The Effects of Using Sulfur and Organic Bedding on the Content of Macro- and Micronutrients and Biologically Active Substances in Winter Garlic Bulbs

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Abstract: Sulfur (S) directly influences the proper development, yield, and biological value of Allium sativum. The sulfuric forms of S are easily leached from the soil due to poor sorption. In this context, we looked at to what extent application of S and biomass of catch crops (CCs) left until spring would cause an increase in the yield; we also looked at the macro- and micronutrient content of garlic plants. The experimental factors included applications of 0 and 20 kg ha−1 S to CCs consisting of Trifolium alexandrinum, Raphanus sativus var. oleiformis, Fagopyrum esculentum, Sinapis alba, and control. The bulbs contained more dry matter and macro- and micronutrients (N, P, K, S, Zn, and Fe) than those without S. Garlic plants cultivated with S accumulated more glutathione and total phenolic acids (TPA), and the extracts showed greater antioxidant activity (AA) than those cultivated without S. In 2019 and 2020, the cultivation of winter garlic with S, in combination with clover contributed to an increase in the content of dry matter, S, TPA, AA in bulbs. In the cultivation with fodder radish garlic plants accumulated more nitrogen (N), S, TPA, AA and glutathione in bulbs. In those cultivated with buckwheat, garlic contained more TPA, AA, glutathione, and with mustard more TPA and AA. However, further research is needed to select the species of CC and to determine the S dose to be applied in the effective biofortification of garlic in a sustainable agriculture system.

Keywords: Allium sativum; sulfur; cover crops; biological value; macro- and micronutrients; glutathione

1. Introduction

Garlic is a vegetable, although it is generally used as a spice, and is known for its medicinal properties. There is increasing interest from the pharmaceutical industry in the genus, Allium. The biological value of garlic is determined by organic sulfur (S) compounds, including sulfoxides found in garlic (alliin) and onion (allicin); glutathione; ajoene; garlic oils; and S-containing amino acids, cysteine, and methionine [1]. Additionally, the nutritional importance of garlic depends on a number of vitamins, such as riboflavin, thiamine, nicotinic acid, and vitamin C. Garlic contains a variety of bioactive substances; it is considered a medicinal plant with broad-spectrum antimicrobial activity. Garlic essential oil has strong bactericidal and fungicidal effects [2], regulates blood pressure, and has positive effects on the digestive and immune systems [3].

Sulfur is mainly taken up by plant roots from soil solutions as an SO4 2− anion. Numerous studies have shown that S fertilization generally increases yield [4−9]. The beneficial effect of various forms of sulfur on garlic yield was demonstrated in various climatic and soil conditions [10−12]. In the cultivation of garlic, the yield-generating effect of S was confirmed [12,13]. Sulfur application was associated with increased production of bioactive compounds [6,14]. By using sulfur during the vegetation periods of plants, the allin content in garlic bulbs significantly increased while high nitrogen doses reduced the content, or simply did not affect the level of organic sulfur compounds in plants [15−17].
It was discovered that S application increases the content of nitrogen (N), phosphorus (P), potassium (K), and S macronutrients in garlic bulbs [17]. In shaping the content of secondary metabolites in Allium plants, the interaction of N with S is emphasized [18,19]. The effective use of N by plants is reduced by S deficiency [6]. A consequence of S deficit in the soil is a reduction in quality, including the sharpness parameter of Allium fistulosum [7].

Only a small fraction of the soil’s total S content is available to plants during the growing season. Despite a significant amount of this component in the form of organic fertilization, S application by plants is low, with a value of about 5–7%, because plants absorbed only the form SO$_4^{2-}$ [20]. Sulfur in plant tissues is transformed thanks to microorganisms that catch the energy in the form of carbon (C) from the decomposition of organic matter, and release sulfur in the form of sulfates [21]. It was discovered that organic C and the availability of S determined the microbiological activity, especially that of bacteria of the genus Thiobacillus, which oxidizes S [22]. In this context, the proper selection of catch crop (CC) species can favor the creation of native inoculum and increase the biodiversity of the soil environment, as pointed out by Cardoso and Kuyper [23].

According to Cheng et al. [9], soil sulfonation reduces the mobility and absorption of S by plants. It was shown that mulching hinders water penetration into the soil and reduces the leaching of soil minerals [24,25]. Organic litter decomposes and enriches the soil with humus, which helps to supply plants with minerals. The beneficial effect of organic mulches on the yield of garlic bulbs was shown in many studies [26–30], and in the cultivation of garlic for bunch harvesting [31].

Catch crops increase the carbon sequestration potential of agroecosystems [32]. Under optimal conditions, the biomass of catch crops can accumulate up to 4.4–5.6 Mg C ha$^{-1}$ in 3–5 months [33]. The change in soil C, insignificant or slight, in a short time, is significant after several years of cultivation. According to Veenstra et al. [32], in the cultivation of tomatoes, using CCs allowed for 1.8–2.3 Mg C ha$^{-1}$ year$^{-1}$. After five years, the total soil C sequestration was 4.5 Mg C ha$^{-1}$ compared to 3.8 Mg C ha$^{-1}$ for standard cultivation systems, while in systems without the net casing, the loss was 0.1–0.4 Mg C ha$^{-1}$.

Fang et al. [34] found that litter decomposition is largely a function of environmental factors, such as soil moisture, temperature, and biological activity, and the nature of biomass, e.g., C:N ratio and lignin content. Biomass with a C:N ratio greater than 30 consumes N when it decomposes. Biomass with a C:N ratio and favorable lignin:N ratios between 10 and 25 release N [35,36]. The decomposition of biomass begins in early spring at temperatures of $-2^\circ$C to $0^\circ$C, but it is fastest at high temperatures of 30$^\circ$C–35$^\circ$C [36]. In hot and humid conditions, the decomposition rate can be four to five times greater than in temperate climates [37]. Fang et al. [34] determined the correlation coefficients between the rate of decomposition of CCs and rainfall, and between the rate of decomposition of CCs and air temperature to be 0.93 and 0.43, respectively.

According to Balkcon and Reeves [38], the decomposition rate of CCs depends on the amount of organic matter used and the biochemical composition. Cherr et al. [36] argue that plant shoots that contain less N, and more lignin and cellulose can decompose up to five times slower than leaves. Research by Snapp and Borden [39] shows that the release of readily available nutrients from the remains of CCs may not coincide with the peak nutrient requirements of the succeeding plant (poor timing). Thomsen and Hansen [40] believe that plants from the Brassicaceae family undergo a much slower mineralization process. As CCs, Brassica rapa, Sinapis alba, and Raphanus sativus can take up mineralized nutrients: S, P, K, and calcium (Ca), and part of the soil N thanks to their root exudates [41]. Justes et al. [42] believe that Brassicaceae plants provide less abundant biomass than legumes due to the moderate C:N ratio (range = 15–25), resulting in slower mineralization of CC residue after incorporation into the soil. Fabaceae plant residues are more effective as soil covers due to their low C:N ratio (range = 10–15), which induces faster mineralization and ultimately releases bound N to succeeding plants more quickly [43]. Cherr et al. [36] and Möller et al. [44] believe that they have a beneficial effect on the microbiological life of the soil. During the subsequent decomposition of their remains, they release nutrients used
by the succeeding plant. According to Wendling et al. [45], the fertilization value of CCs results largely from the CC and the biomass it produces, in particular from the content of macronutrients (i.e., N, P, and K), which are brought into the soil. It is because, after introducing biological macronutrients (along with plant biomass), the farmer may limit or even give up fertilization with macronutrients of mineral origin [46].

Sulfur recycling technology via undersown intercrops is a new topic in horticultural practice. Sulfur is first accumulated organically and then gradually released [24]. In the cultivation of CCs, nutrients—especially N—may become immobilized, determining a reduction in the size and quality of the crop [47]. Bloem et al. [48] point out that a lack of balance in the N to S ratio in garlic cultivation may harm the yield’s size and quality. In comparison, Zhao et al. [49] believe that, due to the risk of sulfate leaching, S fertilization in an optimal regimen should only take place when plants need it, in a manner balanced with N fertilization and organic matter in the soil.

To minimize the risk of S losses through leaching, the suitability of such species of CCs for cultivation with garlic should be tested, characterized by a high demand for this ingredient, and should not compete for water and nutrients. In this study, we hypothesized that the biomass of CCs left until spring would leach, with a final positive effect on the quality of bulbs. Therefore, the research analyzed the extent to which S in the cultivation of winter garlic affects the uptake and content of macro- and micronutrients and bioactive substances in bulbs. The second major research problem was determining whether it was possible to influence the content of bioactive substances in garlic through elemental S and the appropriate selection of CC species.

