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Effect of Soil and Foliar Silicon Application on the Reduction of Zinc Toxicity in Wheat

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Abstract: The aim of the study was to compare soil and foliar application of Si to relieve stress in wheat caused by excess Zn in the soil. Two pot experiments were carried out in which the soil was contaminated with zinc sulphate at the dose of 600 mg kg⁻¹ Zn before sowing. Si was applied in the soil in the following doses 200 mg kg⁻¹ and 400 mg kg⁻¹ Si and as foliar spraying in concentrations 2 mM L⁻¹ and 6 mM L⁻¹ Si in the form of sodium silicate. The applied dose of Zn was toxic to wheat and caused a significant decrease in the biomass of shoots and roots. Soil application of Si reduced the negative effect of Zn on plants and significantly increased the biomass of the tested organs. The foliar application of Si did not reduce the decrease of plant biomass. Soil contamination with Zn caused a drastic increase in Zn concentration in shoots and roots, while Si applied in the soil significantly decreased this concentration. The increase in soil pH, which was caused by sodium silicate, also affected the decrease in Zn concentration in plants. The plants absorbed Si applied to the soil, which is indicated by an increase in the Si content in shoots compared to the control. In the case of foliar spraying, only a higher dose of Si increased its concentration in the plants. The application of Si in the soil, in contrast to foliar application, reduced the transfer of Zn from roots to shoots. The higher effectiveness of soil application of Si than foliar application in alleviating the toxicity of Zn was associated with both an increase in pH and a higher uptake of Si by plants.

Keywords: wheat; Zn stress; Si; method of application

1. Introduction

Environmental pollution with heavy metals is a consequence of industrial development and urbanisation. The main sources of excess Zn in the soil are dusts emitted from non-ferrous metal smelters, burnt coal and oil and municipal solid waste [1]. Zn contamination can also come from the metallurgical and paint industries [2]. Zinc contamination of the soil is an environmental problem that occurs all over the world. Most Zn is mined in China, where soil contamination with this metal often occurs [3]. In Europe, high levels of Zn in the soil are found in the Canary Islands, central-western Spain, France, northern Italy, Slovenia and Greece [4]. Furthermore, in Poland, although only 1.4% of soils are contaminated with Zn [5], some areas with an excess of this element can be found.

Zn is easily taken up by plants from polluted soils, and its excess in the plant interferes with many metabolic and physiological processes and consequently limits yield [6,7]. Too high Zn content inhibits seed germination, plant growth and root development and causes leaf chlorosis. Recent studies have shown a negative effect of Zn stress on photosynthesis, chlorophyll content and chloroplast ultrastructure in plants [8,9].

Although Si was not considered an essential element for plants, it has been shown to be beneficial for the healthy growth and development of many plant species, in particular, rice and sugar cane [10,11].

Several authors believe that in the near future, Si may be considered as an essential element for plants [12,13].

Si is taken up by the roots of plants in the form of H_4SiO_4 [14] and its uptake by leaves is debatable and sometimes questioned. Some authors believe that this element is mostly or even completely taken up by the roots [15,16], while others report a high effectiveness of foliar Si application [17–19].

The beneficial effects of Si are particularly evident in plants exposed to abiotic and biotic stress [16,20,21]. Over the last two decades, many studies have been carried out to clarify the role of Si in increased tolerance and resistance of plants to stress. World literature reports on the role of Si in increasing plant tolerance to drought stress [22,23], salinity stress [24,25] and disease stress [26].

Research has also been conducted on the influence of Si on stress relief caused by excess heavy metals [27]. Many studies concerned Cd [28–33], while fewer Cr [34,35], As [36,37] or Cu [38,39]. Si was also reported as a Zn stress reducing factor. The researchers reported that the excess of Zn in the substrate decreased the yield, whereas the application of Si reduced the decrease in plant biomass [8,9]. The excess of Zn also led to the excessive concentration of Zn in various plant organs, while the addition of Si significantly reduced Zn accumulation in plants [8,40–43]. Zn decreased the chlorophyll content in leaves, whereas Si alleviated these changes [8,9,42]. Si also mitigated the harmful effect of Zn on the ultrastructure of chloroplasts [9]. The excess of Zn led to an increase in the level of MDA in plants, while the application of Si decreased this level [8]. The excess of Zn in the substrate caused oxidative stress in plants, which changed the activity of antioxidant enzymes, such as SOD, CAT and APX. In this situation, the addition of Si modified the activity of enzymes, which contributed to the reduction of stress [8,44]. The application of Si also led to the immobilization of Zn in the substrate, thus reducing its toxicity to plants [40,45].

