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Bamboo Biochar and Zinc Oxide Nanoparticles Improved the Growth of Maize (*Zea mays* L.) and Decreased Cadmium Uptake in Cd-Contaminated Soil

Yan Zha [1,*], Bo Zhao [2] and Tianxin Niu [1]

[1] Institute of Crop and Ecology, Hangzhou Academy of Agricultural Sciences, Hangzhou 310024, China
[2] Institute of Biotechnology, Hangzhou Academy of Agricultural Sciences, Hangzhou 310024, China
* Correspondence: 160507302@stu.cuz.edu.cn; Tel.: +86-189-6911-0730

Abstract: Cadmium (Cd) has attained top priority among all the toxic trace elements, and it easily accumulates in the human body through various pathways. The current pot study was focused on the impacts of foliar spray zinc oxide nanoparticles (ZnO NPs) (0, 50, 75, 100 mg·L^{-1}), alone or combined with soil-applied bamboo biochar (1.0% *w*/*w*), on the maize growth and Cd and Zn accumulations in the grains of maize under Cd-contaminated soil. The results showed that the maize-growth, photosynthesis, and gas-exchange attributes were accelerated by the foliar-applied ZnO NPs, and this effect was further enhanced by the bamboo biochar application in combination with ZnO NPs. All the amendments decreased the electrolyte leakage (EL) and malondialdehyde (MDA) and hydrogen peroxide (H_2O_2) contents, and they enhanced the activities of the antioxidant enzymes in the leaves and roots of the maize more than the control. The Cd concentrations in the shoots decreased by 74.55%, in the roots 66.38%, and in the grains by 76.19% after the bamboo biochar combined with a foliar spray of 100 mg·L^{-1} ZnO NPs. The current study concluded that the combination of the foliar spray of ZnO NPs and soil-applied bamboo biochar is a feasible strategy for safely growing crops on Cd-contaminated soils.

Keywords: maize; bamboo biochar; zinc nanoparticles; cadmium; chlorophyll contents

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1. Introduction

The rapid development of urbanization and industrial automation over the last few years has promoted the issue of environment degradation [1,2]. The metal contamination of agricultural soils is one of the most serious challenges facing agricultural production, and it is seriously damaging arable land resources, leading to severe soil degradation [3]. The heavy metal contamination of soil is more serious in China. The National Soil Pollution Survey of China in 2014 reported that about 7.0% of the total arable areas within China were contaminated by cadmium (Cd). Characterized by high mobility, toxicity, and extensive circulation and enrichment over large areas, Cd takes top priority over other toxic trace elements [4]. Atmospherically deposited Cd in contaminated soils is highly mobile and toxic, and it can easily be taken up by plants via the roots and translocated to different plant parts [5,6], thereby inducing serious negative effects on the crop growth by reducing the chlorophyll synthesis, crop yields, and photosynthetic pigment production, as well as causing ultrastructural alternations [7,8]. As an important grain, as well as a forage crop, maize (*Zea mays* ssp. *mays* L.) shows a higher Cd uptake rate and faster Cd translocation to the aerial part compared with other cereals, leading to higher Cd concentrations [9]. A national statistical bulletin showed that the maize-planting area reached 4126 hm^2, accounting for about 35.3% of the total grain-planting area. It is imperative now to find an efficient and environmentally friendly method to control the transfer of Cd from soil to maize plants.

Biochar is a carbon-rich biological charcoal that is produced by the slow pyrolysis (limited oxygen) of organic residues at a high temperature [10,11], and it has a high surface area, high nutrient- and water-holding capacities, resists decomposition in soil, and retains specific effects for a longer time. Previous studies have demonstrated that biochar can greatly elevate the soil pH values, increase the organic content, and reduce the Cd uptake by plants [12,13]. It is therefore an effective adsorbent for soil heavy metals to mitigate the impacts of climate change by reducing CH_4 emissions and environmental pollution [14]. As a fast-growing plant, bamboo is widely distributed in China [15]. Bamboo charcoal is a recently developed biomass adsorbent; it serves as an alternative to wood-based activated carbon. The unique microporous structure on the surface of bamboo biochar possesses distinctive biological properties and a large surface area. Therefore, it could be a promising way to achieve maize security by growing low-grain Cd maize varieties in combination with the application of bamboo biochar to Cd-contaminated soils.

Nanoparticles (NPs), which range in size from 1 to 100 nm, have unique properties attributed to quantum effects, larger surface areas, and the ability to self-assemble [16]. In recent years, ZnO NPs have been widely used as novel materials in various fields. ZnO NPs have been applied as a fertilizer to improve the Zn availability to crops. In seed germination, ZnO NPs have positive effects on the seedling growth and generation of biomass on onion [17], green pea (*Pisum sativum*) [18], cotton (*Gossypium hirsutum* L.) [19], and moringa (*spicy wood*) [20]. Moreover, a report has shown that the Cd uptake by wheat plant was reduced with the supply of ZnO NPs [21]. In addition, the application of ZnO NPs will result in a higher level of antioxidant enzyme activities and reduce the oxidative damage to various plant species [22–24].

Zn is an essential element for all living organisms, plants, and animals, all of which need Zn to function. It is also a cofactor in many enzymes, thereby playing critical roles in various physiological processes, such as photosynthesis, respiration, electron transport, protein metabolism, chlorophyll synthesis, and hormonal regulation [25]. Therefore, any Zn deficiency can reduce the crop yield and will be manifested in the form of micronutrient deficiencies in humans [26]. The development of Zn-efficient cultivars is thus an effective method to maintain the crop yield and alleviate micronutrient deficiencies. The soil for this pot experiment was from Wangyan village, in which only Cd surpasses the threshold level. The sown land is specifically for agricultural use and is mainly used for maize and wheat planting. As maize is an important global grain and is widely cultivated in Zn-deficient soils throughout China, this study aims to assess the effectiveness of ZnO NPs, as well as the combined use of ZnO NPs and bamboo biochar, on concentrations of various substances so as to enhance the growth of maize in Cd-contaminated soil and its accumulation of Cd and Zn.

