Effect of foliar application of silicon, selenium and zinc on heavy metal accumulation in wheat grains in field studies

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ABSTRACT

Foliar application technology is commonly used in soil remediation for rice, but few attempts on wheat. The heavy-metal food risk of wheat is a major concern recently. In addition, most prior experiments were conducted in pots and lacked consecutive results of years. Therefore, two consecutive years of field positioning tests were conducted to explore the influence of three kinds of mineral foliar application (Si, Se, and Zn) on the heavy-metal content of wheat grains. The results showed that foliar application with silicon (Si) largely increased wheat yield and plant height, and reduced (Arsenic) As and (Lead) Pb contents. Foliar application with selenium (Se) and zinc (Zn) prominently reduced heavy metals Cd, As and Pb. Se application could not only reduce the heavy-metal content in crops but also improve the Se content in the edible parts of crops, thereby, as suggested, applying it in the low and medium polluted soils.

1 Introduction

With the rapid development of industrialization, urbanization and agricultural intensification, the pollution of heavy metals in farmland soil and the food-chain risk of heavy-metal content in agricultural products have become increasingly serious in China [1]. Reducing heavy-metal pollution in farmland soils and excessive heavy metal in crops are of great importance. At present, foliar application technology has obtained more and more recognition in soil remediation, by which heavy-metal content in plants can be effectively reduced [2]. There are three kinds of mechanisms: (1) The improvement of the antioxidant effect of plants. Heavy-metal stress can interfere with the antioxidant system of plants, affect the normal physiological metabolism of plants, and cause a decrease in biomass and quality. But Zong et al. [3] found that foliar fertilizers application increased antioxidant enzyme activity in plants, which could effectively remove free radicals generated by plant stress, thus keeping cell integrity and reducing the influence of heavy metals on plant photosynthesis. Ding et al. [4] also discovered that the activities of antioxidant dismutase (SOD) and ascorbate oxidase (APX) in vegetable leaves were enhanced to protect cells from heavy-metal stress after spraying silicon (Si) and Selenium (Se). Therefore, foliar fertilizers have an important effect on the plant antioxidant defense system. (2) The segregation of heavy metals. Relevant studies found that heavy metals in organelles such as cell walls or vacuoles could be maintained by foliar fertilizers, thus reducing the concentration of heavy metals in the cytoplasm. Liu [5] found that under cadmium (Cd) stress, rice mesophyll cells showed symptoms of structural damage, with concentrated cytoplasm, separation of plasma wall, severe damage to cell membrane system, and a large amount of Cd deposits in the plasma membrane by using transmission electron microscopy. However, the damages to mesophyll cells was alleviated to some extent after spraying with sulfur and phosphorus foliar fertilizers. Cadmium was primarily confined in the cell walls and vacuole. (3): Chelation. Studies found that organic foliar fertilizers could reduce the concentration of free heavy-metal ions in cells by chelating with heavy metals to form stable chelates [6–9]. In addition, foliar fertilizers have the advantages of high utilization rate, convenience, cheapness, and reduced soil pollution, thus are becoming more and more popular among farmers.

Excluding the common nutrient elements (N, P, K, Ca, NA, Mg, Fe, etc.) of foliar fertilizers, mineral elements have been increasingly applied in foliar fertilizers [10]. Mineral elements can not only promote the growth and development of plants, but also participate in various metabolic activities in plants, they play an important role in plant structure, metabolism and cell osmotic regulation. Silicon (Si) can deposit in the endoplasm reticulum, cell walls, or the intercellular space of amorphous

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hydrates, which can form complexes with polyphenols and thereby strengthen cell walls instead of lignin [11,12]. Using Si-containing foliar fertilizers, the stem strength and lodging resistance of plants can be enhanced, and metals can be maintained in the roots and stems of plants to prevent the transfer to grains, thus reducing the content of metals in brown rice in mildly contaminated farmland [13–15]. Selenium is an essential element of glutathione peroxidase, superoxide enzymes, thyroid hormone deiodinase and thioredoxin reductase in human and animal cells, with its function of improving the antioxidant capacity of animals and plants and protecting the integrity of cell membranes by scavenging free radicals [16,17]. Foliar application with Se, not only have important effects on the growth, development and quality of crops, but also can reduce the contents of metals in plants [2]. Zinc (Zn) is an essential element for plants and animals. Zinc-containing foliar fertilizers could localize Cd in plant tissues, increase plant biomass and enzyme activity, thus decreasing the intake of Cd by plants [18].