Almost all above-mentioned studies were carried out under hydroponic conditions, where Zn and Si were added to the nutrient solution. Studies conducted in water cultures provide precise answers, but do not reflect the conditions under which plants actually grow. In agricultural practice, farmers can apply Si to the soil or on the plant list, which is completely different from nutrient solution in aquatic cultures. Therefore, research with the use of soil instead of the nutrient solution and with the application of Si, which can be used in practice by farmers, are necessary.

The aim of our research was to investigate the effect of soil and foliar application of Si on reducing Zn stress for young wheat plants growing in pots filled with soil brought from the field.

2. Materials and Methods

2.1. Pot Experiment

In order to examine the effect of Si fertilisation of wheat on the reduction of stress caused by the Zn concentration in the soil, two identical pot experiments were carried out in the greenhouse, one in spring (III–V) and one in autumn (IX–X) 2018. In both experiments, pots were filled with 2.3 kg of the same soil brought from a field located in Jelcz-Laskowice near Wrocław, Poland. Physical and chemical properties of the soil are presented in Table 1. Winter wheat of Lindbergh (SAATEN-UNION GmbH, Isernhagen, Germany) cultivar was used as a test plant.

Table 1. Properties of soils used in the experiment.

| pH | Sand | Silt | Clay | Corg | P ¹ | K ¹ | Mg ² | Zn ³ |
|-----|------|------|------|---------------------|----------------|----------------|-----------------|-----------------|
| KCl | % | | | mg kg ^{−1} | | | | |
| 6.5 | 70 | 26 | 4 | 0.7 | 150 | 284 | 116 | 33 |

sand: 2.0–0.05 mm, silt: 0.05–0.002 mm, clay: <0.002 mm, Corg-organic carbon, ¹ Enger-Rhiem, ² Schachtschabel, ³ aqua regia.

In the experiment, the soil was artificially contaminated with Zn because the aim was to focus on Zn, whereas naturally occurring contamination usually involves several elements at once. Zn was

added directly to the soil before sowing in the form of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Si was added to the soil before sowing or applied as a triple foliar spray in the form of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$. Six experimental treatments were tested, each in 4 replications:

- (1) 0: control without Zn and Si
- (2) Zn: 600 mg kg^{-1} Zn applied to the soil
- (3) ZnSi1-soil: 600 mg kg^{-1} Zn to the soil + 200 mg kg^{-1} Si to the soil
- (4) ZnSi2-soil: 600 mg kg^{-1} Zn to the soil + 400 mg kg^{-1} Si to the soil
- (5) ZnSi1-foliar: 600 mg kg^{-1} Zn to the soil + triple foliar spray with 2 mM L^{-1} Si
- (6) ZnSi2-foliar: 600 mg kg^{-1} Zn to the soil + triple foliar spray with 6 mM L^{-1} Si

First Zn was added to the soil and then Si after 3 weeks of incubation, each time carefully mixing the additives with the soil. All the time the soil moisture was kept at the level of 60% of the field water capacity. Wheat was sown one week after the introduction of Si into the soil. Two weeks after sowing, plant thinning was done down to 25 plants per pot. Si as foliar spray was applied three times at weekly intervals using the SG11 hand sprayer (Andreas Stihl AG & Co. KG, Waiblingen, Germany). The first application was made a few days after the plant thinning. Plants from each pot were sprayed separately. The solution was applied to completely cover the plants without forming drops on the edge of leaves.

The plants were harvested 2 weeks after the last Si application (60 days after sowing). The aboveground parts of wheat were cut 2 mm above the ground and rinsed with distilled water. The roots were removed from pots, cleaned from the soil, initially rinsed with tap water and then rinsed for 2 h with distilled water using a rotary mixer. Aboveground parts and roots were dried for 24 h at 40°C , then carefully weighed and finely ground. Soil samples were taken from each pot at the same time as the roots. They were dried at room temperature, ground in a mortar and passed through a sieve with a diameter of 2 mm.

2.2. Chemical Analysis

Soil texture was evaluated by the aerometric method [46]; pH was established potentiometrically in $1 \text{ mol KCl} \cdot \text{dm}^{-3}$ [47]; total organic carbon in soil (TOC) was determined by Tiurin method using potassium dichromate [48]; P and K were determined using the Enger–Riehm method [49,50] and Mg by Schachtschabel method [51]. The total Zn concentration in the soil was determined using aqua regia. After the digestion, Zn was determined using the flame atomic absorption spectrometry FAAS (flame atomic absorption spectrometry) method [51]. The available Zn in the soil was determined by Mehlich 3 method [52–54].

Zn in shoots and roots was determined by the FAAS method, having first dry ashed the material in a muffle furnace and digested it with 20% nitric acid [55]. A standard reference material IPE 952 (International Plant-Analytical Exchange) from Wageningen (Netherlands) was used for quality control purposes. Crude SiO_2 in shoots and roots was determined by gravimetric method. Plant samples were digested with nitric acid and filtered. The filter paper and residue were dried, calcined in a muffle furnace at 1000°C , then cooled and weighed [56].