2. Materials and Methods

2.1. Materials and Field Experiment

The soil was collected from the agricultural land of Wangyan Village, which is located downstream of a mine site; the soil samples obtained from this area have been subjected to polluted surface runoff from the mine for 30 years. The initial properties of the selected agriculture land soil were only contaminated with Cd, and the other elements were below the threshold levels in the soil. The random soil sampling was conducted at a depth of 0–20 cm by using a stainless-steel spade. Five sampling points were decided on within the collection area in an "S" pattern. In order to guarantee homogeneity, the soil was air-dried for 7 days, and then it was sieved via a sieve with a pore size of 2 mm and characterized. The soil pH and EC values were 6.78, and 1.58 $dS \cdot m^{-1}$, respectively. The organic matter content was 0.92%. The total concentrations of Cd, Pb, Zn, Cu, Mn, and Fe were 4.15, 3.02, 30.98, 29.48, 53.15, and 101.62 $mg \cdot kg^{-1}$ DW (dry weight), respectively. The test bamboo charcoal was purchased from Henan Lize Environmental Protection Technology Company, and it was carbonized at 700 °C. Its properties were as follows: a pH of 6.78, organic carbon content of 634.15 $g \cdot kg^{-1}$, total nitrogen content of 7.74 $g \cdot kg^{-1}$, total phosphorus content of 1.58 g·kg^{-1}, total potassium content of 9.24 g·kg^{-1}, and an AB-DTPA-extractable Cd concentration of 0.74 mg·kg^{-1}. After the soil analysis, 20 kg of dried soil was put into each pot.

The ZnO NPs were purchased from Alfa Aesar, with a purity of 99%, 20–30 nm APS powder, and a density of 5.606 g·cm^{-3}. Four levels of ZnO NPs (0, 50, 75, 100 mg·L^{-1}) were prepared with deionized H_2O and were ultrasonicated for about 30 min to separate and homogenize the particles.

2.2. Experimental Setup

The experiment was conducted in the greenhouse at the Zhijiang base of Hangzhou Academy of Agricultural Science (30°09′19′′ N, 120°05′18′′ E). The test area is located in the northern part of the southeastern coast of China, which is characterized by a subtropical monsoon climate with four distinct seasons and an abundant rainfall pattern. The average annual temperature is 17.8 °C, the average relative humidity is 70.3%, and the annual precipitation and sunshine are 1454 and 1765 h, respectively. The designed treatments were as follows: T0: control; T1: bamboo biochar mixed in half pots at a rate of 1.0% (*w*/*w*); T2: 50 mg·L^{-1} ZnO NPs; T3: 75 mg·L^{-1} ZnO NPs; T4: 100 mg·L^{-1} ZnO NPs; T5: BC (1.0%, *w*/*w*) + 50 mg·L^{-1} ZnO NPs; T6: BC (1.0%, *w*/*w*) + 75 mg·L^{-1} ZnO NPs; T7: BC (1.0%, *w*/*w*) + 100 mg·L^{-1} ZnO NPs.

A total of 48 pots (36 cm height and 25 cm width) were filled with 20.0 kg of sieved soil per pot. The maize seeds (variety: Qianjiang 3-2017) were disinfected for 5 min in hydrogen peroxide (2.5%, *v*/*v*) solution and then rinsed with d-H_2O. Then, the maize seeds were sown in the soil bamboo biochar, mixing in the soil. Five seeds were sown in each pot, and after 6 days of germination, three seedlings with good growth were selected, and fertilizers (K_2SO_4-DAP-Urea) were used at a dose of 120-50-25 kg·ha^{-1} with irrigation water. Urea fertilizer was applied in two applications (i.e., once with other fertilizers, and the second time after 15 days). The first foliar application of ZnO NPs (0, 50, 75, 100 mg·L^{-1}) was performed by using a hand-held sprayer after two weeks of germination. In total, seven sprays were applied in the whole experiment, with a one-week interval. In the pots, the soil surface was treated with a plastic cover to avoid the directly entry of ZnO NPs to the soil, and replicates of the same treatment were grouped during each spray to maximize the contact of the plants with the NPs.

2.3. Plant Harvesting

After 82 days, the maize plants were harvested. The plant heights, spike heights, lengths, and widths were recorded at the harvesting stage, while the shoot and root dry weights were measured later. The washed samples were dried at a temperature of 65 °C for a constant weight and were stored for further use.

2.4. Determination of Chlorophyll and Gas-Exchange Parameters

Fresh maize leaf samples were taken to determine the chlorophyll contents. The samples were placed in a dark place and continuously shaken at 4 °C in acetone (85% *v*/*v*) solution [27]. The absorbance of the extracted solution at selected wavelengths (470, 647, and 664.5 nm) was recorded using a spectrophotometer, and the chlorophyll concentration of the maize leaves was measured using coefficients. A portable infrared gas analyzer (Analytical Development Company, Hoddesdon, UK) was used to measure the stomatal conductance, photosynthetic rate, and transpiration rate prior to harvesting the plants.

2.5. Determination of Electrolyte Leakage (EL) and Antioxidant Enzymes

About 200 mg of fresh maize leaves were thoroughly rinsed with distilled water to avoid surface contamination, before a 1.0 g leaf sample was added to 8.0 mL deionized water. The tubes were positioned in a water bath for two hours at 32 °C to record EC1. Then, the cylinders were placed in the water bath for twenty minutes at 121 °C to record EC2.

Finally, the electrolyte leakage was estimated through the given formula by Dionisio-Sese and Tobita [28] (electrolyte leakage = (EC1/EC2) $*$ 100).

Fresh leaves were ground into a slurry with 2 mL of prechilled phosphate buffer in a prechilled mortar placed in an ice bath. Then, the slurry was transferred into a 10 mL centrifuge tube. The mortar was rinsed with phosphate buffer, and any remnant slurry was also added to the centrifuge tube. The tube was then centrifuged at 10,000$\times$ *g* for 30 min at 4 °C. The supernatant was collected and stored at 4 °C until analyzed. The H_2O_2 content was calculated in accordance with the method described by Qi [29], while the malondialdehyde content was determined by the thiobarbituric acid method, and the peroxidase activity was determined by the guaiacol method. In addition, the superoxide dismutase activity was determined by the nitrogen blue tetrazolium method, the chloramphenicol acetyltransferase activity by the ultraviolet absorption method, and the ascorbate peroxidase activity in accordance with the method described by Nakano et al. [30].