Rice is the major grain crop of China, and the technology of foliar fertilizers has been widely used in rice, but few studies were applied to wheat [19]. Different crops have different metal accumulation capacities, and the performance of foliar fertilizers on different crops may be different. Wheat is the main grain crop in north China, which ranks second in China in terms of its cultivation and total output. But the results found that the heavy-metal contents in wheat from Gansu, Henan, Hebei and Jiangsu exceeded the standard (GB 2762–2017) to some extent [20–23]. Li et al. [24] did a wheat sample survey in the plain area of Jiyuan City (Henan province) and discovered that the contents of Cd and Pb of 74.2% and 10.8% soil samples exceeded the screening value of farmland soils risk (GB 15618–2018), respectively, and the contents of Cd and Pb of 61.3% and 40.9% wheat samples exceeded the national food safety limit standard, respectively. Therefore, the risk of heavy metals in wheat food chain in China cannot be ignored, the application of foliar fertilizers is needed to reduce the content of heavy metals on wheat grains.

In the current studies, the application of foliar fertilizers to block heavy metals are mostly potted experiments with consistent conditions [13,25]. In field conditions, the metal content in wheat grains can be easily influenced by various factors such as soil properties, pollution levels, temperature, precipitation, et al. [26]. Therefore, field plot experiments with multiple years are needed to eliminate the influence of these conditions as much as possible [27].

Therefore, in this study, the effects of different kinds of mineral foliar fertilizers on heavy-metal content in wheat grains were investigated through two consecutive years of field positioning experiments.

2 Materials and methods

2.1 Field experiment

The field design experimental plots were set as follows: each plot was 100 m² (10 m × 10 m), with an interval of 0.5 m. Each treatment was repeated with 3 plots, and over 0.5 m protection rows were set outside the plots. The trials were conducted in 2019 and 2020. The soil pH was 6.02, and the total amount of Cd, As, Pb and Hg in the soil was 0.87 mg kg⁻¹, 18.5 mg kg⁻¹, 58.1 mg kg⁻¹ and 0.134 mg kg⁻¹. The wheat variety was Ningmai 13. Agricultural measures, water and fertilizer control, disease and insect pest control and other management measures refer to local customs.

The climate here is subtropical, ocean and monsoon, with four distinct seasons, mild climate and abundant rainfall, and average annual temperature is 15.7°C and average rainfall is 1100 mm.

2.2 Foliar fertilizers

The foliar fertilizers Y1 containing Si, Y2 containing Se and Y3 containing Zn were purchased in the markets. Foliar fertilizers were applied according to product instructions at the stages tillering, flowering, filling and milk ripening. Due to the high noon temperature in sunny days and large evaporation, it is according to select sunny mornings and evenly spray on the leaves, young stems and ears of crops.

2.3 Sample collection and determination

In the wheat harvest season of 2019 and 2020, soil and plant samples were collected in each plot by using 5-point sampling method. The wheat was stored in the net bag, while the corresponding soil samples stored in the cloth bag. The wheat samples were brought back to the laboratory for air drying, and the grains were separated, dried at 70°C to constant weight, and crushed with a stainless steel mill. The soil samples were dried and ground, respectively through 2 mm and 0.15 mm nylon sieve, and were stored for use. The contents of Cd, Mercury (Hg), As and Pb, were detected in soil and rice samples. Cd and Pb were determined by ICP-MS (7700x, Agilent Technologies, Santa Clara, CA), while Hg and As were determined by Atomic Fluorescence (Beijing Baode instrument Co., LTD).
2.4 Data analysis

All data are expressed as mean ± standard error (SE). Significant differences were determined by one-way analysis of variance (ANOVA) for single-species test data. Mean values were compared using Duncan’s multiple range test at the 5% protection level. Statistical analysis was conducted using Microsoft Excel 2010 and the SPSS 21.0 software package (SPSS Inc., Chicago ILL).

3 Results and discussion

3.1 Effects of grain yield and seed performance on wheat

As shown in Tables 1 and 2, the application of mineral foliar fertilizers, especially Si, made the wheat yield and height significantly increase. The yield increased by 8.12% and 10.3% in 2019 and 2020, and the wheat height increased by 3.92% and 2.74% in 2019 and 2020. Wheat is a silicon-loving crop. Silicon applied on plant leaves has the advantages of quick effectiveness and low cost, which can improve plant lodging resistance and increase wheat plant height [25,28]. Hattori et al. [29] found that Si can improve the dry matter quality, root shoot ratio, the relative water content, leaf area and leaf thickness, thus promoting the growth of plants. Besides, Si can increase the content of chlorophyll in wheat flag leaf, promote wheat photosynthesis, assimilate more photosynthates and transport them to grains, thus making wheat grain heavier [15]. The application of Se and Zn also raised wheat production, which may be due to the supplementation of micronutrients required by wheat, thus promoting the growth of wheat [30,31].