2.3. Calculation of the Bioaccumulation and Translocation Factor

In order to compare metal accumulation in plants, bioaccumulation coefficients (BF) of shoots and roots were calculated by the following formulas according to Melo et al. [57]:

$$\text{BF}_{\text{shoot}} = \frac{\text{Zn concentration in shoots } (\text{mg kg}^{-1})}{\text{Zn concentration in soil } (\text{mg kg}^{-1})} \quad (1)$$

$$BF_{\text{root}} = \frac{\text{Zn concentration in roots (mg kg}^{-1}\text{)}}{\text{Zn concentration in soil (mg kg}^{-1}\text{)}} \quad (2)$$

The transfer of metals from roots to shoots was determined based on the translocation factor (TF) expressed by the formula [57]:

$$TF = \frac{\text{Zn concentration in shoots (mg kg}^{-1}\text{)}}{\text{Zn concentration in roots (mg kg}^{-1}\text{)}} \quad (3)$$

2.4. Statistical Analyses

As the results of the spring and autumn experiments were very similar to each other, it was decided to average them. All results of plant biomass and Zn and Si concentration were given as the means from these two experiments. ANOVA calculations were performed using the Statgraphics v 5.0 software (StatPoint Technologies, Inc., Warrenton, VA, USA). Multiple comparisons among groups were made with Tukey's honest significant difference test ($p < 0.05$).

3. Results

3.1. Plants Biomass

The dose of 600 mg kg⁻¹ Zn had a toxic effect on wheat and caused a 44% decrease in shoot biomass and the same decrease in root biomass compared to a control treatment without Zn (Figure 1). Soil application of Si reduced considerably the negative effect of Zn and caused a 23–25% increase in shoot biomass and a 12–17% increase in root biomass in comparison to the Zn treatment without Si.

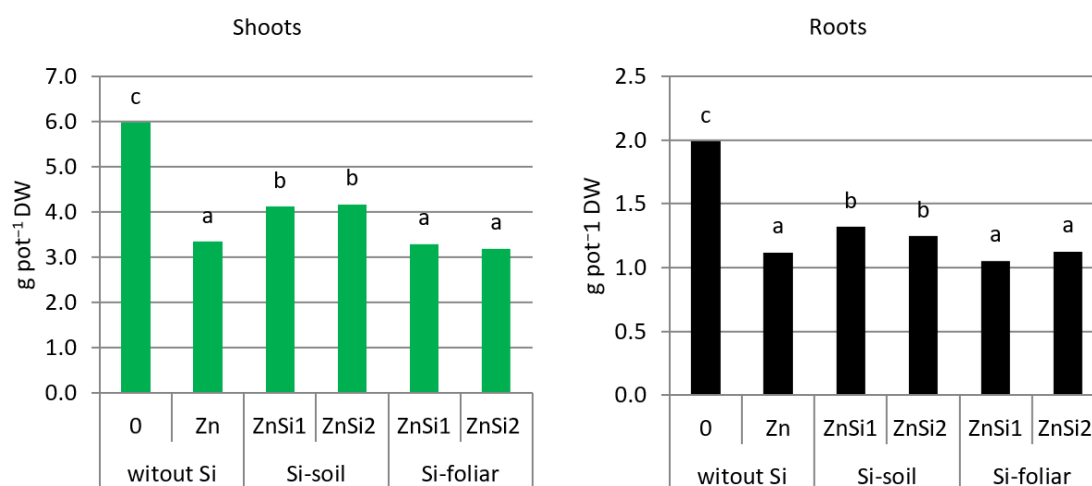


Figure 1. Biomass of wheat shoots and roots. Values marked with the same letters indicate no significant difference according to Tukey's test ($p < 0.05$).

In contrast, foliar application of Si did not reduce Zn toxicity to wheat. Biomass of shoots and roots from the treatments ZnSi1-foliar (2 mM L⁻¹ Si) and ZnSi2-foliar (6 mM L⁻¹ Si) was almost the same as from the treatment with only Zn without Si.

3.2. Zn Concentration in Shoots and Roots

The wheat shoots from the control treatment contained 38 mg kg⁻¹, while roots 119 mg kg⁻¹ Zn. Soil application of 600 mg kg⁻¹ Zn caused a 40-fold increase in the Zn concentration in shoots and roots (Figure 2). Soil application of Si resulted in a significant reduction in Zn content, whereas the dose of 400 Si mg kg⁻¹ (ZnSi2-soil) gave a considerably bigger effect than 200 mg kg⁻¹ Si (ZnSi1-soil).

The concentration of Zn in shoots decreased by 41–56%, and in roots by 24–41%, respectively, to the Si dose.