2. Materials and Methods

2.1. Description of the Station’s Location

Agronomic experiments were conducted between 2018 and 2020 at the University of Life Sciences research station in Lublin, in southeastern Poland (51.23° N, 22.56° E). Determination of the chemical composition was conducted at the Department of Vegetable and Herb Crops, University of Life Sciences in Lublin.

2.2. Experimental Design and Management Practices

In the cultivation of winter garlic cv. Arcus, undersown crops left after freezing as natural soil mulch were Alexandrian clover (Trifolium alexandrinum L.), oilseed radish (Raphanus sativus var. oleiformis), buckwheat (Fagopyrum esculentum L.) of ‘Kora’ cv., and white mustard (Sinapis alba L.) of ‘Borowska’ cv. Plots without cover plants were the control.

The experiment was set up as a two-factor split-plot design with four replications. The factors of the experiment were the catch crops (CCs) and sulfur (S) fertilization. The following combinations were used: clover × S; fodder radish × S; buckwheat × S; mustard × S; control × S; clover × no S; fodder radish × no S; buckwheat × no S; mustard × no S; and control × no S. The area of each plot with a CC was 8.0 m² (2.0 × 4.0 m). Garlic cloves were planted at a row spacing of 0.40 × 0.12 m. There were 166 garlic plants in each combination in one repetition.

The elemental S dose (100%) for all CCs and the control plot (without CCs) was 20 kg ha⁻¹. The S was applied on the day the garlic cloves were planted: 25 September 2018, and 20 September 2019. No additional mineral fertilization or chemicals were used in the cultivation of garlic.

The experiment was carried out in monoculture for three consecutive years in the same field. The paper presents results from the last two years of experience. In the year preceding the experiment’s assumption, i.e., in 2017, a preliminary experiment was established (the results were not published due to the different methodology of carrying out analyses of the chemical composition of garlic) in an identical arrangement, as in this study.

The main physical characteristics of the soil (0–20 cm) were the following (in %): sand, 35.2; silt, 25.8; clay, 39; and organic matter, 1.6. The chemical composition of the soil before planting garlic is shown in Table 1.
Table 1. The chemical composition of the soil before planting garlic (in mg dm$^{-3}$, except for soil pH).

| Years | pH in H$_2$O | N-NO$_3$ | P-PO$_4$ | K   | Ca   | Mg   | S-SO$_4$ | Zn   | Mn   | Fe   | B   |
|-------|--------------|----------|----------|------|------|------|----------|------|------|------|-----|
| 2018  | 6.3          | 27.7     | 105      | 150  | 684  | 60   | traces   | 8.8  | 4.7  | 5.1  | 0.7 |
| 2019  | 6.1          | 42.4     | 90       | 133  | 664  | 90   | traces   | 9.4  | 6.4  | 5.9  | 0.7 |

The cover plants were sown at the beginning of August (2018 and 2019). After freezing (November–December), the grown mass of plants constituted mulch covering the soil surface. In each year of the study, garlic cloves were planted in the grown mass of green cover plants to a depth of 6 cm, previously delineating the rows so that they were 40 cm apart. The garlic cloves were planted: 25 September 2018, and 20 September 2019.

Finally, garlic was harvested once: 4 July 2019 and 6 July 2020 (mature plants). Samples of garlic bulbs were collected for chemical analysis.

2.3. Soil Chemical Analyses

Soil samples were taken on 5 August 2019, and 8 August 2020, before sowing the CCs. Before sampling, plant debris was removed from the soil surface. The samples were taken—ten evenly spaced individual samples using a steel soil probe from a depth of 0–20 cm. The combination of individual samples constituted the aggregate sample. The samples were numbered, tightly closed, secured against contamination, and transported to the laboratory.

The pH$_{H2O}$ was determined in a soil suspension in distilled water with a glass electrode in a 1:5 ratio ($v/v$) [50].

Soil samples were subjected to chemical analyses using the universal method of Nowosielski [51,52]. Extraction of the content of N-NO$_3$, S-SO$_4$, Ca, Mg, Zn, B, Fe, and Mn was carried out in an extract of 0.03 M CH$_3$COOH with the ratio of the weight of the soil to the extraction solution ($v/v$) as 1:10, i.e., of 0.03 M CH$_3$COOH, with extraction for 30 min [52]. After extraction was determined: S-SO$_4$ content was determined by the BaCl$_2$ nephelometric method; N-NO$_3$-microdestilation according to Bremner in Stark’s modification, B by the AAS method [52]. The available forms of Zn, Fe, and Mn were determined using Lindsay’s solution [53]. Determination of elements in extracts and solutions after mineralization was performed by spectrophotometric method on a Shimadzu Spectrophotometer UV-1800 UV–Vis (Shimadzu Schweiz GmbH, Reinach, Switzerland).

Phosphorus and K compounds were extracted with a buffered solution of calcium lactate and the lactic acid at pH 3.55 (Egner–Riehm method) [54]. The P content was determined colorimetrically; while K was by the AAS method [55].

2.4. Sample Preparation and Analyses

The samples were frozen, and phytochemical tests were performed successively for one week. Immediately before performing chemical analyses, the plant material was ground. In garlic bulbs, dry weight was determined by drying to constant weight at 105 °C [56].

To determine the content of macro and micronutrients, the plant material was mineralized in concentrated sulfuric acid. After mineralization of the plant material, these determinations were made: N—by distillation according to Kjeldahl’s in the Parnas–Wagner apparatus; content of calcium (Ca), potassium (K), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn)—spectrophotometrically [57]; boron (B) content spectrophotometrically (ICP–MS) [58]; S content, nephelometric with BaCl$_2$ [57].

In the prepared samples, the content of ascorbic acid was assessed by Tillman’s titration method [59], which involved the extraction of ascorbic acid from the product with oxalic acid, and then its oxidation to dehydroascorbic acid in an acidic environment with a standard blue dye 2.6-dichlorophenolindophenol (DCIP).
2.5. Total Phenolic Acids Content

The sum of phenolic acids, expressed as caffeic acid, was determined using Arnov’s reagent [60]. To a 10 mL measuring test tube, 1.0 mL of water extract was weighed out, as well as 1 mL of hydrochloric acid (18 g L$^{-1}$), 1 mL of Arnov’s reagent, 1 mL of sodium hydroxide (40 g L$^{-1}$), and that was topped up with water to 10 mL (solution A). Then, the solution absorbance was measured at 490 nm, applying a mixture of reagents without the extract as reference. The contents of phenolic acids (%) was determined in conversion to coffee acid ($C_9H_2O_4$), assuming absorbability $a \times l%/l \text{ cm} = 285$, according to the formula:

$$X = A \times 3.5087/m,$$

where $A$ means absorbance of solution A, $m$—a weighted sample of raw material in 100 g.

2.6. DPPH Radical Scavenging Activity Assay

The determination was performed according to the method given by Yen and Chen [61]. To prepare a reagent containing a solution of radicals 0.012 g DPPH (2,2'-diphenyl-1-picrylhydrazyl) was weighed out, transferred to a measuring flask of the capacity of 100 mL, filled up with methanol (100%), then it was dissolved in an ultrasound washer for 15 min. The blind assay (Ar) was prepared as follows: 1 mL of distilled water was measured out into a test tube (pH > 5), as well as 3 mL of methanol (100%) and 1 mL of DPPH solution. Having stirred it, after 10 min it was read on a spectrophotometer at 517 nm, against methanol (100%). To perform the examined assay (At), 1 mL of a sample was diluted in methanol and 3 mL of methanol (100%) was added, as well as 1 mL of DPPH solution. The sample was stirred, and after 10 min, it was read on a spectrophotometer at 517 nm, against methanol (100%). DPPH radical scavenging activity was expressed as µmol TE/g of fresh matter (FM).

2.7. Glutathione Analysis

The reduced form of glutathione was measured by the method of Guri [62]. Three extraction samples were taken from each combination. Glutathione was extracted from 3 g of plants with 6 mL of a mixture of ethylenediaminetetraacetic acid and trichloroacetic acid (Sigma-Aldrich, Poznań, Poland) (0.18612 g/L EDTA in 3% TCA was taken). The solution was adjusted to pH 7.0 with potassium phosphate buffer (Sigma-Aldrich, Poznań, Poland) and centrifuged for 10 min in the Rotofix 32 A, Hettich Zentrifugen, Tuttingen, Deutschland. The reduced glutathione content was determined spectrophotometrically with Ellman’s reagent (5.5-dithio-bis-2-nitrobenzoic acid (DTNB), Sigma-Aldrich, Poznań, Poland) with the UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan). The absorbance of the solution was measured at 412 nm. Glutathione was quantified from a calibration curve obtained using L-glutathione as the standard calibration curve.