3.2 Effects on heavy-metal content in wheat grains

3.2.1 Effects on Cd content in wheat grains

Without the application of foliar fertilizers, the content of Cd in wheat grains exceeded the limit standard of 0.1 mg kg⁻¹ in 2019 and 2020 (GB 2762–2017). These results indicated that this area might have wheat Cd food chain risk. The content of Cd in wheat grains significantly decreased after applying Se and Zn fertilizers, but the effect of Si fertilizers on the content of Cd in wheat grains was not significant (Figure 1). This was not consistent with the results in rice [9,13,14]. Wang et al. [9] made a conclusion that spraying foliar nano-silicon during the rice planting period (seedling stage, tillering stage, heading stage) significantly reduced the content of Cd in grains. The difference may be due to different crop types and different types of silicon fertilizer. Therefore, the differences in plant varieties should be given more attention when applying foliar fertilizers in production practice. Meanwhile, foliar fertilizers combined with the new material could significantly increase efficiency. The efficiency of nano-silicon is obviously higher than that of ordinary silicon fertilizer due to its high bioavailability [9]. Zinc-foliar fertilizers had the most significant effects in 2019 and 2020, with the reduction rates near to 40% (Table 3–4). This may be caused by the antagonism effect of Zn to Cd. Zinc is an essential trace element for plant growth, which can promote plant growth and compete with the absorption sites of Cd on cell membrane surface, thus reducing the intake of Cd. Meanwhile, Zn and Cd are generally transported by the same transporter [32,33]. When Zn content in plants increases, it will compete the heavy-metal binding site on the transporter with Cd, resulting in the decrease of Cd content in plants [34,35]. In 2020, Selenium-foliar fertilizers had the best effects of

| Table 1. Effects of different kinds of foliar fertilizers on wheat yield and seed performance in 2019. |
|---------------------------------------------------------------|
| Treatment | Yield (t hm⁻²) | Stem length (cm) | Ear length (cm) | Thousand seed weight (g) |
|------------|----------------|------------------|-----------------|--------------------------|
| CK         | 3.573 ± 0.101b | 58.6 ± 0.361ab   | 7.800 ± 0.346a  | 37.0 ± 0.200a            |
| Y1         | 3.863 ± 0.049a | 60.9 ± 1.531a    | 8.167 ± 0.289a  | 37.2 ± 0.764a            |
| Y2         | 3.650 ± 0.147ab| 58.1 ± 0.902a    | 8.000 ± 0.200a  | 36.6 ± 0.603a            |
| Y3         | 3.713 ± 0.068ab| 58.8 ± 0.551ab   | 8.300 ± 0.361a  | 36.8 ± 1.058a            |

Note: CK indicated control treatment, Y1 indicated the application of Si, Y2 indicated the application of Se, Y3 indicated the application of Zn. Different lowercase letters in a column indicated significant differences among treatments at P < 0.05 and P < 0.01 levels.

| Table 2. Effects of different kinds of foliar fertilizers on wheat yield and seed performance in 2020. |
|---------------------------------------------------------------|
| Treatment | Yield (t hm⁻²) | Stem length (cm) | Ear length (cm) | Thousand seed weight (g) |
|------------|----------------|------------------|-----------------|--------------------------|
| CK         | 3.600 ± 0.056b | 58.3 ± 0.057ab   | 7.933 ± 0.404a  | 36.4 ± 0.929a            |
| Y1         | 3.970 ± 0.112a | 59.9 ± 1.36a     | 8.300 ± 0.264a  | 37.7 ± 0.764a            |
| Y2         | 3.714 ± 0.065b | 58.1 ± 0.264b    | 8.433 ± 0.681a  | 37.0 ± 1.01a             |
| Y3         | 3.744 ± 0.062b | 59.0 ± 0.208ab   | 8.067 ± 0.306a  | 37.2 ± 0.800a            |

Note: Different lowercase letters in a column indicated significant differences among treatments at P < 0.05 and P < 0.01 levels.
Figure 1. The heavy metal content in wheat grains. Note: Data were shown as mean ± standard deviation. The black letters represented the significance level of heavy metal contents in wheat after application of different foliar fertilizers in 2019, and red letters represented the significance level of heavy metal content in wheat after application of different foliar fertilizers in 2020 (P < 0.05) and (P < 0.01).