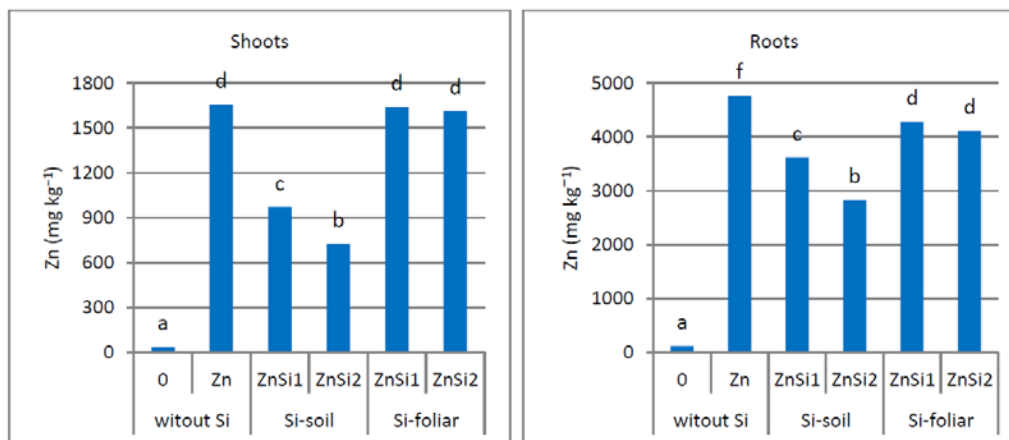


Figure 2. Zn concentration in shoots and roots of wheat. Values marked with the same letters indicate no significant difference according to Tukey's test ($p < 0.05$).

Foliar application of Si did not have such a beneficial effect on the concentration of Zn in plants as the soil application. Triple spraying with 2 mM L⁻¹ (ZnSi1-foliar) and 6 mM L⁻¹ Si (ZnSi2-foliar) did not cause any changes in Zn in shoots and only 10–14% decrease in Zn in roots compared to the treatment Zn without Si.

3.3. Si Concentration in Shoots and Roots

The Si concentration in both treatments without Si (0 and Zn) was similar to each other and ranged between 2.1–2.3% SiO₂ in shoots and 11.8–12.4% SiO₂ in roots of wheat (Figure 3). Soil application of Si significantly increased Si amount in shoots. The dose of 200 mg kg⁻¹ Si (ZnSi1-soil) increased Si concentration by 55%, while dose 400 mg kg⁻¹ Si (ZnSi2-soil) by 77% compared to the control. The increase in Si concentration in roots was smaller than in shoots. Only 400 mg kg⁻¹ Si increased Si concentration by 29%, while 200 mg kg⁻¹ Si caused a 9%, a statistically insignificant increase in Si concentration compared to the control treatment.

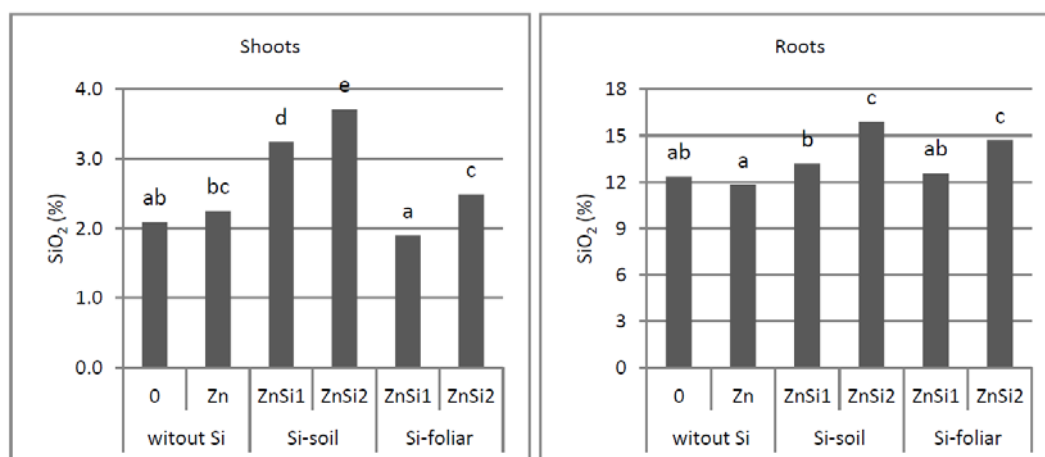


Figure 3. SiO₂ concentration in shoots and roots of wheat. Values marked with the same letters indicate no significant difference according to Tukey's test ($p < 0.05$).

Foliar application of Si much less increased Si concentration in wheat plants than the soil application. Spraying with 2 mM L⁻¹ Si (ZnSi1-foliar) did not produce any results, while spraying

with 6 mM L⁻¹ Si (ZnSi2-foliar) caused a 19% increase in the concentration of this element both in wheat shoots and roots.