2.6. Determination of Cd and Zn Concentrations

The dry weights (0.5 g) of the shoot, roots, and grains of the maize were subjected to di-acid digestion using nitric acid (HNO_3) and perchloric acid ($HClO_4$) in a 1:3 ratio, respectively, followed by heating on a hot plate at 250 °C [31,32]. Samples were later filtered and analyzed for the Cd and Zn analyses using an atomic absorption spectrophotometer (AAS) (z2000, Hitachi, Tokyo, Japan). The postharvest soil was analyzed for the pH and AB-DTPA-extractable Cd, as given in the previous section, as the characterization of the soil and amendments.

2.7. Statistical Analysis

The significance of the differences between the treatments was analyzed by one-way and two-way analyses of variance (ANOVA) using IBM SPSS Statistical software, version 21.0. Differences between the treatments were detected, and the mean values were compared by the Tukey's range test ($p = 0.05$). The analysis of correlation was performed by using a Pearson's correlation test by considering $p < 0.05$ as significant (two-tailed).

3. Results

3.1. Plant Growth and Photosynthesis

In this study, the effects of treating soil with bamboo biochar and the foliar spraying of ZnO NPs were recorded for maize grown under Cd stress (Table 1). Compared with the control, the shoot and root dry weights per plant significantly increased by 31.52%, 49.63%, 71.37%, 54.09%, 52.79%, and 32.40% during the application of 100 mg·L^{-1} ZnO NPs alone, and increased by 40.32%, 57.12%, 82.53%, 64.38%, 68.67%, and 36.28% in the ZnO NPs (100 mg·L^{-1}) + bamboo biochar treatments. Separately, they had a significant impact on all the parameters, whereas the combined effects of ZnO NPs and bamboo biochar were not significant. The foliar spraying of ZnO NPs had a significant effect on the spike length and width ($p < 0.001$), plant height, spike height, and shoot and root dry weights ($p < 0.01$). Soil treated with bamboo biochar had a significant effect on the plant height, spike length, root dry weight ($p < 0.001$), spike height and width, and shoot dry weight ($p < 0.01$). Overall, the combined application of bamboo biochar and the foliar spraying of ZnO NPs greatly improved the resistance of maize to Cd toxicity.

The application of ZnO NPs alone or in combination with bamboo biochar enhanced the chlorophyll concentrations, photosynthesis rate, stomatal conductance, and transpiration rate (Figure 1). The chlorophyll "a" (Figure 1A) and "b" (Figure 1B) concentrations in the 50, 75, and 100 mg·L^{-1} ZnO NPs alone treatment increased by 20.21%, 40.41%, and 62.18%, and 23.36%, 31.78%, and 64.49%, respectively; they increased by 32.12%, 53.89%, and 73.46%, and 34.58%, 47.66%, and 76.64%, respectively, in the same NP treatments with bamboo biochar. At the highest application rate for the foliar spraying of ZnO NPs alone, the photosynthetic rate (Figure 1C), stomatal conductance (Figure 1D), and transpiration rate (Figure 1E) increased by 61.95%, 57.14%, and 31.47%, respectively, compared with those of the control. The combined treatments with the bamboo biochar and foliar spraying of ZnO NPs at 100 mg·L^{-1} had a significant impact on the photosynthetic rate, stomatal conductance, and transpiration rate, which increased by 68.43%, 86.12%, and 36.55%, respectively, when compared with those for the control. A two-way ANOVA revealed that the combined effects of ZnO NPs and bamboo biochar were not significant. The foliar spraying of ZnO NPs and soil treated with bamboo biochar had the same significant effect on the chlorophyll a and b, photosynthetic rate, stomatal conductance, and transpiration rate ($p < 0.001$).

Table 1. Growth responses of corn by using bamboo biochar and foliar application of ZnO NPs.

Treatments	Plant Height (cm)	Spike Height (cm)	Spike Length (cm)	Spike Width (cm)	Shoot Dry Weight (g)	Root Dry Weight (g)
CK	150.72 ± 4.51 e	58.51 ± 1.63 e	18.37 ± 1.35 f	3.79 ± 0.13 e	23.68 ± 1.15 d	6.45 ± 0.25 c
T1	167.58 ± 4.08 cd	67.34 ± 1.17 cd	19.89 ± 1.08 ef	4.01 ± 0.25 ef	27.04 ± 1.77 cd	6. 94 ± 0.24 bc
T2	174.04 ± 5.86 bc	70.01 ± 2.82 cd	21.56 ± 1.21 e	4.71 ± 0.18 d	29.61 ± 1.94 bc	7.66 ± 0.33 ab
T3	185.92 ± 5.42 ab	80.38 ± 2.77 c	27.75 ± 1.07 d	5.12 ± 0.12 cd	32.14 ± 1.09 b	7.78 ± 0.26 a
T4	192.26 ± 6.09 ab	87.55 ± 2.51 bc	31.48 ± 1.25 cd	5.84 ± 0.21 cd	36.18 ± 1.66 b	8.54 ± 0.44 ab
T5	186.45 ± 5.09 ab	77.46 ± 2.78 bc	25.48 ± 1.32 bc	5.05 ± 0.27 bc	31.88 ± 1.31 ab	8.13 ± 0.47 a
T6	198.49 ± 4.55 ab	83.47 ± 2.07 ab	29.31 ± 1.11 ab	5.63 ± 0.18 abc	34.95 ± 1.08 ab	8.35 ± 0.37 a
T7	211.77 ± 5.66 a	91.93 ± 2.83 a	33.53 ± 1.24 a	6.23 ± 0.28 a	39.94 ± 1.08 a	8.79 ± 0.67 a
BC	0.000 ***	0.025 **	0.000 ***	0.048 **	0.027 **	0.000 ***
ZnO NPs	0.036 **	0.047 **	0.000 ***	0.000 ***	0.024 **	0.041 **
BC × ZnO NPs	ns	ns	ns	ns	ns	ns

Note: T1–T7: T1: 2.0% co-composted BC (hereafter termed BC); T2: 50 mg·L^{-1} ZnO NPs; T3: 75 mg·L^{-1} ZnO NPs; T4: 100 mg·L^{-1} ZnO NPs; T5: 2.0% co-composted BC + 50 mg·L^{-1} ZnO NPs; T6: 2.0% co-composted BC + 75 mg·L^{-1} ZnO NPs; T7: 2.0% co-composted BC + 100 mg·L^{-1} ZnO NPs. Values are means of four replications, and bars represent standard deviations. Different letters demonstrate significant differences among treatments. In the table: ns: nonsignificant; ** significant at 0.01, and *** significant at 0.001 levels.

