium (and other elements) by plants. At the same time, potassium can have a negative effect on the accumulation of nitrogen and different nitrogen compounds in plants [15]. This happens most often when the soil is deficient in potassium, which, by participating in water uptake, affects the uptake of nitrogen and other elements by plants [14]. The reverse situation is also possible, when an excess of nitrogen in the soil (mostly derived from fertilizers)—and especially the particularly persistent presence of the NH_4^+ ion in the soil—limits the uptake of potassium by plants [8,47]. The translocation of K^+ ions in plants is influenced by both NH_4^+ and NO_3^- . The rate of potassium translocation from roots to shoots of plants decreases with increasing $\text{NH}_4^+/\text{NO}_3^-$ in the rhizosphere [8].

In view of the above, it is extremely important to adjust the doses of fertilizers to the fertilization needs of particular plant species while taking into account the direct and indirect effects of fertilizers on the course of physiological and biochemical processes in plants. Fertilization with ammonium nitrogen, nitrate nitrogen and potassium in appropriate proportions has a particular influence on the uptake of nitrogen by plants and the synthesis of organic nitrogen compounds [48,49]. The content of nitrogen in wheat is strictly correlated with the dose of N fertilizer [50,51] and the time of its application [35]. Postponed wheat sowing and later application of N fertilizer have been found to contribute to increased nitrogen content in plants, which has a positive influence on plant yield [38]. An experiment conducted by Wysocka et al. [52] showed that differentiated N fertilization, within the whole range of applied doses, caused an increase in the value of technological parameters describing wheat grain. Reducing N fertilization reduces the content of nitrogen in wheat and barley grains [53], an effect that is generally confirmed in this study, especially in the cultivation of spring wheat and spring rape.

According to Hao et al. [48], the application of N fertilizers containing both nitrate nitrogen and ammonium nitrogen can produce higher crop yields than those containing only one of these forms of nitrogen. An example of the former is urea and ammonium nitrate, whose positive effect on plant growth, development and chemical composition was observed in this study. The application of potassium in interaction with phosphorus improves the utilization of ammonium nitrogen, especially when ammonium nitrate fertilizers are used. The final effect is an increase in the crop yield. Excessive N fertilization, especially with N-NH_4^- and N-NO_3^- , can reduce the uptake of calcium by plants [54]. In a study by Hao et al. [48], the greatest effect of nitrogen on plant biomass was achieved with a ratio of $\text{NH}_4^+:\text{NO}_3^-$ of 50:50. Fertilizers applied in such proportions had a beneficial effect on plant roots increasing their length, surface area, diameter, volume and xylem, as well as on the leaf stomata—their aperture, conductivity, rate of photosynthesis and its products or transpiration. However, it should be noted that in some plant species, the antagonism between the NH_4^+ ion and NO_3^- can be pronounced, which leads to a decrease in the transport of nitrate and other macroelements from the roots to the aerial parts and their utilization. The photosynthetic capacity of the leaves and, consequently, the accumulation of plant biomass are then reduced. This is particularly evident in the early stages of plant development, such as in wheat [55].

However, NH_4^+ ions in the soil are less leached from the soil than NO_3^- ions due to its sorption in the soil and after its denitrification with the emission of N_2O and N_2 into the air [22]. Emissions can be reduced by adding inhibitors, which can increase crop yields (e.g., wheat) by several percent [20]. The effect of high levels of NH_4^+ in the soil on plants is related to the competitive uptake of cations. In the study by Kong et al. [56], the effect of excess NH_4^+ on wheat showed a reduction in the cellulose and lignin content of the vascular bundles in plants and their mechanical strength, which consequently reduced the efficiency of N remobilization and the rate of grain filling with nitrogen, as well as the

potassium content (by 36%). According to ten Hoopen et al. [57], the negative effects of NH_4^+ ions result from the disturbance of the ionic balance related to the reduced uptake of cations, such as K^+ , Mg^{2+} and Ca^{2+} , which determines the uptake of water and thus of other elements. In addition, the NH_4^+ ion can be transported in plants through the same channels as the K^+ ion, which is particularly unfavorable when the soil and plants are low in potassium [58]. It is therefore important to provide plants with adequate amounts of potassium in the form of fertilizers. The addition of potassium significantly alleviated the negative effects of NH_4^+ , resulting in increased grain filling and nitrogen remobilization, as well as increased potassium content [56]. According to Lai et al. [59], a high level of soil nitrogen reduces potassium availability and increases magnesium availability to plants. High levels of phosphorus can reduce potassium and calcium uptake.