3.4. Zn Concentration in Soil

The soil from the control treatment contained 33 mg kg⁻¹ of total Zn and 13 mg kg⁻¹ of available Zn, determined with Mehlich 3 method. Adding 600 mg kg⁻¹ Zn to the soil increased the total Zn in the soil to a level of 668–700 mg kg⁻¹, while available Zn to 568–607 mg kg⁻¹ (Figure 4). The Si application did not significantly affect the Zn content of the soil.

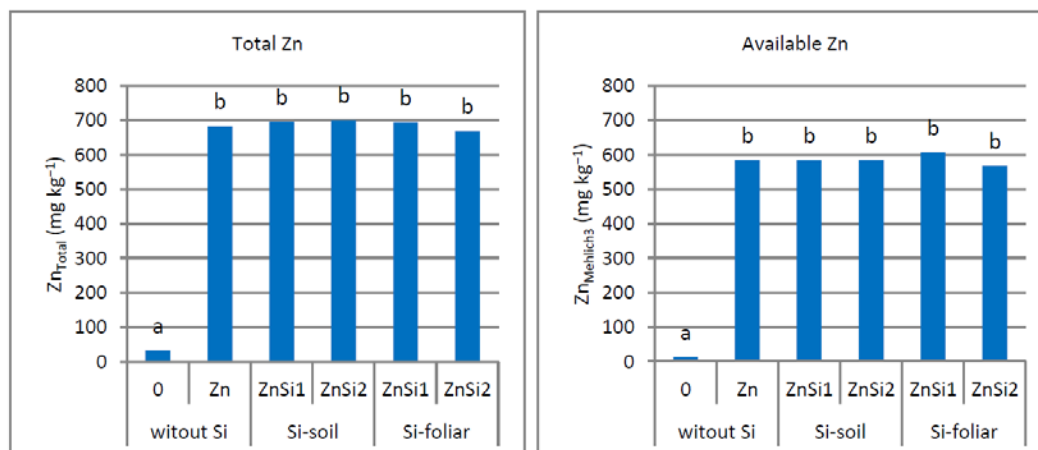


Figure 4. Zn concentration in soil. Values marked with the same letters indicate no significant difference according to Tukey's test ($p < 0.05$).

3.5. Soil pH

The initial pH of the soil in the control treatment was 6.5 (Figure 5). Zn application decreased pH to the level of 5.7–5.9 in 3 treatments: Zn, ZnSi1-foliar, and ZnSi2-foliar. The soil application of Si (ZnSi1-soil and ZnSi2-soil) counteracted the pH decrease and kept it at a level close to the control treatment.

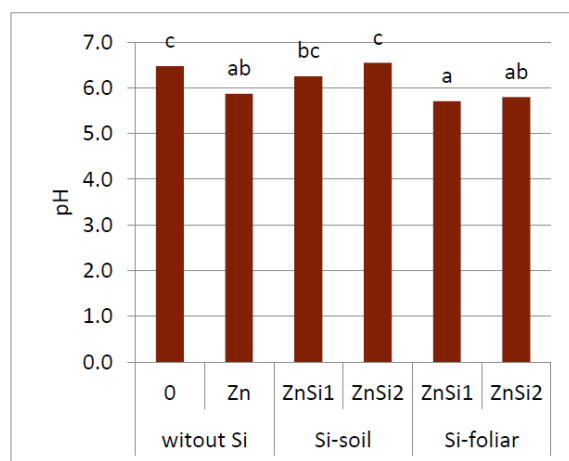


Figure 5. Soil pH. Values marked with the same letters indicate no significant difference according to Tukey's test ($p < 0.05$).

3.6. Zn Bioaccumulation and Translocation

Bioaccumulation factor for shoots (BF_{shoot}) ranged within 1.1–2.4, while for roots (BF_{root}) it was much higher, fluctuating within 4.2–7.0 (Table 2). This indicates a higher accumulation of Zn in roots

than in shoots. BF_{shoot} in Zn-without Si treatment amounted to 2.4 and decreased to the level of 1.1–1.4 as a result of the soil Si application. Foliar Si application did not reduce the value of BF_{shoot} , which remained at the level of 2.4. BF_{root} , similarly as BF_{shoot} , being the highest in the Zn-without Si treatment. In the roots, however, unlike in the shoots, both soil and foliar application of Si lowered the BF value. The value of BF_{root} fell from the level of 7.0 to 4.1–5.2 in the case of soil application and down to the level 6.2 in the case of foliar application.

Table 2. Bioaccumulation and translocation factors of Zn.

| Treatment | BF_{shoot} | BF_{root} | TF |
|---------------|--------------|-------------|------|
| Zn-without Si | 2.42 | 7.00 | 0.35 |
| ZnSi1-soil | 1.39 | 5.21 | 0.27 |
| ZnSi2-soil | 1.08 | 4.08 | 0.26 |
| ZnSi1-foliar | 2.35 | 6.17 | 0.38 |
| ZnSi2-foliar | 2.39 | 6.16 | 0.39 |

BF_{shoot} —Bioaccumulation factor for shoota; BF_{root} —Bioaccumulation factor for roots; TF—Translocation factor.