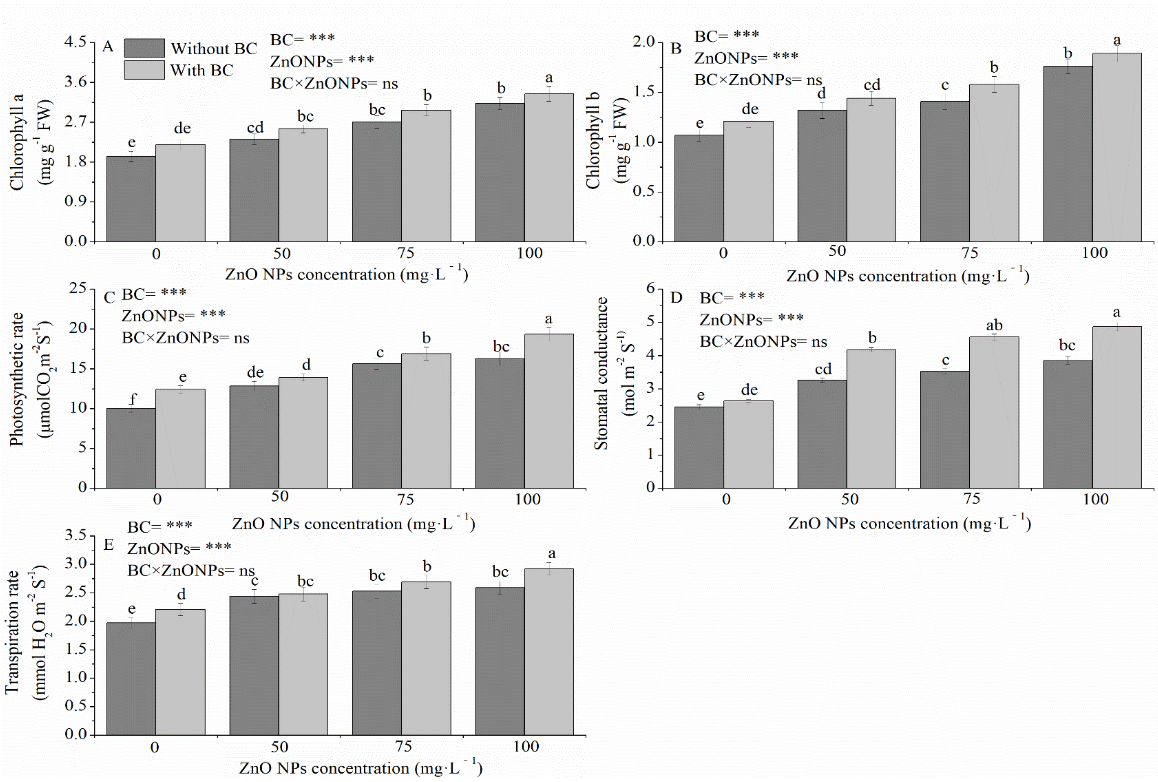

Figure 1. Effects of foliar-applied ZnO NPs alone and combined with bamboo biochar on (**A**) chlorophyll a, (**B**) chlorophyll b, (**C**) photosynthetic rate, (**D**) stomatal conductance, and (**E**) transpiration rate in maize plant under Cd stress. Bars show standard deviations of four replications. Different letters on the bars demonstrate the significant differences between treatments at $p \leq 0.05$. In the figures: ns: non-significant; and *** significant at 0.001 levels.

3.2. Oxidative Stress and Antioxidant Enzymes of Maize Leaves and Roots

The effects of ZnO NPs with and without bamboo biochar on the MDA, H_2O_2, EL, and antioxidant enzymes in maize leaves are shown in Figure 2. At the 100 mg·L^{-1} foliar application of ZnO NPs alone, the MDA (Figure 2A) and H_2O_2 (Figure 2B) contents and EL (Figure 2C) in the maize leaves decreased by 39.91%, 42.96%, and 56.44%, respectively, while those during the combined application of bamboo biochar and 100 mg·L^{-1} ZnO NPs decreased by 61.47%, 51.56%, and 61.25%, respectively, compared with those of the control. A two-way ANOVA revealed that the foliar application of ZnO NPs and the addition of bamboo biochar to the soil had the same significant effect on the MDA and H_2O_2 contents and EL in the maize leaves ($p < 0.001$), while the combined effects of ZnO NPs and bamboo biochar did not significantly affect the H_2O_2 content and EL in the maize leaves; however, the combined effects of ZnO NPs and bamboo biochar had a significant effect on the MDA content ($p < 0.05$).