Table 3. The reduction rates of different kinds of foliar fertilizers on heavy metals of wheat grains in 2019.

| Treatment | Cd (mg kg⁻¹) | As (mg kg⁻¹) | Pb (mg kg⁻¹) | Hg (mg kg⁻¹) |
|-----------|--------------|--------------|--------------|--------------|
| CK        | 0b           | 0c           | 0c           | 0a           |
| Y1        | −7.79 ± 3.52b| 11.1 ± 2.13ab| 30.8 ± 2.31b | 0.348 ± 1.13a|
| Y2        | 29.1 ± 4.67a | 16.0 ± 2.58a| 31.3 ± 2.01b | 0.565 ± 0.482a|
| Y3        | 39.1 ± 3.27a | 8.33 ± 2.24b | 49.8 ± 3.94a | 0.161 ± 0.676a|

Note: Different lowercase letters in a column indicated significant differences among treatments at P < 0.05 and P < 0.01 levels.
decreasing Cd in wheat, and the reduction rate was 38.7%. Selenium are essential for plant antioxidant systems, it can resist the oxidative stress of Cd on plants and maintain Cd in the cell wall of leaves, thus blocking the migration of Cd to grains [4,16]. In conclusion, Se- and Zn-foliar fertilizers showed significant effects on decreasing Cd content in wheat grains to the limit range, and had positive effects on wheat production and seed performance in two consecutive years, thus we suggest applying in production practice.

### 3.2.2 Effects on As content in wheat grains

In this study, the content of As in wheat grains ranged from 0.0640 to 0.0793 mg kg⁻¹, which was greatly lower than the national limit standard of 0.2 mg kg⁻¹ (GB 2762–2017), thus in this area, the food-chain risk of wheat As was low. The content of As in wheat grains decreases significantly after the application of foliar fertilizers (Figure 1). In 2019, foliar application with Si, Se and Zn decreased grains As by 13.4%, 5.63% and 19.1%, respectively, and Zn-foliar fertilizers showed the best effect. In 2020, Si-, Se- and Zn-foliar fertilizers decreased grains As by 11.1%, 16.0% and 8.33% respectively, and Se-foliar fertilizers showed the best effect. Selenium-foliar fertilizers showed stable effects in 2019 and 2020. Generally, As can be chelated with phytochelatins and fixed in the vacuole of plant cells, reducing the toxic effect on plant cells [36]. Selenium can promote the synthesis of plant chelates in root cells, increase the vacuolar binding of As to plant chelates, and thus reduce the transport to the shoot [36,37]. In addition, selenium could alleviate As toxicity by increasing the antioxidant capacity of plants [38,39]. Selenium is an important element for glutathione peroxidase (GSH-PX), which catalyzes the reduction of toxic peroxides to non-toxic compounds containing hydroxyl groups and decomposition of H₂O₂, thereby reducing reactive oxygen species and alleviating oxidative stress. Hasanuzzaman et al. [40] found that the activities of peroxidase (POD), catalase (CAT), SOD and lipid peroxidation (MDA) were decreased after spraying Se-foliar fertilizers on rapeseed. Photosynthetic parameters in leaves may also lead to the difference in arsenic content in grains. Results found that after the application of Se- and Si-foliar fertilizers, photosynthetic parameters such as photosynthetic rate, stomatal conductance and intercellular CO₂ concentration of plants were significantly increased, which could reduce the effects of As on plant photosynthesis [41,42]. Meanwhile, Se and Si can improve photosynthetic efficiency by repairing the damaged chloroplasts and increasing chlorophyll content [43,44]. But different types of Se-foliar fertilizers have different effects on As reduction. Yang [45] found the As reduction effects of Se (IV) in the roots and shoots of rice seedlings were 4.3 and 3.5 times higher than that of Se (VI). Above all, Se (IV) is recommended as a foliar fertilizer of selenium source for As reduction.