2.8. Statistical Analysis

The Shapiro–Wilk test was used to test the assumption of normality. Cochran’s test was used to test for homoscedasticity, following which, the data were subjected to a two-way analysis of variance (ANOVA) based on a factorial combination of ten levels of sulfur × cover crop. Means were separated by the least significant difference (LSD) test when the F-test was significant. Data were evaluated by the HSD Tukey test at $p < 0.05$. The Pearson correlation coefficients for selected pair of parameters were also estimate. All calculations and analyses were performed using Statistica 10.0 PL (StatSof Inc., Tulsa, OK, USA).

3. Results

3.1. Impact of Climatic Condition

The weather during the growing season of winter garlic in 2018–2020 differed from the average thermal and humidity conditions in the region (Figure 1). In the 2018–2019 cultivation season, the average annual air temperature was 2.5 °C higher than the average for 1951–2010. The garlic-growing season 2019–2020 was exceptionally warm, during
which the average annual air temperature was 3.1 °C higher than the long-term average. The experiment's years were characterized by only a slightly higher amount of rainfall compared to the average total for the years 1951–2010. In the first season, the annual rainfall accounted for 109%, and in the second season, 108% of the average total for the years 1951–2010. A large diversity of humidity conditions characterized the experiment's years during the growing season of winter garlic. In the 2018–2019 cultivation season, there was a shortage of rainfall in June and July. The sum of precipitation constituted 56% and 48% of the long-term value in 1951–2010 for those months, respectively. However, in 2020, a huge amount of rainfall was recorded in May and June. In May, the sum of precipitation was 170%, and in June, 255% of the long-term average for these months. July was also characterized by a shortage of rainfall. The sum of precipitation in that month only constituted 35% of the average long-term sum in July.

![Figure 1. Average air temperatures and total rainfall during the experimental trials (2018–2019). Data were obtained from the Meteorological Station in Felin, 51.13° N; 22.37° E.](image_url)

3.2. Yield

The yield of winter garlic in cultivation with sulfur (S) and catch crop (CC) plants is shown in Figure 2. In 2019, in cultivation with S, higher garlic was obtained with clover (6.5 kg m⁻²), lower with mustard (2.4 kg m⁻²). The yield in cultivation with clover was higher by 109% in those cultivated without CCs. In cultivation without S, a higher yield of garlic bulbs was obtained with radish and clover (4.7 and 4.5 kg m⁻², respectively) than with buckwheat, without CCs and mustard (3.7, 2.9, and 2.5 kg m⁻², respectively). Production of garlic with S applied to clover resulted in yield that exceeded that of garlic grown without S applied to clover by 44%. However, production of garlic, when no S was
applied to clover in fall, was still superior to production of garlic without CC. In this case, the yield difference was 45%. In 2020, when using S, the garlic yield was the highest in cultivation with clover (7.4 kg m$^{-2}$), lower with buckwheat, mustard, and without CCs (3.8, 3.8, and 3.6 kg m$^{-2}$, respectively). The yield in cultivation with clover was higher by 105% in those cultivated without CCs. In cultivation without S, the marketable yield was higher with clover (5.5 kg m$^{-2}$) than with radish, mustard, and buckwheat (3.9, 3.5, 3.2 kg m$^{-2}$, respectively). The yield in cultivation when no S was applied to clover was higher by 161% in those cultivated without CCs. Production of garlic with S applied to clover and radish resulted in yield that exceeded that of garlic grown without S applied to clover, by 34% and 33%, respectively.

Figure 2. Yield of winter garlic cultivated under sulfur and catch crops in 2018–2020. * Clo: clover; Fod: fodder radish; Buc: buckwheat; Mus: mustard; Con: control (without cover crop); S: sulfur, noS: no sulfur. Different letters (a–d) indicate a significant difference between the experimental factors: sulfur × CCs; no sulfur × CCs ($p \leq 0.05$).
In 2019 and 2020, in cultivation with clover, both with and no S, compared to cultivation without CCs, the yield was higher by 109% and 106%, respectively.

3.3. Bioelements Analysis

The use of S had a significant effect on the dry matter of garlic bulbs (Table 2). In 2019 and 2020, in samples cultivated with S and clover, the bulbs were characterized by a higher dry matter in those cultivated without S. In 2020, the content dry matter was higher in samples cultivated with S and CCs and without CCs in comparison to those cultivated without S.

### Table 2. Dry matter and macronutrient analysis of winter garlic bulbs cultivated under sulfur and catch crops in 2018–2020.

| Source of variation | 2019          | 2020          | Mean         | 2019          | 2020          | Mean         | 2019          | 2020          | Mean         | 2019          | 2020          | Mean         |
|---------------------|---------------|---------------|--------------|---------------|---------------|--------------|---------------|---------------|--------------|---------------|---------------|--------------|
| (F)                 | *             | *             | *            | *             | *             | *            | *             | *             | *            | *             | *             | *            |
| (CC)                | NS            | NS            | *            | NS            | NS            | NS           | NS            | NS            | NS           | NS            | NS            | NS           |
| (F) × (CC)          | *             | *             | *            | *             | *             | *            | NS            | *             | NS           | NS            | NS            | NS           |

*F: fertilizer; S: sulfur; nS: no sulfur; ** CC: catch crop; *** dry matter (%); macronutrient (N, P, and K) amounts were expressed as % of dry matter (DM). Different letters (a–d) indicate a significant difference between the experimental factors: sulfur × CCs; no sulfur × CCs (p ≤ 0.05). Different letters (A, B) indicate a significant difference between the fertilizer; S: sulfur; nS: no sulfur (p ≤ 0.05). NS: no significant.

The content of N in garlic bulbs was higher in those cultivated with S compared to cultivation without S. In 2019, more N was found in garlic cultivated with S and with CCs, especially radish, buckwheat, and mustard, and in garlic cultivation without CC, compared to cultivation without S, by 64%, 37%, 27%, and 46%, respectively. In 2020, more N was produced in garlic bulbs through the use of S in cultivation coordinated with radish and in cultivation in bare soil compared to cultivation without S, by 162% and 33%, respectively.

In 2019, the garlic phosphorus (P) was higher in cultivated with S than no S, while S did not significantly affect the level of garlic P in 2020. In 2019, a diverse effect of S application on P accumulation by garlic plants was demonstrated. In cultivation with S and buckwheat, garlic plants accumulated significantly more P in bulbs than in cultivation without S, by 54%. However, the S application combined with the clover resulted in a reduction in the amount of P in the garlic bulbs compared to the cultivation without S, by 56%. In 2020, CC type had a substantial effect on garlic P content. Garlic P content was highest when grown under terminated buckwheat and lowest under the control treatment with the values of 0.52% and 0.38%, respectively. Apart from buckwheat, there was no difference in P content of the control treatment and other CC types.

Garlic bulbs contained more potassium (K) when cultivated with S than without S. In 2019, more K was produced in garlic bulbs through the use CCs in cultivation. Garlic K was highest when grown with clover than without CCs with the values of 58% and 38%, respectively. However, in the cultivation with radish, buckwheat, and mustard, garlic also contained significantly more K compared to the control. In 2020, the K content in bulbs was even recorded in samples cultivated with and without S. Only the plants grown with S and buckwheat accumulated slightly more K in the bulbs.
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No clear effect of S on the accumulation of calcium (Ca) and magnesium (Mg) in garlic plants was found (Table 3). In 2019 and 2020, the Ca content was higher in bulbs grown without S with biomass from clover than with S, by 40 and 33%, respectively. In 2020, the use of S increased the level of Ca in bulbs in the cultivation coordinate with mustard compared to cultivation without S, by 16%.