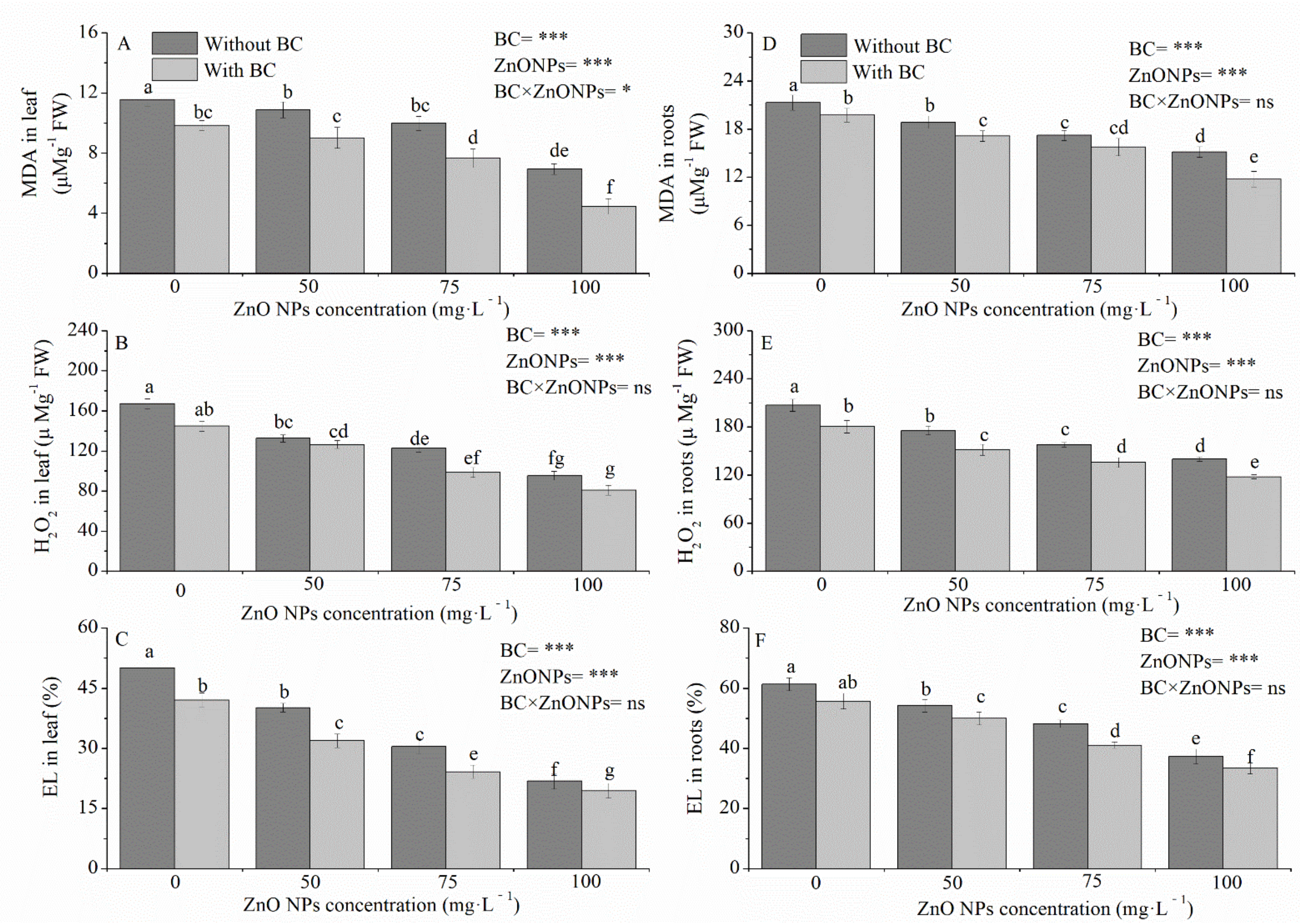

Figure 2. Effects of foliar-applied ZnO NPs alone and combined with bamboo biochar on MDA in (**A**) leaves, (**B**) H_2O_2 in leaves, (**C**) El in leaf, (**D**) MDA in root, (**E**) H_2O_2 in root, and (**F**) El in root in maize plants under Cd stress. Different letters on the bars demonstrate the significant differences between treatments at $p \leq 0.05$. In the figures: ns: non-significant; * significant at 0.05, and *** significant at 0.001 levels.

The results of the impacts of the applied treatments on oxidative stress are shown in Figure 2, which shows that the application of ZnO NPs alone can significantly reduce the MDA (Figure 2D) and H_2O_2 (Figure 2E) contents and EL (Figure 2F) in maize roots. As the concentration of ZnO NPs increased, the EL and H_2O_2 and MDA contents decreased correspondingly. Upon the application of 100 mg·L^{-1} Zn NPs alone, the EL and H_2O_2 and MDA contents decreased by 39.13%, 32.56%, and 28.87%, respectively, compared with those of the control. The bamboo biochar + 100 mg·L^{-1} ZnO NPs enhanced the EL and H_2O_2 and MDA contents in the maize roots by 45.57%, 44.84%, and 43.16%, respectively, compared with the control. A two-way ANOVA revealed that separate applications of the foliar spraying of ZnO NPs and the addition of bamboo biochar in the soil had the same significant effects on the EL and H_2O_2 and MDA contents in the maize roots ($p < 0.001$), while the effects of the combined application of ZnO NPs and bamboo biochar were not significant.

3.3. Antioxidant Enzymes of Maize Leaves and Roots

As shown in Figure 3, the foliar application of ZnO NPs improved the activities of the antioxidant enzymes in the leaves under all treatments. The SOD activity in the leaves increased by 21.08%, 71.86%, and 91% with applications of 50, 75, and 100 mg·L^{-1} ZnO NPs (Figure 3A), respectively, compared with that in the control. At the application of 100 mg·L^{-1} ZnO NPs alone, the POD (Figure 3B), CAT (Figure 3C), and APX activities (Figure 3D) in the maize leaves increased by 53.54%, 142.55%, and 44.89%, respectively, compared with those of the control. The maximum values of the antioxidant enzymes in the leaves were achieved under the combined bamboo biochar and foliar application of 100 mg·L^{-1} ZnO NPs, which enhanced the SOD, POD, CAT, and APX activities in the maize leaves by 112.53%, 92.92%, 186.10%, and 59.52%, respectively, compared with those of the control. A two-way ANOVA revealed that the foliar application of ZnO NPs had a significant effect on the SOD, POD, CAT, and APX activities ($p < 0.001$), while the addition of bamboo biochar to the soil had a significant effect on the SOD, POD, CAT ($p < 0.001$), and APX activities ($p < 0.01$). The combined effects of the ZnO NPs and bamboo biochar on the SOD, POD, CAT, and APX activities in the maize leaves were not significant.