### 3.2.3 Effects on Pb content in wheat grains

The content of Pb in wheat grains ranged from 0.0114 to 0.0321 mg kg⁻¹, which was far lower than the national limit standard of 0.2 mg kg⁻¹ (GB 2762–2017), thus in this area, the food-chain risk of Pb in wheat was also low. The content of Pb in wheat grains decreased significantly after the application of foliar fertilizers (Figure 1). In 2019, Si-, Se- and Zn-foliar fertilizers decreased grains Pb by 41.0%, 38.0% and 52.5%, respectively. In 2020, Si-, Se- and Zn-foliar fertilizers decreased grains As by 30.8%, 31.3% and 49.8%, respectively. Selenium-foliar fertilizers showed stable and obvious effects on grains Pb reduction in 2019 and 2020. Compared with the reduction rates of other metal elements, these foliar fertilizers had the most obvious reduction effects on Pb. Lead poisoning can cause DNA damage, the malfunction of chromosomal, the inhabitation of DNA for synthesis and repair, and cause serious irreparable damage primarily to kidney and intestinal system [46]. Studies have proven that Se can combine with Pb²⁺ to form Pb-Se protein complex, which can be excreted through metabolism, thus alleviating Pb toxicity [47]. Zhang et al. [48] also discovered that the absorption of Si through leaves could not only reduce Pb enrichment in leaves, but also reduce the absorption of Pb from soil by roots. The Pb absorbed by roots was enriched in stems and rice husks, thus reducing the content of Pb in grains. In the prior studies, there were few studies focusing on the reduction of Pb content in wheat by Zn-foliar fertilizers. Foliar application with Zn could significantly reduce both the content of Cd and Pb in wheat grains, which may be a new strategy for wheat Cd and Pb pollution.

### 3.2.4 Effects on Hg content in wheat grains

In this study, the Hg content in wheat grains varied from 0.0011 to 0.0013 mg kg⁻¹, far lower than the national limit standard of 0.02 mg kg⁻¹ (GB 2762–

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**Table 4. The reduction rates of different kinds of foliar fertilizers on heavy metals of wheat grains in 2020.**

| Treatment | Cd    | As   | Pb    | Hg   |
|-----------|-------|------|-------|------|
|           | 0b    | 0c   | 0c    | 0a   |
| Y1        | 4.79 ± 3.631b | 13.4 ± 5.00ab | 41.0 ± 6.21ab | 0.607 ± 1.91a |
| Y2        | 38.7 ± 10.1a  | 5.63 ± 2.616bc | 38.0 ± 4.88b  | 0.913 ± 1.08a  |
| Y3        | 34.6 ± 4.99a  | 19.1 ± 2.29a   | 52.5 ± 4.50a  | 0.267 ± 0.814a |

Note: Different lowercase letters in a column indicated significant differences among treatments at P < 0.05 and P < 0.01 levels.
2017), which indicates the food-chain risk of Hg in wheat in this region was also low. Application of foliar fertilizers (Figure 1) had no significant effects on Hg content in wheat grains, which may be due to the low Hg content in soils and less Hg available for wheat intake. It is necessary to strengthen the test of wheat foliar fertilizers on Hg contaminated soils.

Although there were many interference factors in the field experiment, the continuous planting of two cropping wheat demonstrated that the foliar fertilizers could not only improve the yield and seed performance of wheat, but also significantly reduce the content of heavy metals in wheat grains. It also should be noted that foliar fertilizers are only appropriate for low and medium levels of soil heavy-metal pollution, however. Other measures should be combined to reduce crop heavy-metal risk in highly contaminated soils [2]. Selenium-foliar fertilizers showed stable and significant effects on the reduction of heavy metals Cd, As and Pb in wheat grains. Selenium is closely related to human health, which is an essential factor in important physiological processes such as collective immunity, anti-aging and anti-cancer [49]. More than 15% of the population in the world has suffered from Se deficiency [50], and about 72% of land area in China has suffered from Se deficiency (< 0.05 mg kg−1). The potential Se deficiency of Chinese residents is prominent [51,52]. The application of Se on plants is an economical, feasible and safe agricultural technology, which can not only reduce the heavy-metal content in crops, but also improve the Se content in the edible parts of crops, thus overcoming the dietary Se deficiency [53]. Selenium can also increase protein content in grains, and Se-rich foods have potential health benefits for humans [43]. Therefore, it is necessary to strengthen the use of Se-foliar fertilizers on low and medium polluted soils to realize the safe utilization of agricultural products and the supplement of Se required by human body.

4 Conclusion

In this study, the effects of foliar application of mineral element Si, Se and Zn on heavy-metal content in wheat grains were investigated through two consecutive years of field positioning experiments. Foliar application with Si could significantly increase the production and plant height, and reduce the content of As and Pb in wheat grains. Foliar application with Se and Zn can significantly reduce heavy metals like Cd, As and Pb. Among them, Se foliar fertilizers have the most obvious reduction effect on grains As in wheat, and Zn foliar fertilizers have the most obvious reduction effect on grains Cd and Pb in wheat. Foliar application with Se fertilizers could not only reduce the heavy-metal content in crops, but also improve the Se content in the edible parts of crops. It is suggested to apply it in low and medium polluted soils.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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