Table 3. Macronutrient analysis of winter garlic bulbs cultivated under sulfur and catch crops in 2018–2020.

| F *  | CC **  | Ca *** | Mg | S |
|------|--------|--------|----|----|
|      |        | 2019   | 2020 | Mean | 2019 | 2020 | Mean | 2019 | 2020 | Mean | 2019 | 2020 | Mean |
| S    | Clover | 0.60 b | 0.56 b | 0.58 cd | 0.11 a | 0.16 ab | 0.16 a | 0.56 bc | 0.56 bc | 0.56 b |
|      | Fodder radish | 0.59 b | 0.67 b | 0.63 b | 0.08 b | 0.18 ab | 0.13 ab | 0.75 a | 0.72 ab | 0.74 a |
|      | Buckwheat | 0.60 b | 0.65 b | 0.63 b | 0.10 b | 0.10 bc | 0.10 ab | 0.46 c | 0.84 a | 0.65 a |
|      | Mustard | 0.57 b | 0.57 b | 0.57 cd | 0.10 b | 0.11 bc | 0.11 ab | 0.64 b | 0.71 ab | 0.68 a |
|      | Control | 0.55 b | 0.37 c | 0.46 ef | 0.06 c | 0.07 c | 0.07 b | 0.54 bc | 0.49 cd | 0.52 b |
|      | Mean | 0.58 A | 0.56 A | 0.57 A | 0.09 A | 0.12 A | 0.10 A | 0.59 A | 0.66 A | 0.63 A |
| nS   | Clover | 0.84 a | 0.84 a | 0.84 a | 0.10 b | 0.19 a | 0.15 ab | 0.40 d | 0.30 d | 0.35 c |
|      | Fodder radish | 0.44 b | 0.53 b | 0.49 ef | 0.09 b | 0.13 ab | 0.11 ab | 0.62 b | 0.32 d | 0.47 b |
|      | Buckwheat | 0.50 b | 0.54 b | 0.52 cd | 0.10 b | 0.11 bc | 0.11 ab | 0.43 c | 0.30 d | 0.37 bc |
|      | Mustard | 0.49 b | 0.49 c | 0.49 ef | 0.10 b | 0.10 bc | 0.10 b | 0.65 b | 0.39 cd | 0.52 b |
|      | Control | 0.43 b | 0.45 c | 0.44 f | 0.09 b | 0.09 bc | 0.09 b | 0.40 d | 0.30 d | 0.35 c |
|      | Mean | 0.54 A | 0.57 A | 0.56 A | 0.10 A | 0.12 A | 0.11 A | 0.50 B | 0.32 B | 0.41 B |

Source of variation

- *(F): fertilizer; S: sulfur; nS: no sulfur; ** CC: catch crop; *** macronutrient (Ca, Mg, and S) amounts were expressed as % of dry matter (DM).
- Different letters (a–f) indicate a significant difference between the experimental factors: sulfur × CCs; no sulfur × CCs (*p ≤ 0.05). Different letters (A, B) indicate a significant difference between the fertilizer; S: sulfur; nS: no sulfur (*p ≤ 0.05). NS: no significant.

In 2019, garlic bulbs contained more Mg when cultivated with S and clover. In those cultivated with S but without CCs, the Mg content in bulbs was much lower than in those cultivated without S and organic mulch. In 2020, CC type had a substantial effect on garlic Mg content. Garlic Mg content was highest when grown under terminated clover and lowest under the control treatment with the values of 0.18 and 0.08%, respectively. Apart from clover, there was no difference in Mg content of the control treatment and other CC types.

The application of S had a significant effect on the level of this element in garlic bulbs. In 2019, garlic S in cultivation with application of S was higher by 15%, while in 2020 by 113%, in those cultivated without S. In 2019, a high and stable amount of garlic S was ensured by S combined with the clover and radish CCs in comparison to samples cultivated with these CCs without S by 40% and 20%, respectively. In cultivation with S without CCs, the S content was also higher than in the cultivation without S on bare soil by 35%. In 2020, the use of S combined with CC significantly increased the level of S of bulbs compared to cultivation without S (with buckwheat, radish, clover, mustard by 180%, 125%, 86%, 82%, respectively). In the cultivation with S without CCs, the S content was also higher than no S by 63%.

When S was used in 2019 and 2020, plants accumulated more zinc (Zn) in bulbs (Table 4). In 2019, garlic bulbs contained more Zn in those cultivated with S and fodder radish, buckwheat, and mustard biomass than in those cultivated with no S (by 5% to 14%). Garlic plants grown in uncovered soil with and without S accumulated significantly less Zn in bulbs. In 2020, no significant effect of S and CCs on garlic’s Zn content was found.
Table 4. Micronutrient analysis of winter garlic bulb cultivated under sulfur and catch crops in 2018–2020.

| Source of variation | F * | CC ** | Zn *** | Cu | Mn | Fe | B |
|---------------------|-----|-------|--------|----|----|----|---|
|                     | 2019 | 2020 | Mean   | 2019 | 2020 | Mean | 2019 | 2020 | Mean | 2019 | 2020 | Mean | 2019 | 2020 | Mean | 2019 | 2020 | Mean |
| Clover              | 20.40 b  | 23.77 a  | 22.09 ab | 2.22 b | 3.89 a  | 2.80 a  | 6.83 a  | 5.29 c  | 6.06 b  | 20.50 c  | 33.83 a  | 27.17 bc | 5.23 d  | 6.23 a  | 5.73 d |
| Fodder radish      | 22.43 a  | 21.66 a  | 22.05 ab | 3.04 a  | 2.23 a  | 2.64 a  | 5.15 b  | 6.93 a  | 6.04 b  | 32.49 a  | 24.70 b  | 28.60 ab | 6.91 b  | 7.57 a  | 7.24 ab |
| Buckwheat          | 22.60 a  | 23.93 a  | 23.27 a  | 2.51 b  | 2.37 a  | 2.44 ab | 6.63 a  | 6.66 a  | 6.65 ab | 30.35 b  | 31.55 b  | 31.05 ab | 6.77 b  | 6.77 a  | 6.77 ab |
| Mustard            | 22.55 a  | 23.88 a  | 23.22 a  | 2.50 b  | 2.33 a  | 2.42 ab | 6.68 a  | 6.78 a  | 6.73 a  | 30.38 b  | 33.05 b  | 31.72 a  | 6.76 b  | 7.10 a  | 6.93 ab |
| Control            | 20.00 c  | 21.40 a  | 20.70 ab | 2.20 b  | 2.22 a  | 2.21 b  | 5.16 b  | 5.28 c  | 5.22 c  | 19.70 c  | 25.83 a  | 22.77 c  | 5.18 d  | 6.18 a  | 5.68 ab |
| Mean               | 21.60 A | 22.93 A | 22.26 A | 2.49 A  | 2.51 A  | 2.50 A  | 6.09 B  | 6.19 B  | 6.14 B  | 26.72 A  | 29.79 A  | 28.26 A  | 6.17 B  | 6.77 A  | 6.47 B |
| Clover             | 21.32 b  | 22.91 a  | 22.12 ab | 2.53 b  | 2.22 a  | 2.38 b  | 6.64 a  | 6.51 a  | 6.58 ab | 24.77 b  | 28.10 b  | 26.44 bc | 8.37 a  | 7.37 a  | 7.87 a |
| Fodder radish      | 21.30 b  | 20.64 a  | 20.97 ab | 2.37 b  | 2.30 a  | 2.34 b  | 6.57 a  | 6.44 a  | 6.51 ab | 23.44 b  | 26.77 b  | 25.11 bc | 8.04 a  | 7.38 a  | 7.71 ab |
| Buckwheat          | 19.70 c  | 19.03 a  | 19.37 b  | 2.33 b  | 2.23 a  | 2.28 b  | 6.34 a  | 6.21 b  | 6.28 b  | 21.00 c  | 27.66 b  | 24.33 bc | 7.80 b  | 7.46 a  | 7.63 ab |
| Mustard            | 20.90 b  | 19.03 a  | 19.97 b  | 2.33 b  | 2.30 a  | 2.32 b  | 6.34 a  | 6.21 b  | 6.28 b  | 21.00 c  | 24.33 b  | 22.67 c  | 7.80 b  | 7.46 a  | 7.80 ab |
| Control            | 19.70 c  | 20.56 a  | 20.13 ab | 2.32 b  | 2.20 a  | 2.26 b  | 6.07 a  | 6.00 b  | 6.04 b  | 22.50 c  | 18.50 c  | 20.50 c  | 6.50 c  | 6.17 a  | 6.34 cd |
| Mean               | 20.58 B | 20.43 B | 20.51 B | 2.38 B  | 2.25 B  | 2.31 A  | 6.39 A  | 6.27 A  | 6.33 A  | 22.54 B  | 25.07 B  | 23.81 B  | 7.70 A  | 7.10 A  | 7.40 A |

* F: fertilizer; S: sulfur; nS: no sulfur; ** CC: catch crop; *** Micronutrient (Zn, Cu, Mn, Fe, and B) amounts were expressed as mg kg$^{-1}$ of dry matter (DM). Different letters (a–d) indicate a significant difference between the experimental factors: sulfur × CCs; no sulfur × CCs ($p \leq 0.05$). Different letters (A, B) indicate a significant difference between the fertilizer; S: sulfur; nS: no sulfur ($p \leq 0.05$). NS: no significant.
The use of S did not affect garlic copper (Cu) content. In 2019, only cultivation with S and fodder radish provided higher Cu levels in garlic bulbs than cultivation without S, by 28%.

The effect of S on the manganese (Mn) content was found only in 2019. In 2019, less Mn was determined in bulbs in the cultivation of garlic with S, both with fodder radish and in uncovered soil, than in cultivation without S, by 27% and 17%, respectively. Different dependencies occurred in the content of this element in 2020. More Mn in bulbs was accumulated by crops cultivated with S and buckwheat and mustard CCs compared to cultivation without S. However, plants of garlic accumulated less Mn with S and clover and in cultivation without CCs than in cultivation without S by 23% and 13%, respectively.