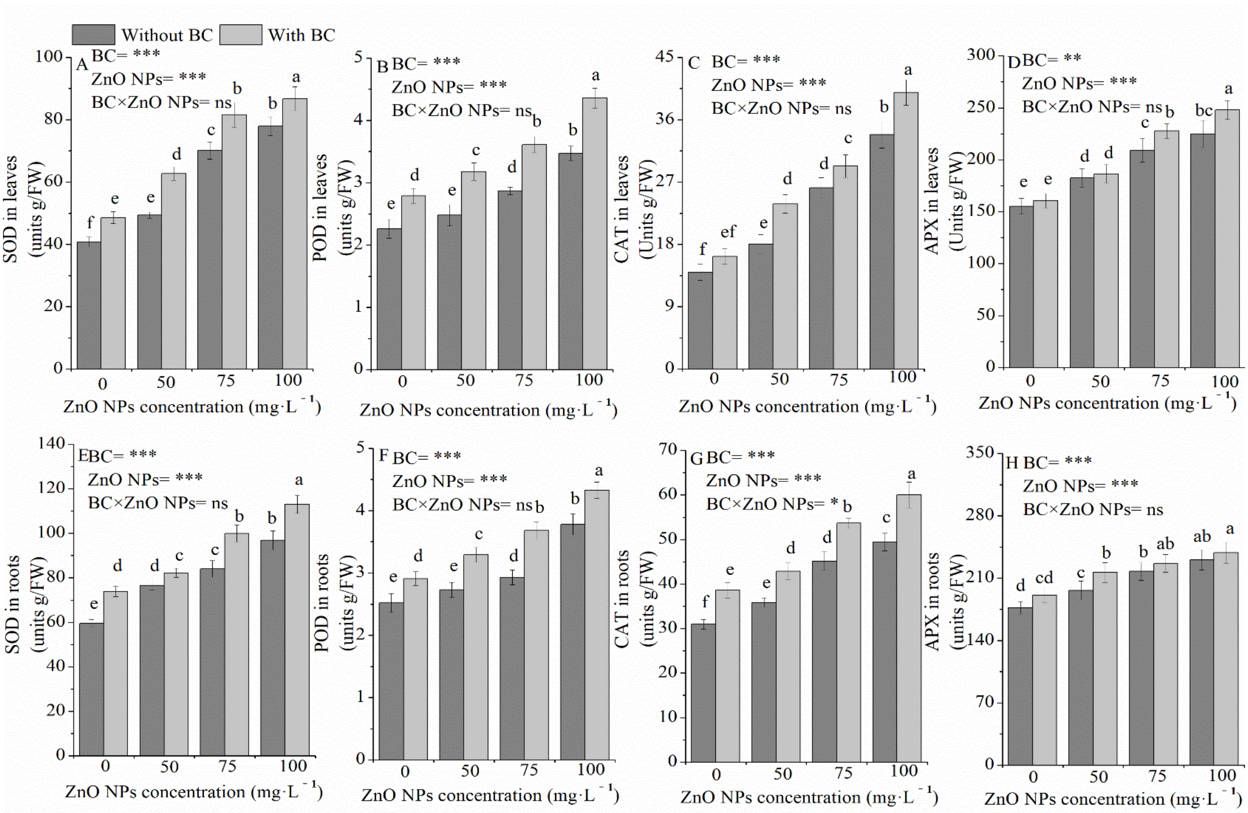

Figure 3. Effects of foliar-applied ZnO NPs alone and combined with bamboo biochar on (**A**) SOD in leaf, (**B**) POD in leaf, (**C**) CAT in leaf, (**D**) APX in leaf, (**E**) SOD in root, (**F**) POD in root, (**G**) CAT in root, and (**H**) APX in root in maize plants under Cd stress. Different letters on the bars demonstrate the significant differences between treatments at $p \leq 0.05$. In the figures: ns: non-significant; * significant at 0.05, ** significant at 0.01, and *** significant at 0.001 levels.

As shown in Figure 3, the foliar application of ZnO NPs improved the activities of the antioxidant enzymes in the roots under all treatments. The SOD activity in the leaves increased by 28.76%, 41.20%, and 62.74% upon the applications of 50, 75, and 100 mg·L^{-1} ZnO NPs alone (Figure 3E), respectively, over the control. At 100 mg·L^{-1} ZnO NPs alone, the POD (Figure 3F), CAT (Figure 3G), and APX activities (Figure 3H) in the maize roots were increased by 50.00%, 59.74%, and 30.43%, respectively, as compared with those in the control. The maximum values of the antioxidant enzymes in the leaves were reached under the combined treatments of bamboo biochar and the foliar application of 100 mg·L^{-1} ZnO NPs, which enhanced the SOD, POD, CAT, and APX activities in the leaves by 89.94%, 71.83%, 93.90%, and 34.85%, respectively, compared with those in the control. A two-way ANOVA revealed that the foliar application of ZnO NPs and the addition of bamboo biochar to the soil had the same significant effect on the SOD, POD, CAT, and APX activities ($p < 0.001$), while the combined effects of the ZnO NPs and bamboo biochar were not significant on the SOD, POD, and APX activities. However, the combined effects of ZnO NPs and bamboo biochar significantly affected the CAT activity in the maize leaves ($p < 0.05$).

3.4. Cadmium and Zn Concentrations in Plants and Post Soil Analysis

As shown in Figure 4, the amendments had a significant impact on the Cd and Zn concentrations in the maize shoots, roots, and grains. The Cd and Zn concentrations were the highest in the roots, followed by those in the shoots and grains. All the treatments reduced the Cd and enhanced the Zn concentrations in the shoots, roots, and grains. In the control treatment, the highest Cd concentrations and lowest Zn concentrations were observed in the maize shoots, roots, and grains. The Cd concentrations in the shoots (Figure 4A), roots (Figure 4B), and grains (Figure 4C) decreased by 81.03%, 80.46%, and 84.62%, respectively, during the application of 100 mg·L^{-1} ZnO NPs alone, as compared with the control. Overall, the combined treatments with the bamboo biochar and 100 mg·L^{-1} ZnO NPs had the most significant effect on the reduction in the Cd concentrations in the maize shoots, roots, and grains, which were reduced by 85.38%, 91.26%, and 88.46%, respectively, compared with those in the control. The Zn concentrations in the shoots (Figure 4D), roots (Figure 4E), and grains (Figure 4F) were reduced by 168.01%, 113.48%, and 50.72%, respectively, in the 100 mg·L^{-1} ZnO NPs alone, compared with the control. Overall, the combined treatments with the bamboo biochar and 100 mg·L^{-1} ZnO NPs had the most significant effect on the increase in the Cd concentrations in the maize shoots, roots, and grains, which were reduced by 132.47%, 184.96%, and 82.29%, respectively, compared with those in the control.

3.5. Soil Bioavailable Cd and pH after Harvesting the Maize

As shown in Table 2, the use of bamboo biochar with and without 100 mg·L^{-1} of ZnO NPs produced the lowest and highest soil pH values, respectively. The soil pH value increased by 0.25 and 0.36 with the use of 75 and 100 mg·L^{-1} of ZnO NPs alone, respectively, and by 0.47 with the use of 100 mg·L^{-1} of ZnO NPs in combination with bamboo biochar, as compared with the control. The control treatments produced the highest soil concentrations of bioavailable Cd. All the treatments significantly reduced the soil concentration of bioavailable Cd. The soil concentration of bioavailable Cd decreased by 36.49% and 41.89% with the use of 75 and 100 mg·L^{-1} of ZnO NPs alone, respectively, as compared with the control. Overall, the combined treatment with bamboo biochar and ZnO NPs further reduced the soil concentration of bioavailable Cd and improved the soil pH.