Translocation factor (TF), showing the ability of plants to transfer metals from the roots to the above-ground parts, was 0.35 in the Zn-without Si treatment. Soil Si application decreased TF to the level of 0.26–0.27, while foliar application increased it slightly to the level of 0.38–0.39.

4. Discussion

4.1. Plant Biomass

In the conducted pot experiments, the addition of 600 mg kg^{-1} Zn to the soil had a toxic effect on wheat, causing an approximately 40% decrease in shoot and root biomass (Figure 1). The addition of 200 and 400 mg kg^{-1} Si to the soil limited the decrease in biomass, while a three-time foliar spraying with 2 mM L^{-1} and 6 mM L^{-1} did not show such effect. It can be assumed that a lower soil dose of Si (200 mg kg^{-1}) was sufficient because both doses used had a similar effect. Furthermore, a bigger effect of Si was observed on limiting the decrease of shoot biomass (23–25%) than of root biomass (12–17%).

Similar results of mitigating the toxicity of Zn by Si were obtained by other authors, but in water culture studies, where Si was added to the nutrient solution, and not to the soil, as in our studies. In the studies of Anwaar et al. [8] the addition of 25 and $50 \text{ }\mu\text{M}$ Zn to the nutrient solution resulted in a significant decrease in the yield of leaves, stems and roots of young cotton plants. The addition of Si increased the ability of plants to cope with Zn excess and reduced the decrease in biomass. On the Zn+Si treatment, the yield of leaves was by 34–76%, of stems by 26–111%, while of roots by 21–62% higher than in the Zn-without Si treatment. Similar results were obtained by Kaya et al. [42], where Si increased the biomass of 5-week-old maize shoots by 42% and the root biomass by 50% compared to the Zn-treatment without Si. In the research of Song et al. [44], Si significantly mitigated the decrease in shoot and root biomass caused by an excess of Zn in two cultivars of rice, and this effect was, as in our research, bigger for shoots than roots. Furthermore, Gu et al. [58] showed a positive effect of Si addition on the biomass of 40-day-old rice plants subjected to Zn stress. This effect was bigger under a higher dose of Si, and similarly to the study by Song et al. [44], stronger for shoots than roots. Similar results were obtained by Mehrabanjoubani et al. [43]. Shoot biomass of young rice plants was significantly higher in $100 \text{ }\mu\text{M}$ Zn + Si treatment in comparison with the $100 \text{ }\mu\text{M}$ Zn without Si treatment, yet no significant effect of Si on root biomass was observed.

Bokor et al. [40] obtained completely different results for maize grown hydroponically. These authors found no beneficial effect of Si in alleviating the symptoms of Zn toxicity. Moreover, they observed a negative effect of Si on the biomass of roots and shoots of 10-day-old corn seedlings subjected to Zn stress. The dose of $182 \text{ }\mu\text{M}$ Zn caused a 38% decrease in shoot biomass as compared

to the control without Zn. The applied doses of Si aggravated this decrease, causing the largest 54% decrease at the dose of 5.0 mM Si.

4.2. Zn Concentration in Shoots and Roots

Excess Zn in the substrate causes excessive concentration of this element in plants, which can interfere with various metabolic processes. The application of Si generally leads to a reduction in the uptake and accumulation of Zn. In our research, the application of 600 mg kg⁻¹ Zn to the soil caused a very large, about 40-fold Zn increase in wheat shoots and roots (Figure 2). Soil application of Si reduced this concentration by 41–56% in shoots and by 24–41% in roots (Figure 1). Although the dose of 400 mg kg⁻¹ Si reduced the concentration of Zn much more than 200 mg kg⁻¹ Si, this fact did not affect the plant biomass, which was similar for both Si doses. The concentration of Zn in wheat tissues was significantly less influenced by the foliar application than the soil application of Si. A three-time spraying did not reduce Zn in shoots and caused only a 10–14% reduction in roots compared to the Zn- without Si treatment. It can be assumed that the lack of Zn decrease in shoots and only a small Zn decrease in roots caused the lack of beneficial effect of foliar application of Si on wheat biomass.