In 2019 and 2020, the S application increased the iron (Fe) content in garlic by 18%. In 2019, garlic plants cultivated with S buckwheat, mustard and radish contained more Fe in bulbs than without S by 45%, 44%, and 30%, respectively. However, garlic plants accumulated less of this element with S and clover intercrop undersown than without S, by 17%. A different relationship occurred in 2020. More Fe was determined in garlic cultivated with S and clover and in uncovered soil compared to without S by 20% and 39%, respectively.

In 2019, the consequence of S was a low level of boron (B) in garlic bulbs. Garlic plants cultivated with S and clover, fodder radish, and in cultivation without CCs contained less B in bulbs than with S, by 60%, 16%, and 25%, respectively. In 2020, there was no effect of S on the B content in bulbs. CC type had substantial effect on garlic Mn content. Garlic Mn content was highest when grown under terminated radish, buckwheat and mustard (with the values of 7.47, 7.11, 7.20 mg·kg\(^{-1}\) DM) and lowest under the control treatment (6.17 mg·kg\(^{-1}\)DM).

### 3.4. Organic Compounds Analysis

In 2019, garlic plants cultivated without S contained more L-ascorbic acid (LAA) in in bulbs than with S (Table 5). A higher LAA content was found in garlic bulbs grown without S with buckwheat and fodder radish CCs compared to the cultivation of those with S by 98% and 44%, respectively. More LAA were also accumulated by plants grown without S and CCs than with S. In 2020, more LAA was determined in bulbs in the cultivation of garlic with S than no S. However, only more LAA were accumulated by garlic plants grown with S and mustard than those cultivated without S by 58%.

### Table 5. Bioactive compound content in bulb winter garlic cultivated under sulfur and catch crops in 2018–2020.

| Source of variation | 2019 Mean | 2020 Mean | 2019 Mean | 2020 Mean | 2019 Mean | 2020 Mean | 2019 Mean | 2020 Mean | 2019 Mean | 2020 Mean | 2019 Mean | 2020 Mean |
|---------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| F       | 14.83 B  | 13.68 A  | 14.26 A  | 97.14 A  | 107.14 A  | 102.14 A  | 0.94 A  | 1.27 A  | 1.10 A  | 14.71 A  | 13.83 A  | 14.27 A  |
| CC **  | 18.18 A  | 11.86 B  | 15.02 A  | 84.91 B  | 90.84 B  | 87.87 B  | 0.57 B  | 0.93 B  | 0.75 B  | 10.96 B  | 9.83 B  | 10.39 B  |

* F: fertilizer; S: sulfur; nS: no sulfur; ** CC: catch crop; *** LAA: L-ascorbic acid; TPA: total phenolic acid; amounts were expressed as mg 100 g\(^{-1}\) of fresh matter (FM); AA: antioxidant activity was expressed as µmol TE/g of fresh matter (FM); glutathione amounts were expressed as mg g\(^{-1}\) of fresh matter (FM). Different letters (a–f) indicate a significant difference between the experimental factors: sulfur × CCs; no sulfur × CCs (p ≤ 0.05). Different letters (A, B) indicate a significant difference between the fertilizer; S: sulfur; nS: no sulfur (p ≤ 0.05). NS: no significant.
The application of S had a significant effect on the content total phenolic acid (TPA) in garlic bulbs. In 2019, much higher TPA amount was determined in the bulbs of garlic grown with S and CCs (by 4% to 21%) and in uncovered soil compared to those cultivated without S by 24%. In 2020, garlic bulbs significantly contained the highest TPA when cultivated with S and clover than those cultivated without S by 39%. Other CCs type had substantial effect on garlic TPA content, likewise (by 6% to 11%).

Furthermore, garlic plant extracts showed higher antioxidant activity (AA) when cultivated with S and CCs and cultivated with S in bare soil than when cultivated without S. In 2019, the significantly highest AA was displayed by garlic extracts from soil cultivation S application and clover, compared to extracts from the other variants of the experiment. In 2020, the extract from the same cultivation variant and the extract from garlic cultivation with S without catch plants had the highest AA.

Garlic bulbs contained more glutathione when cultivated with S than without S. In 2019, the glutathione content in bulbs was much higher in samples cultivated with S and buckwheat, fodder radish, mustard, and clover than in those cultivated with S by 63%, 53%, 32%, and 20%, respectively. In 2020, more glutathione was also found in garlic grown with S and fodder radish, buckwheat, and mustard than in the experimental variants in which no S was used by 71%, 37%, and 15%, respectively. More glutathione was also accumulated by plants grown with S unprotected soil than without S by 77%.

4. Discussion

4.1. Chemical Composition of the Soil

The soil in garlic cultivation in the years 2018–2020 in the 0–20 cm layer was characterized by a high phosphorus (P) content (98 mg P dm$^{-3}$ on average) and magnesium (Mg) (75 mg Mg dm$^{-3}$ on average), (Table 1). The calcium (Ca) and potassium (K) content was respectively lower by 400 and 20 mg dm$^{-3}$ than the optimal values for garlic cultivation [63]. Before the cultivation was established in 2018, the soil was slightly acidic (pH 6.3). In 2019, the soil was slightly acidic (pH 6.1), and the content of nitrogen (N), P, K, Ca was higher. The content of N in the soil was not optimal for garlic, as no mineral fertilization was used in the cultivation. Based on the determined content of macro- and micronutrients for the agronomic category of the soil on which the experiments were conducted, it should be concluded that the content of P and Mg was in the high content class, and the K content in the medium content class [64]. The soil was characterized by a particularly low Ca, zinc (Zn), manganese (Mn), iron (Fe), and boron (B) content.

4.2. Yield

In our research, the average yield of winter garlic bulbs was 4.1 kg m$^{-2}$. The yield was smaller than the yield of 6.1 kg m$^{-2}$ of winter garlic obtained by Rekowska et al. [65]. The difference was probably due to the different climate and cultivation time. In the cultivation of garlic with catch crops (CCs), no reduction in the yield and no negative competitive effect on the yield was noted compared to conventional cultivation. A higher yield of bulbs was obtained in cultivation with clover and sulfur (S). Compared to cultivation without CCs (control), a lower yield was obtained only for cultivation with mustard. These results confirmed the earlier findings on the yield-generating effect of organic mulches on the yielding of garlic in cultivation on the bunch harvest [31].

4.3. Climatic Conditions

In our research, the N available to garlic plants depended not only on the characteristics of the CC, but also on the weather conditions. In 2019, in early spring, under conditions of a favorable moisture content and rapidly warming soil with high average air temperatures, favoring microbial and enzymatic soil activity, the process of mineralization of organic residues was much faster than in 2020. It should be emphasized that S application favored the process of the mineralization of organic matter, the immobilization of N formed, and, as a result, the synergistic uptake of both components by garlic plants,
which contributed to a higher content of N and S, especially in cultivation with fodder radish, buckwheat, and mustard. When S was used, the N content in the bulbs was higher (average 1.92% DM) than without S (1.33% DM).

4.4. Macro- and Micronutrients Enrichment and Their Content

The intensity of the mineralization process of organic compounds is related to the type and amount of plant debris that makes up the soil surface catch [24]. Plant matter left as mulch contains a lot of organic carbon (C), easily absorbed by soil organisms, which protects minerals from being lost [21]. The faster the organic matter is broken down, the faster the nutrients are available to the succeeding plants [24]. The effective use of N, absorbed by organic matter, requires the synchronization of N release from harvest residues and N uptake by plants in the next crop [66].

Sulfur application in the cultivation of garlic increased the dry matter and the content of N, P, K, S, Zn, Mn, and Fe, as well as the total phenolic acids (TPA), antioxidant activity (AA), and glutathione. Simultaneously, it had no significant effect on the level of Ca, Mg, copper (Cu), B, and L-ascorbic acid (LAA) accumulated by plants in bulbs. In the cultivation of garlic with S, the organic mass of CCs quickly decomposed in spring and was mineralized, which favored N uptake by garlic plants. In 2019, in plants cultivated with S, there was a tendency to accumulate N in bulbs with CC plants of clover, radish, buckwheat, and mustard, and in 2020, only with fodder radish. As the mineralization of organically bound N in the soil and its availability for garlic occurred more rapidly with the use of S, in 2019, a similar trend, in the increase in dry matter in garlic bulbs with S and CCs, was expected. This expected tendency was not found because garlic was only cultivated with S and clover with a high and stable dry matter level in bulbs. Fabaceae plants such as *Trifolium incarnatum* are effective CCs, absorb quickly, and release N faster due to their low C:N ratio (range 10–15) as opposed to biomass characterized by a high C:N ratio (*Panacea*, mustard > 30), consuming N in the decomposition process [67].