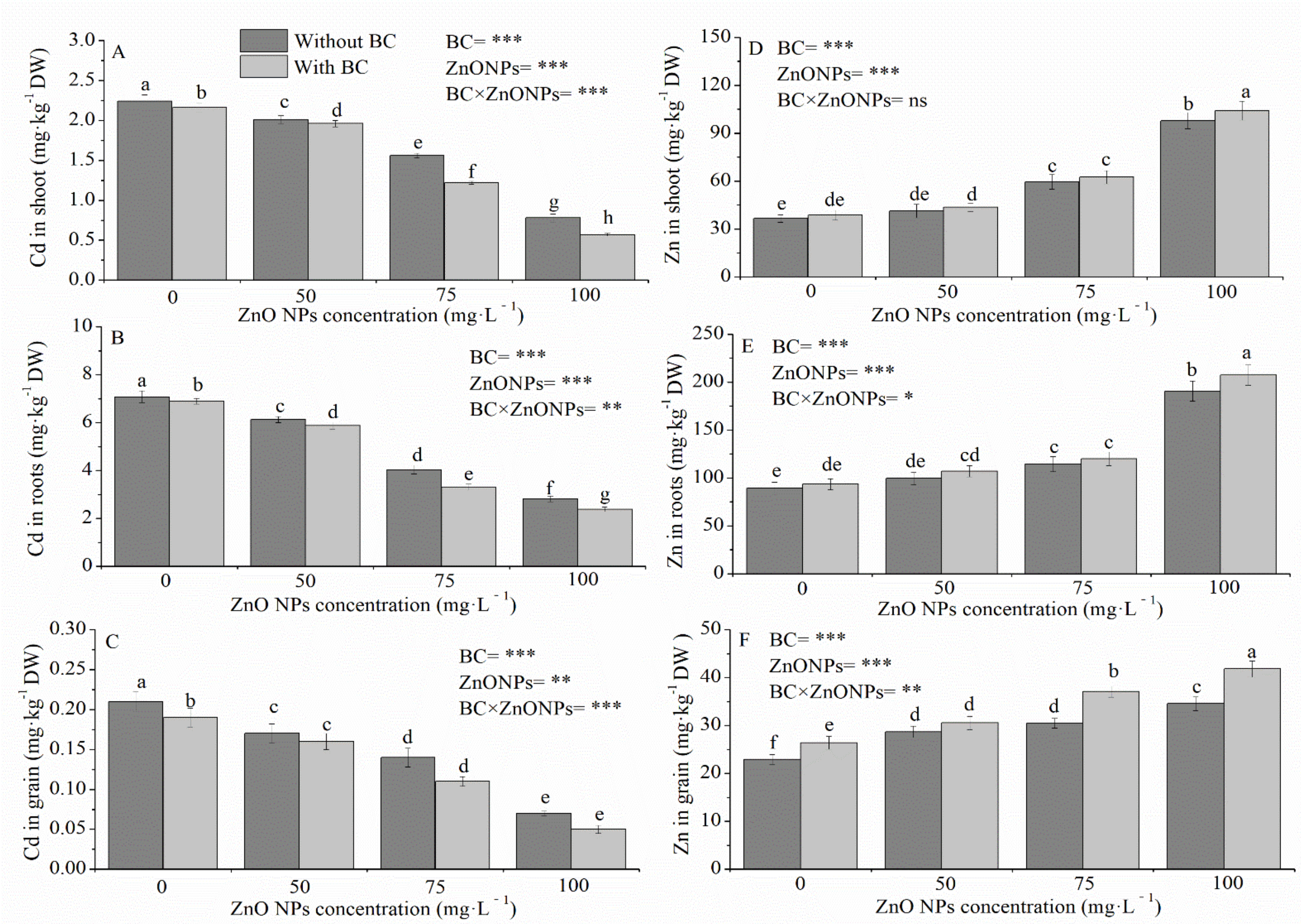

Figure 4. Effects of foliar-applied ZnO NPs alone and combined with bamboo biochar on (**A**) Cd in shoot, (**B**) Cd in root, (**C**) Cd in grain, (**D**) Zn in shoot, (**E**) Zn in shoot, and (**F**) Zn in grain. Different letters on the bars demonstrate the significant differences between treatments at $p \leq 0.05$. In the figures: ns: non-significant; * significant at 0.05, ** significant at 0.01, and *** significant at 0.001 levels.

Table 2. Postharvest soil AB-DTPA-extractable Cd (mg·kg^{-1}) and pH. Values are means of five replications, and different letters demonstrate significant differences between treatments at $p \leq 0.05$.

Treatments	0 (mg·L^{-1})	50 (mg·L^{-1})	75 (mg·L^{-1})	100 (mg·L^{-1})
pH				
Without biochar	6.78 ± 0.09 d	6.87 ± 0.12 cd	7.03 ± 0.05 bc	7.14 ± 0.14 ab
With biochar	6.82 ± 0.096 d	6.98 ± 0.12 cd	6.95 ± 0.11 bcd	7.25 ± 0.09 a
Cd				
Without biochar	0.74 ± 0.07 a	0.63 ± 0.07 abc	0.58 ± 0.06 bcd	0.52 ± 0.08 cd
With biochar	0.71 ± 0.06 ab	0.57 ± 0.12 bcd	0.47 ± 0.09 d	0.43 ± 0.08 d

3.6. Correlation Analysis

Correlation analyses of the maize growth indicators and photosynthesis parameters with the soil pH, extractable Cd concentration, maize leaf and root enzyme activities, and maize (root, shoot, and grain) Cd and Zn concentrations were constructed using Origin 2021 software to obtain correlation heat maps. As shown in Figure 5, the maize plant height, spike length, height, and width, and the shoot and root dry weights, were positively correlated with the leaf and root enzyme activity ($p < 0.001$), and negatively correlated with the shoot, root, and grain Cd concentrations, leaf and root EL, and MDA and H_2O_2 contents ($p < 0.001$). In addition, the grain Zn was negatively correlated with the grain Cd and shoot and root Cd concentrations ($p < 0.001$), and the soil pH was negatively correlated with the shoot, root, and grain Cd concentrations ($p < 0.001$). The leaf and shoot EL and MDA and H_2O_2 contents were negatively correlated with the shoot, root, and grain Zn concentrations, chlorophyll a and b, stomatal conductance, transpiration rate, and photosynthetic rate ($p < 0.001$). However, the soil pH was negatively correlated with the leaf and root EL and MDA and H_2O_2 contents ($p < 0.001$).