Fertilization with potassium caused a higher uptake and content of this element in plants, especially in the early stages of their vegetative growth [60]. According to Gebreslassie [61], potassium is taken up faster than other basic macronutrients (e.g., nitrogen and phosphorus) and sometimes in excessive amounts in the early stages of vegetation. During the subsequent stages of plant growth and development, it is transported to individual plant organs. It is therefore important to supply this nutrient properly during its intensive uptake by plants [62]. In a study carried out by Surányi and Izsáki [63], an increase in the content of nitrogen and potassium was observed in the aerial parts of barley under the influence of N fertilization, but the contents of calcium, magnesium and sodium were not affected. High levels of potassium in soils can reduce the availability of magnesium and sometimes nitrogen for plants. Among the interactions of potassium with other macroelements, the relationship with nitrogen seems to be the most important. Coskun et al. [64] showed the antagonistic effect of potassium on nitrogen nutrition in the form of NH_4^+ , and the synergistic effect between K^+ and NO_3^- ions. A deficiency of potassium or other nutrients in the soil can limit the content of potassium and other elements in plants, such as nitrogen, calcium and sometimes phosphorus [65]. Therefore, when N fertilization is limited, the potassium content in plants increases and the calcium content decreases. It is also worth mentioning that other soil properties, such as high zinc content, can contribute to the accumulation of macro- and microelements and their content in plants [66]. The synergistic effect of zinc on nitrogen, potassium and manganese, and the antagonistic effect on phosphorus, calcium and some microelements (e.g., Fe, B or Cu) have been observed. Negative effects are caused by disturbances in translocation from roots to aerial parts of plants, which is connected with interference of Zn with P, Ca, Fe and Cu in absorption on the surface of roots, as well as competition with the same places of adsorption of soil particles, as well as on root surfaces. Therefore, the correct choice of proportions between the components is a very important element in planning rational fertilization of plants.

According to Duncan et al. [67], fertilization with nitrogen, phosphorus, potassium and sulfur in optimal proportions, which have certain interactions with each other, does not lead to a strong increase in nitrogen content in cereal grain, nor to its decrease with increasing yield, which is related to the so-called dilution effect. By ensuring balanced availability of the abovementioned fertilizer components, it is possible to reduce the doses of N fertilizers in the cultivation of wheat and other crops, as nitrogen seems to accumulate more efficiently in grain or seed of plants.

This was confirmed by our own research, which reported an antagonistic effect of potassium on nitrogen and magnesium content, but generally a synergistic effect on potassium and sulfate-sulfur (VI) content in usable plant parts. The strength of the effect depended on the crop species. The effect of N dose on the content of macronutrients in plants was smaller than that of potassium, but usually antagonistic to the latter element. The presence of NH_4^+ and NO_3^- ions balanced their effect on the elemental content. The influence and direction of the fertilizer effects on the other elements depended on the soil quality. The elemental content of plants depends not only on fertilization, but also on soil quality. Soil pH is important because at higher pH, slightly acidic or near neutral, the proportion of available forms of macronutrients in the soil is highest. The soils selected for

our study were characterized by such a pH. However, other properties are also important, such as the sorption complex of the soil, which is more developed in good soils and also has a positive effect on growth and development, or the chemical composition of plants [68]. Better-quality soils tend to contain more macronutrients (also in plant-available forms) than poorer soils. The mobility of individual nutrients is also important, as phosphorus and other cations are fairly easily immobilized and fixed in the soil, while anions (e.g., nitrates, anions other than phosphorus) are more mobile and can be easily moved to deeper soil layers [69–71] and the right moisture content [72], as well as the presence of microorganisms and enzymatic activity [73], which create the right conditions for the transformation (cycling) and uptake of elements by plants. Macronutrients are taken up by plants in greater quantities from higher-quality soils [69]. This has been confirmed by our own research, where higher plant macronutrient contents were found on the better-quality soils at most sites, especially for wheat and spring rape. However, the differences in the element content of the plants were not very large due to the fact that the soils were sand and loamy sand.

The results obtained in this research were therefore a natural reaction of the plants resulting from antagonisms and synergisms between elements in soil and plants and seem to provide benefits from the point of view of both agronomy and environmental science.

5. Conclusions

The improved soil quality resulted in a significant increase in the calcium (as opposed to magnesium) content of the three crops, in the nitrogen and sulfate–sulfur (VI) content of spring wheat grain and spring rapeseed, and in the phosphorus content of spring rapeseed and maize aerial parts. The effect of the richer soil was greatest in the case of calcium content (+46%) in spring rapeseed and sulfate–sulfur (VI) content (+100%) in spring wheat grain compared to the poorer soil.

Reducing the N dose had a negative effect on the nitrogen content of spring wheat and on the sulfate–sulfur (VI) content of spring wheat, spring rape and maize. The N 2 dose caused the greatest reduction of 31% in the content of sulfate–sulfur (VI) in the grain of spring wheat on the richer soil compared to the optimal (N 1) dose. The effect of the N dose on the plant macronutrient content was the smallest among the experimental factors analyzed, usually irregular and depending on the plant species.

The increase in N:K:S ratio had a small but usually antagonistic effect on the nitrogen content of all plant species, but a synergistic one on the potassium content of spring wheat, maize and partly of spring rape, and especially on the content of sulfate–sulfur (VI) of the plants. It was greatest in the case of sulfate–sulfur (VI) content in the grain of spring wheat (2.5–3 times) and maize (3–5 times). On the other hand, the antagonistic effect of the N:K:S ratio on the magnesium content was particularly high in the aerial parts of maize, where it reached a maximum of 41% with respect to the control (without K and S). The effect of the soil type and the application of fertilizers with different N:K:S ratios on the content of the other macroelements depended on the species of crop.

The new fertilizer with the N:K₂:S₂ ratio had the greatest effect on the content of the macronutrients tested in spring wheat, spring rape and maize. In order to confirm the obtained dependencies, it seems justified to carry out field experiments.

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