It is generally believed that applying S to soil may have a synergistic relationship with the bioavailability of N released from organic matter to garlic plants, determining higher yields and a better quality [48]. The results of many studies indicate the existence of interactions between S and N and their effective positive influence on the yield in *Allium sativum* and *Allium cepa* [5,6,9,18]. Literature data show a decrease in the weight of bulbs in *Allium cepa* through the use of S [68], a decrease in the yield of *Allium fistulosum*, and an increase in the sharpness of the onion flavor [7].

In the presented research, the application of S increased the content and uptake of P and K by garlic plants. This factor, which increases garlic’s P levels, signals an additive effect of S. Our findings on the greater availability of P for garlic plants under the influence of S follow other authors’ statements [10]. Jaggi et al. [69] found that S reduces the pH of alkaline soil and may improve the P and micronutrient availability for succeeding crops. González-Morales et al. [70] emphasize that the soil reaction and moisture determine the intensity of uptake of P ions from the soil solution. The effectiveness of P use by plants is influenced by an appropriate S:P:Se balance. The authors mentioned above explained that the absorption of orthophosphoric ions (H$_2$PO$_4^-$ and HPO$_4^{2-}$) by plants largely depends on the S and Se balance in the soil sorption complex. According to Gransee and Führs [71], the soil’s optimum pH for P uptake is wide (pH ranging from 5 to 7).

This study showed a higher P content in garlic in 2020 because, during intensive plant growth (May–June), more rainfall, and a higher air temperature (June) than in this period in 2019 were recorded. There was a significant interaction effect of S fertilization × type of CC on the P content in garlic bulbs in individual years of research. In 2019, when S was used, the P content in bulbs was only higher when grown with buckwheat. However, in the cultivation with S and clover, the P level in garlic bulbs was lower than in the cultivation without S. Moreover, buckwheat cultivated as a CC combined with S was an efficient source of N (in 2019), P (in 2019 and 2020), and K (in 2020) for garlic plants, as the content of this macronutrient was the highest in bulbs. According to Zarzecka et al. [72], buckwheat
enriches the soil with P and K by releasing organic acids from the roots into the substrate and, consequently, increasing the bioavailability of elements for the succeeding plant. As the soil pH decreases by the release of H+ ions from the decomposition of organic acids, the absorption of the maximum amount of orthophosphate ions and available forms of K increases. In this study, more P in cloves was determined in cultivation with S (0.42% DM on average) without mineral fertilization than without S (0.38% DM on average). Jiku et al. [73] determined the P content in garlic cloves at the level of 0.15% DM in cultivation without K fertilization (K0) and 0.35% in cultivation with K 200 kg ha\(^{-1}\). The above-cited authors also showed that potassium increases the N content in garlic bulbs. With increasing doses of potassium (K0, K200, K175, K250), the content of N (1.5, 2.4, 2.5, 2.1% DM) in garlic bulbs increased.

In our research, using S had a positive effect on the availability of K for garlic plants. Similarly, Youssif et al. [10] found a high K accumulation efficiency in garlic leaves when S was used in foliar fertilization. However, in our research, the CC (on average, in 2019 and 2020) did not affect and the availability of this element for garlic plants. The uptake of N, P, and K, depending on S and the type of CC, can be associated with slight differences in the dry matter content of garlic bulbs, as the content of these elements mainly affects the dry weight of plants. It can be assumed that growing conditions, mainly temperature, could have influenced the dry matter content in the tested garlic. The content of dry and organic S compounds in Allium crops depends on the characteristics of the cultivar, plant organs, length of the growing season, and environmental factors, such as water stress, light quality, duration, and temperature in the growth and root zones [74,75]. In our experiment, using S significantly increased the level of K (0.52% DM) in bulbs compared to cultivation without S (0.44% DM). Other authors obtained significantly higher values. According to Jiku et al. [73], the K content of garlic with the applied K fertilization (K200 kg ha\(^{-1}\)) was 2.88% DM. The average content of this element was also high in garlic leaves and amounted to 17.35–27.99 g kg\(^{-1}\) DM [76]. High variability of K in bulbs was found in 14 ecotypes of Greek garlic (ranging from 446 to 675 mg 100 g\(^{-1}\) FW) [77]. Driba-Shiferaw [78] believe that the K content of garlic depends on fertilization and soil properties.

In this study, there was no effect of S on the Ca and Mg uptake by garlic plants and the content of these components in bulbs. There was a tendency to accumulate greater amounts of Ca in the bulbs in an S-free crop with clover. In cultivation with S, a higher Ca level in bulbs was only recorded in 2020 in cultivation with fodder radish and buckwheat. In this situation, Ca’s content and uptake could limit the use of S in cultivation with other CCs. Earlier studies found that sulfate sulfur (S-SO4) can precipitate in the form of Ca, which reduces the availability of Ca to garlic plants [47,79,80]. This statement is also supported by the fact that in cultivation without S, the generally used biomass from CCs increased Ca’s availability in the soil and its absorption by succeeding crops [81]. In our study, garlic cloves were characterized by a similar Ca content (0.37–0.84% DM) compared to the amount (0.62–0.78% DM) determined by Jiku et al. [73]. Much smaller amounts of Ca were determined in garlic leaves (7.55–28.96 g kg\(^{-1}\) DM) [76]. In the studies by Petropoulos et al. [77], significant differences in the Ca content (from 163 to 963 mg 100 g\(^{-1}\) FW) in garlic were associated with varietal differences. In these studies, applying S to the soil had a synergistic effect in cultivation with clover biomass, as the garlic plants accumulated more magnesium (Mg) in the bulbs. Zhao [49] pointed out that Mg in the soil in a form available to plants only occurs in soil solution. The release of this element from organic matter depends on the precipitation in the season. In our research, a higher Mg content in garlic bulbs was demonstrated in 2020, in which, during the bulbs’ formation period, more favorable humidity conditions for plant growth were noted. The use of S in the cultivation of garlic on bare soil decreased the Mg content in bulbs. Similar results proving that Mg is leached more rapidly from the top layers of bare soil were obtained in earlier studies by Melakeberhan et al. [82]. In the presented study, garlic bulbs were characterized by low and similar Mg levels in cultivation with S (0.10% DM) and without S (0.11% DM). Jiku et al. [73] found a higher Mg content in garlic 0.20–0.23% DM in cultivation with
mineral fertilization. Piątkowska et al. [76] showed a higher content of this component in garlic leaves, amounting to 0.85–1.32 g kg\(^{-1}\) DM. Depending on the garlic ecotype, the Mg content ranged from 23.1 to 63.1 mg 100 g\(^{-1}\) FW [77].

Using S had a positive effect on the amount of S in garlic bulbs. Such a phenomenon should be considered favorable due to the improvement in garlic bulbs’ quality [15,16]. The basic and primary product in incorporating S into organic compounds in the plant is cysteine, which is a precursor to sulfuric amino acids [9]. In this study, in both years of research, using S in cultivation with clover and fodder radish, and in 2020, with buckwheat and mustard, increased the S level in bulbs. Our finding that the highest amounts of S in bulbs were found in garlic grown with CCs follows others’ results [82]. Bloem et al. [16] believe that the sorption of sulfates by organic matter occurs in humic complexes with aluminum (Al) and iron (Fe). Several factors cause seasonal changes in the availability and bioavailability of S for plants: the rate of mineralization of organic matter, leaching, and sorption processes [17].

In our research, more S was accumulated by plants with S fertilization (0.63% DM) than in cultivation without S (0.41% DM). The obtained results do not differ from those obtained by other authors. In the studies of Bloem et al. [48], the content of this component ranged from 2.9 to 7.0 mg g\(^{-1}\) DM, while according to Jiku et al. [73], garlic contained 0.43–0.50% DM. The content of this component in garlic leaves was higher, ranging from 2.41 to 6.22 g kg\(^{-1}\) DM [76]. Fertilization with S and N (N90S60 kg ha\(^{-1}\)) increased the content of S in garlic bulbs in the range from 3.5 to 5.0 mg 100 g\(^{-1}\) DM [19]. Simultaneously, the authors mentioned above suggest that pre-harvest factors, such as cultivar selection, and N and S fertilization determine the size and quality of garlic bulbs yield.

Some have also noted that the yield-generating effect of S in the cultivation of Allium plants depends on Zn’s availability for plants [83]. The bioavailability of Zn for garlic plants is largely determined by the soil’s texture and the content of organic carbon in the soil [10].