It is not possible for us to compare the effects of soil and foliar application of Si on the reduction of Zn in plant tissues with the results of other authors because there are no similar studies. The studies of other authors concern water cultures, where Si is applied directly to nutrient solution contaminated with Zn. Nevertheless, these authors prove the reduction of Zn in plant tissues under the influence of Si addition to the nutrient solution. In the studies of Anwaara et al. [8], the addition of Si resulted in a significant reduction of Zn in leaves, stems and roots of young cotton plants exposed to stress caused by excess Zn. Furthermore, Mehrabanjoubani et al. [43], Kaya et al. [42] and Gu et al. [58] observed a significant reduction of Zn concentration in the shoots and roots of rice seedlings as a result of the addition of Si under conditions of excess Zn in the nutrient solution. Moreover, as in our research, Gu et al. [58] found that the higher dose of Si (1.8 mM) was more effective than the lower one (0.5 mM), causing a greater decrease in Zn content in plants. Bokor et al. [40] also proved higher efficacy of high doses than low doses of Si. In the study with 10-day maize seedlings, they showed that addition of 5 mM Si caused almost twice as much decrease of Zn concentration in roots as the addition of 1 mM Si.

Song et al. [44] achieved different results. In the study with two cultivars of rice, they observed a significant increase in Zn concentration in the shoots and roots of 14-day-old seedlings growing on Zn-contaminated nutrient solution. The addition of Si to the nutrient solution resulted in a continued increase in Zn concentration in roots and a significant Zn decrease in shoots. These results were confirmed by later studies by the same authors [9]. They suggest the influence of Si on the accumulation of Zn in roots and limiting its transport to shoots.

4.3. Si Concentration in Shoots and Roots

The soil doses of Si used in our experiments were 200 mg kg⁻¹ (Si1-soil) and 400 mg kg⁻¹ (Si2-soil), while foliar doses were 2 mM L⁻¹ (Si1-foliar) and 6 mM L⁻¹ (Si2-foliar). Similar soil doses of Si in pot tests were used by Habibi [59], Liang et al. [28], Naaem et al. [29], Vieira da Cunha et al. [45] and Zhang et al. [35]. Similar to ours, Si concentrations for foliar spraying were used by Shahid et al. [60], Bukhari et al. [22], Kamenidou et al. [61], and Pilon et al. [62].

Our results showed that the Si concentration was several times higher in wheat roots than in the shoots. This applied to all treatments—control without Zn and Si, Zn without Si, and Zn+Si (Figure 3). Different results for 10-day hydroponically grown maize seedlings were presented by Bokor et al. [40]. In their study, there was more Si in shoots than in roots in the control treatment and at lower Si doses (1 and 2.5 mM). However, under the highest dose of Si (5 mM), this proportion changed, and there was more Si in the roots than in the shoots. This applied both to Si without Zn treatments, and to Si + Zn treatments.

The results of our experiments showed that both soil and foliar application of Si significantly increased its concentration in wheat shoots and roots, yet soil application was more effective (Figure 3).

Moreover, in both ways of application, the Si2 doses caused a higher increase in Si in plant tissues compared to the Si1 doses. Soil application of 400 mg kg⁻¹ Si (ZnSi2-soil treatment) increased its concentration by 77% in shoots and by 29% in roots, while application of 6 mM L⁻¹ (ZnSi2-foliar treatment) increased Si in both shoots and roots by only 19%.

On the basis of the plant biomass and Zn and Si concentration in wheat tissues, it can be assumed that the soil dose of 200 mg kg⁻¹ Si was sufficient. Although the dose of 400 mg kg⁻¹ Si increased the Si content and decreased the Zn content in wheat tissues more than the dose of 200 mg kg⁻¹ Si, but this fact did not affect the plant biomass. (Figures 1–3). Different conclusions should be drawn about the foliar Si doses. Due to the fact that in most cases, only the S2-foliar concentration worked, it can be assumed that a concentration higher than 6 mM L⁻¹ would be more effective.

4.4. Zn Concentration in Soil

Several authors report that the application of Si in the form of silicates to nutrient solution or to the soil contaminated with metals, can lead to the immobilization of metals, and thus reduce the availability of metals for plants. Bokor et al. [40] report on precipitation of insoluble Zn₂SiO₄ under the application of Si and Zn to the nutrient solution in a water culture experiment. Furthermore, Liang et al. [28] found Cd immobilization in the soil in result of the soil application of 400 mg kg⁻¹ Si in the form of Na₂SiO₃ in a pot experiment. This dose caused a decrease in available Cd in soil, determined in CaCl₂, compared to the treatment without Si. Moreover, these authors observed less exchangeable Cd and more Cd in forms specifically adsorbed or bounded with Fe and Mn oxides in the soil in the treatments with Si application compared to the treatments without Si.

In contrast, in our experiments, soil applications of 200 and 400 mg kg⁻¹ Si did not affect the concentration of available Zn in soil, determined by Mehlich 3 (Figure 4). Perhaps such an effect would have been revealed by using a weaker extractant than Mehlich 3.

4.5. Zn Transfer from Roots to Shoots

Soil Si application decreased the Zn transfer from roots to shoots by 23–27% (Table 2). This protected the photosynthetic apparatus, which was probably the reason for limiting the yield decrease. The foliar application did not reduce the transfer from roots to shoots, and there was even a tendency to increase it by 9–11%. This is probably the reason for the lack of the beneficial effect in biomass of foliar Si application.