In this work, using S increased the bioavailability of Zn to garlic plants. In 2019, the CCs fodder radish, buckwheat, and mustard generated abundant organic matter, with a high organic carbon content, which, it should be assumed, affected the subsequent use of Zn by garlic plants. In 2020, such a beneficial effect of S combined with CCs on Zn’s bioavailability for garlic was not recorded. As shown by the research conducted by White and Broadley [84], the content of Zn in plants is strongly correlated with the content of this element in the soil and the soil pH. The content of Zn in plants decreases with an increasing soil pH. Zn uptake by plants may reduce S and Fe oxides in the soil [85]. In the presented research, when S was used, plants accumulated on average more Zn (22.26 mg kg\(^{-1}\) DM in bulbs and 20.5 mg kg\(^{-1}\) DM on average) in cultivation without S. The results obtained in this study confirm the regularities observed by other authors who report a high level of Zn in Allium plants, in leaves of A. sativum 9.32–13.78 mg kg\(^{-1}\) DM [76], in bulbs (0.55–1.18 mg 100 g\(^{-1}\) FW) [77], in pseudo-steams A. porrum (11.96–23.97 g kg\(^{-1}\) DM) [86].

In our research, no subsequent influence of S and CCs on the Cu concentration in bulbs was found. In the first year, the factor influencing the solubility, migration, and bioavailability of Cu for garlic plants was S with CC of oilseed radish. It is generally believed that Cu is a slow-moving element, strongly absorbed by plant roots, both with deficiency and excess of the element [83]. It is believed that low-weight organic compounds released during the decomposition of organic matter increase Cu’s mobility, and thus its uptake from the soil solution [87]. The above-cited authors have shown that Cu uptake from soil by plants only decreases under conditions of strong absorption by Al, Fe oxides, and Mn oxides, and by the organic matter under alkaline conditions. Since S lowers the soil pH, the absorption of Cu indirectly increases because of the dissolution of compounds that chelate it strongly [88]. In our research, the slight differences in the interaction of S fertilization × type of CC do not indicate such an action of the organic substance limiting the absorption of Cu by garlic plants because this micronutrient content in bulbs was even recorded in 2019 and 2020. Using S increased the Cu content (2.50 mg kg\(^{-1}\) DM
on average) in garlic compared to cultivation without S (2.31 mg kg\(^{-1}\) DM on average). However, higher values were given by Golubkina et al. [86] in pseudo-steams of \textit{A. porrum} 3.46–7.18 g kg\(^{-1}\) DM.

In bulbous vegetables, Mn positively affects the yield and increases the N use efficiency by plants [89]. In this study, the consequence of S used in the first year was a low Mn level in bulbs cultivated with radish and in the second year, in those cultivated with clover. Moreover, using S in the cultivation of garlic without CCs lowered the Mn level in bulbs. Although, in the second year of research, using S with CCs of buckwheat and mustard increased Mn’s concentration in bulbs, the movement of this element and its uptake could be limited by S. The antagonism of S towards Mn limits \textit{Allium cepa} plants’ availability in a controlled greenhouse experiment [5]. In soil, using S may only indirectly affect Mn’s availability for plants, as it may lower the soil pH and, thus, conducive the bioavailability of this element. The availability of Mn-available forms for plants also depends on the soil moisture status because strong soil moisture promotes accessibility to plants, and drought caused Mn’s transition from the Fe form to the form of dioxide unavailable to plants [90].

Under the conditions of our experiment, the soil moisture level could have affected a slightly higher level of Mn in garlic bulbs in 2020 because of greater rainfall during the period of intense weight gain of the bulbs (May–June).

More Mn was accumulated by plants in cultivation without S (6.33 mg kg\(^{-1}\) DM) than with S (6.14 mg kg\(^{-1}\) DM). Less Mn was determined in pseudo-steams in another species of \textit{A. porrum} in the range from 6.93 to 23.15 mg kg\(^{-1}\) DM. It is presumed that, besides the differences in species characteristics, the differences in the content of this component were also influenced by the cultivation conditions, mainly the soil. In shaping the Fe content in plants, S’s role is emphasized, which reduces the amount of this element in conditions of S deficiency or increases the level of Fe in the plant with a good S supply [70].

In the cultivation of onions, S antagonizes Fe and Zn [5]. The solubility and availability of Fe for plants depend on the soil pH, and as the soil pH increases, the amount of Fe available to plants decreases. The availability of Fe in the soil is also strongly influenced by oxidation and reduction reactions, the course of which depends on soil moisture [91].

In our research, CCs combined with S had a different effect on the Fe content in garlic bulbs. In 2019, using S and the CCs fodder radish, buckwheat, and mustard increased the bioavailability of Fe in the cultivation of garlic, as the level of this element in the bulbs was higher than in those cultivated without S. In 2019, the application of S and clover reduced the Fe in bulbs, and in 2020, increased the content of this element. The positive effect of S application on the Fe level in bulbs was also visible in the second year with garlic cultivation without using plant biomass. Based on these results, it is difficult to generalize unequivocally because deficiencies of this component are usually observed in alkaline soils due to the appearance of sparingly soluble iron hydroxides. In these studies, the soil’s pH (pH\(_{H_2O}\) 6.1–6.3) before the experiment was set up was slightly acidic, so using S could have contributed to lowering the soil pH and increased the concentration of this element in garlic cloves. In the cultivation with S, cloves of garlic contained more Fe (28.26 mg kg\(^{-1}\) DM) than in the cultivation without S (23.81 mg kg\(^{-1}\) DM). Much lower values were obtained by Petropoulos et al. [77] in fresh plant material (2.89–5.45 mg per 100 g) and also Piątkowska et al. [76] in the dry matter of garlic leaves (3.48–85.71 g kg\(^{-1}\)).

In these studies, in 2019, the consequence of S was a low level of B in garlic bulbs, especially in plants cultivated with clover and fodder radish, and in those cultivated without CCs. In 2020, there was no effect of S on the B content in onions. Since, in June 2019, there was a shortage of rainfall, it can be assumed that using S in such weather conditions contributed to a reduction in the B content in garlic bulbs. Coolong et al. [5] showed that the uptake of B by \textit{Allium cepa} plants may be difficult during drought and S fertilization. Similarly, Ozturk et al. [92] showed that the availability of B to plants is limited by drought and the alkaline pH of the soil. The uptake of B by plants may also be influenced by the
content of organic matter in the soil, as a greater amount usually increases the overall abundance of this element [93].

Under conditions of the experiment, in cultivation without S, B was determined in bulbs much more (7.40 mg kg\(^{-1}\) DM) than with S (6.47 mg kg\(^{-1}\) DM). A lower B content characterized garlic from the Kushtia province in Bangladesh; the content of this component in bulbs was 21–23 µg g\(^{-1}\), in leaves 26–28 µg g\(^{-1}\) [73]. According to Hatwal [94], the use of S in the form of ZnSO\(_4\) (0.4%), or elemental (25 kg ha\(^{-1}\)), and vermicompost (15 t ha\(^{-1}\)) increases the garlic yield. It has a positive effect on the content of garlic bioactive substances. In this study, an increase in secondary metabolites' content in garlic bulbs was expected due to S. However, it can be seen that this was not found for the LAA content (for two-year mean values). In previous studies, Salata et al. [25], whilst investigating the cultivation of garlic for bunch harvesting, found an average reduction in LAA levels of 10% in bulbs and leaves cultivated with serradella, buckwheat, and millet CCs compared to those cultivated in bare soil. In shaping the level of secondary metabolites, the role of environmental factors is emphasized. According to Maggio et al. [95], the levels of antioxidants such as LAA increase or decrease, responding to environmental stress. In our research, the produced biomass reduced soil heating in various ways, thus reducing evaporation and promoting water absorption and infiltration. On this basis, it can be assumed that the LAA level was more influenced by the weather factor and the type of mulch than by S. A higher LAA content was determined in garlic bulbs in 2019; in this year, during the spring-summer period, there were more favorable thermal conditions than in the same period in 2020. In 2019, the application of S with fodder radish and buckwheat and without CCs lowered the LAA levels in bulbs. In 2020, the combined use of S and mustard biomass resulted in a higher LAA level in garlic bulbs.

4.5. L-ascorbic Acid, Total Phenolic Acid, Antioxidant Activity, Glutathione Content

In these studies, it was revealed that S fertilization with the applied CCs allows for garlic with a higher total phenolic acid (TPA) content in bulbs to be obtained. It is evidenced by the positive and high correlation coefficient between TPA and using S in garlic cultivation. The value of the coefficient of determination (R2) explains 62% of the variability. Simultaneously, it was found that garlic extracts with a higher TPA content exhibited higher antioxidant activity (AA). Imen et al. [96] also found that the S fertilization of rosy garlic (Allium roseum L.) plants has a beneficial effect on the taste and results in an increase in the TPA content and a reduction in the amount of reduced carbohydrates. Gorai et al. [97] found that a low S concentration (1.0 mM SO\(_4^{2-}\)) increases, and high concentration (4.5 mM SO\(_4^{2-}\)) reduces, the total phenolics content in Allium ampeloprasum plants.

In these studies, S and CCs increased the glutathione content of garlic bulbs. In 2020, using S also increased the amount of glutathione in garlic grown without CCs. It is reported in the literature that increasing the amount of sulfate (S-SO\(_4^2-\)) in the soil increases the content of alliin and glutathione in the leaves and bulbs of A. cepa and A. sativum, both under dry [98] and temperate [16,19] conditions. Bloem et al. [15,16] found that, based on studies with garlic, the content of cysteine, sulfoxides, glutathione, and glucosinolates is modified with S. However, the effect of S application on the content of S-containing metabolites in garlic bulbs is strongly correlated with the environmental conditions (light, temperature, and carbohydrate content) and genotype [17]. In our research, garlic bulbs had a higher content of bioactive substances in 2019, when the garlic bulbs grew under more favorable thermal conditions. According to Bloem et al. [16], another important factor is a garlic harvesting term essential for the quality of the crop. According to the quoted author, S-containing metabolites are synthesized in the leaves and move to the garlic bulbs. When all of the aboveground parts of the plants dry, there is a greater accumulation of S-containing compounds in the bulbs.

Plant species that can be introduced in co-cultivation with plants grown in the main crop are required. Appropriate selection of the species and the date of sowing the seeds of this plant should consider the plant’s low competitiveness in the main crop and the
Phytomeliorative and phytosanitary functions. During the research period, it was observed that oilseed radish (*Raphanus sativus*) plants formed a bulky biomass and increased soil nutrients in early spring. Garlic cloves (on average, in both years of research) cultivated with fodder radish and S contained more N, S, TPA, and glutathione than those cultivated with clover, buckwheat, and mustard. In the literature on the subject, Thorup-Kristensen et al. [41] explained that fodder radish plants (narrow C:N ratio < 15) quickly bind soil minerals and release them in spring, but do not increase the organic matter, unlike CCs with high C:N ratios (*Panacea, Hordeum vulgare > 30*).

4.6. Correlations

The correlation coefficient for glutathione was positive and very high, indicating a strong relationship between the content of this component and using S in garlic cultivation (Table 6). The coefficient of determination (R2) explained 75% of the variability in glutathione content. The correlation between dry matter, N, K, S, Zn, B, AA, and TPA and using S in garlic cultivation was positive and high. The coefficient of determination (R2) explained 33–64% of the variability. The values of the correlation coefficients for the content of P and Ca in bulbs indicated an average relationship between their content and using S. The value of the correlation coefficient for the relationship between the yield size and using CCs was very high, and for the relationship between the content of Ca, Mg, and B and the CC plants, it was high. The correlation coefficient for K, Cu, Fe, TPA, AA, and glutathione was average and indicated a poor relationship between their content and CC plants. Multiple regression analysis showed that using S caused a decrease in the B content (0.53 mg kg\(^{-1}\) DM). The used CCs decreased the content of Cu, Mn, and B in garlic bulbs.

| Component | \(\text{R}^2\) | Structure of Significance Coefficients | Standard Regression Coefficient **** |
|-----------|--------------|----------------------------------------|-----------------------------------|
|           | F** | CC*** | Years | b\(_1\) | b\(_0\) | Years |
| Yield     | 0.528 | 0.449 * | 0.746 * | 0.087 | 2.296 * | 6.525 * | 1.300 | -0.085 * | -0.462 * | 0.036 |
| Dry Matter | 0.485 | 0.623 * | 0.346 | 0.223 | 2.873 * | 4.831 | 0.913 | -1.328 * | -1.771 | 0.567 |
| Macronutrient | | | | | | | | | | |
| N         | 0.528 | 0.609 * | 0.451 * | 0.212 | 2.415 * | 4.787 * | 1.882 | -0.544 * | -1.062 * | -0.227 |
| P         | 0.438 | 0.355 * | 0.066 * | 0.518 * | 1.993 * | 3.361 | 0.498 | -1.203 * | -0.881 | 2.441 * |
| K         | 0.339 | 0.538 * | 0.296 | 0.090 | 2.658 * | 1.335 | 1.738 | -2.379 * | 3.010 | -0.489 |
| Ca        | 0.404 | 0.347 | 0.544 * | 0.213 | 2.093 | 6.011 | 0.987 | -1.003 | -5.092 * | 0.865 |
| Mg        | 0.374 | 0.031 | 0.501 * | 0.334 * | 1.448 | 4.528 * | 0.850 * | 0.447 | -13.367 * | 5.678 * |
| S         | 0.541 | 0.740 * | 0.070 | 0.159 | 2.501 * | 3.309 | 1.748 | -1.914 * | -0.591 | -0.475 |
| Micronutrient | | | | | | | | | | |
| Zn        | 0.330 | 0.546 * | 0.084 | 0.153 | 3.946 * | 1.695 | 0.658 | -0.114 * | 0.061 | 0.039 |
| Cu        | 0.351 | 0.290 | 0.404 * | 0.348 * | 2.503 | -1.531 * | 3.334 * | -0.425 | 1.919 * | -0.776 * |
| Mn        | 0.544 | 0.255 | 0.742 | 0.007 | 0.714 | -6.298 * | 1.539 | 0.125 | 1.480 * | -0.008 |
| Fe        | 0.349 | 0.491 * | 0.288 | 0.246 | 2.394 * | 1.778 | 0.937 | -0.034 * | 0.046 | 0.021 |
| B         | 0.649 | 0.607 * | 0.640 | 0.017 | -0.358 * | -2.594 * | 1.435 | 0.267 * | 0.804 * | 0.009 |
| Bioactive compound | | | | | | | | | | |
| LAA       | 0.262 | 0.082 | 0.007 | 0.398 * | 1.371 | 2.967 | 2.111 * | 0.008 | 0.002 * | -0.041 |
| TPA       | 0.627 | 0.628 * | 0.351 | 0.429 * | 5.882 | 3.643 * | 0.241 | 0.030 | -0.022 * | 0.018 |
| AA        | 0.598 | 0.555 * | 0.374 * | 0.469 * | 2.072 * | 3.974 * | 0.917 | -0.621 * | -1.058 * | 0.683 |
| Glutathione | 0.751 | 0.848 * | 0.332 | 0.192 | 3.279 * | 4.562 | 1.957 | -0.144 * | -0.126 | -0.037 |

* represents significance at \(p \leq 0.05\); ** F: fertilizer; *** CC: catch crop; **** b\(_1\): the slope of the line, b\(_0\): the intercept.

5. Conclusions

The use of sulfur (S) in the cultivation of winter garlic significantly increased the yield of bulbs. The results clearly showed that the quality of garlic depended on two groups of factors: the first was related to the use of S, and the second to the selection of different species of cover crops (CCs). However, these two groups of factors should not be considered separately, because they interact with each other, which affects the quality of the garlic cloves.
The results indicated a strong beneficial effect of S in the cultivation of winter garlic on the uptake of minerals (N, P, K, S, Zn, and Fe) by plants, and on the accumulation of dry matter, total phenolic acid (TPA), antioxidant activity (AA), and glutathione in garlic cloves, which was associated with the fertilization efficiency of elemental S in biomass mineralization and the availability of minerals for garlic plants. The process of biomass mineralization depended on different weather conditions in 2019 and 2020. In 2019, rainfall and a high temperature activated organic matter’s mineralization and contributed to the rapid release of nutrients.

Using S in the cultivation of winter garlic significantly increased the yield of bulbs in the cultivation of garlic with CCs, no reduction in the yield and no negative competitive effect on the yield was noted compared to conventional cultivation. In the cultivation of garlic with clover, the yield was higher by 50.1% compared to cultivation without CCs. Only in cultivation with mustard was there no yield-generating effect of this plant’s biomass. The possibility of using the CCs clover, fodder radish, and buckwheat, which can become an integral part of ecological and diversified agriculture, is promising in this respect. In 2019 and 2020, S application and fodder radish in the co-cultivation with winter garlic increased the average content of nitrogen (N), S, TPA, and glutathione in bulbs; with clover dry matter, increased the S, TPA, and AA; with buckwheat, increased the TPA, AA, and glutathione; and with mustard, increased the TPA and AA.

The controlled use of S with CCs may contribute to the effective biofortification of garlic into bioactive substances. The proper balance of S used with CCs can significantly impact the yield and chemical composition of garlic bulbs, which may contribute to the control and manipulation of the content of organosulfur compounds that determine the quality and health-promoting value of garlic.

From a gardening practice viewpoint, the decision to use S in the cultivation of winter garlic should be considered based on the specificity of soil and climate conditions. However, further research is necessary for the practical determination of the S dose and the appropriate selection of species of CC in winter garlic cultivation.

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