Other authors also report the role of Si in limiting the transfer of heavy metals from the roots to the aerial parts [23,29,32]. The studies of Shi et al. [31] confirmed the reduction of metal translocation from roots to shoots by Si. These authors, using an electron microscope, showed a strong deposition of silicon in the vicinity of the root endoderm of young rice seedlings. The physical barrier created in this way, can reduce the porosity of the cell walls of the inner root tissues, thus blocking Cd transport through the apoplast. However, Bokor et al. [40] demonstrated that the reduced Zn translocation from roots to shoots caused by Si did not reduce the toxicity of Zn in young maize plants under aquatic culture conditions. These authors suggest that caution should be taken when generalizing and formulating conclusions about the alleviating effects of Si on metal toxicity.

4.6. The Joint Effect of Si and pH Changes in Alleviating Zn Toxicity

Application Zn to the soil in the form of zinc sulfate resulted in a decrease in pH by 0.6 units compared to the control treatment (Figure 5). It should be assumed that the decrease in pH increased the Zn bioavailability, and thus contributed to its higher toxicity. The increase in availability of Zn for plants due to the decrease in pH is a well-known phenomenon [63]. Soil application of Si in the form of sodium silicate counteracted the decrease in pH, which undoubtedly contributed to limiting Zn uptake on ZnSi1-soil and ZnSi2-soil treatments. The fact that the pH in treatments with foliar Si application was similar to that in the Zn-without Si treatment confirms the influence of sodium silicate introduced into the soil on the increase in soil pH. The impact of Na₂SiO₃ to the increase of soil pH is

reported also by other authors [28,35]. It can therefore be assumed that the beneficial effect of reducing the toxicity of Zn in the treatments with soil application of Si was caused not only by the effect of silicon, but also by an increase in pH. The evidence that it was not only the effect of pH, but also the effect of Si, can be a significant increase in Si concentration in wheat shoots and roots in the treatments ZnSi1-soil and ZnSi2-soil (Figure 3). Such an increase also occurred in the ZnSi2-foliar treatment, but it was considerably lower than in the case of soil application and did not manage to compensate for the decrease in pH in this treatment. Taking into account that the lower concentration of Si (2 mM L^{-1}) did not cause the increase of this element in plants, it can be assumed that a larger foliar supply of Si than in the treatment ZnSi2-foliar (6 mM L^{-1}) could alleviate the toxicity of Zn.

Changes in soil pH and Si concentration in plants due to application ZnSO_4 and Na_2SiO_3 observed in our experiments, and their effect on the reduction of Zn toxicity to plants, are difficult to compare with the results of other authors. Other studies on alleviating Zn toxicity by Si were carried out in water cultures where Zn and Si were added to the nutrient solution [8,9,40,42–44,58,64]. There is a lack of research on plants growing on Zn-contaminated soil, where Si would be applied into the soil or to the leaves. However, there are studies describing the effect of Si on the alleviation of Cd toxicity. Liang et al. [28], similarly to us, showed an increase in pH due to application of Si in the form of Na_2SiO_3 to the soil contaminated with Cd. In their conclusion, however, they state that Si itself can effectively alleviate the Cd toxicity in maize. The alleviative effect of Si on Cd toxicity can be attributed not only to Cd immobilization in soil and its low phytoavailability resulting from pH rise in the Si-amended soil, but also to the Si-mediated Cd detoxification in plants.

5. Conclusions

Soil Si application alleviated Zn toxicity for young wheat plants, while foliar application did not cause beneficial effects in the form of reducing the decrease of biomass. Soil application of Na_2SiO_3 increased the Si concentration and decreased the Zn concentration in the shoots and roots, as well as limited the translocation of Zn from the roots to the shoots compared to the Zn-without Si treatment. Both soil doses of Si (200 and 400 mg kg^{-1}) gave a similar effect, which allows to presume that a lower dose was sufficient. It can be assumed that the reduction of Zn toxicity to plants by the soil applied sodium silicate was caused both by a slight increase in soil pH and the uptake of Si by plants. The addition of Na_2SiO_3 to the soil increased the soil pH by 0.4 – 0.7 units.

The foliar application of Na_2SiO_3 reduced the Zn concentration in the roots less than the soil application and did not reduce Zn concentration in the shoots. The foliar application did not limit the translation of Zn from roots to shoots. Only a higher dose of Si (6 mM L^{-1}) increased its concentration in shoots and roots, while a lower dose (2 mM L^{-1}) did not give this effect. This suggests that the supply of Si in a triple spray of sodium silicate at a concentration of 2 mM L^{-1} was too low. It can be assumed that a higher concentration of Si or more sprayings would give better results.

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