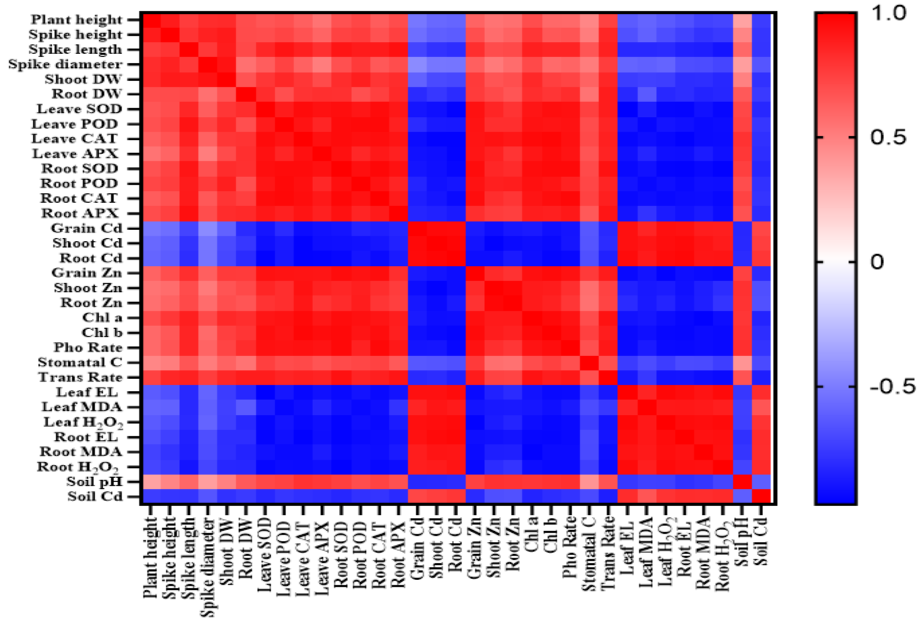

Figure 5. Correlations between different parameters. DW: dry weight; EL: electrolyte leakage; H_2O_2: hydrogen peroxide; MDA: malondialdehyde; SOD: superoxide dismutase; POD: peroxidase. All the above indexes showed extremely significant correlations at the 0.01 level.

4. Discussion

The study revealed that the maize growth and biomass accumulation were accelerated by the foliar spraying of ZnO NPs, and this effect was further enhanced during the combined bamboo biochar in combination with ZnO NPs treatment (Table 1). Previous studies have shown that Cd causes stress in plants, as demonstrated by the decreased vigor and biomass under these conditions [33,34]. Therefore, the lower biomass in the control group may be attributed to the higher Cd concentrations in the maize. In this study, a correlation analysis revealed that the maize biomass and growth were negatively correlated with the Cd concentrations in the shoots, roots, and grains, as well as with the EL and MDA and H_2O_2 levels in the leaves and roots. Therefore, the lower maize plant biomass observed in the control group was related to the elevated levels of MDA, H_2O_2, and EL in both the above and below ground groups (Figure 3).

This study showed that the gas exchange and chlorophyll content were comparatively lower in the control maize leaves (Figure 1). Spraying ZnO NPs on the maize leaves increased the photosynthetic rate, which may be attributed to the reduction in the oxidative stress and increased enzyme activity [35]. Pullagurala et al. (2018) [36] reported that ZnO NPs have a positive effect on plant growth. Zinc NPs and Zn have positive effects on the growth and plant nutritional status of sorghum [37]. The growth and antioxidant enzyme activities are promoted when ZnO NPs are applied to mustard plants [38]. Several studies have confirmed that bamboo biochar reduces oxidative stress in many plant species [6,34], which is consistent with the findings of this study. A further correlation analysis revealed that the maize photosynthetic parameters were significantly and negatively correlated with the oxidative stress and enzyme activities (Figure 5). In our study, the bamboo biochar application in combination with ZnO NPs minimized the oxidative stress and enhanced the enzyme activity in the maize plants. Under metal stress, ZnO NPs reduced the oxidative stress in *Leucaena leucocephala* [22]. The reduction in ROS and the increase in the antioxidant enzyme activity may have been due to the maintenance of the plant membrane structure. The increase in the antioxidant enzyme activity and decrease in the oxidative stress markers in maize leaves may be a stress-tolerance mechanism in maize under Cd stress. Our results suggested that the Cd tolerance in maize can be improved by foliar spraying with ZnO NPs and the soil application of biochar.

The similarity between the essential nutrient Zn and nonessential nutrient Cd further indicates the importance of Zn in the soil–plant system [9]. A moderate amount of Zn in the soil can alleviate the Cd toxicity in plants. Zn can reduce the accumulation of Cd in plants owing to the mutual antagonism of these metals [39]. Previous studies have reported that ZnO NPs reduce the Cd levels in wheat [40], while a more recent study found that soybean and tomato plants absorbed Zn in any form ($ZnSO_4$, ZnO nanoparticles, and bulk ZnO) when applied via foliar sprays [41]. Read et al.'s (2020) [42] study found that the leaf cuticles of wheat and sunflowers were the main pathway for the uptake of ZnO NPs, and the adhesion of the NPs to the leaves restored the Zn levels. Therefore, ZnO NPs are a more effective and slow-releasing source of Zn compared with conventional fertilizers [43,44]. Our results showed that the Zn content linearly increased (Figure 4C–E) and the Cd content linearly decreased in the maize plants (Figure 4A–C) with the application of ZnO NPs. A correlation analysis revealed that the higher Cd content in the maize seeds might be highly positively correlated with the soil concentration of bioavailable Cd (Figure 5), while the combined application of biochar and NPs further reduced the Cd concentration in the maize plants (Figure 4A–C). The lower Cd concentrations in the maize plants treated with NPs were because of the high plant biomass (Table 1), which may have caused a dilution effect.

The soil pH after harvest in the control group was slightly higher than the initial soil value, and it increased after corn growth without any amendments, which could have been due to changes caused by the application of nitrogen, phosphorus, and K fertilizers [7]. Siebers (2013) [45] reported that the application of phosphorus fertilizer increased the soil pH. Several other studies have shown that the application of biochar significantly increased the soil pH [12,46]. Liu et al. (2018) [13] found that the application of bamboo biochar at 1–5% markedly enhanced the soil pH by 1.17–40.3%. Ma et al. (2021) [12] indicated that bamboo biochar contains a large amount of carbonate phosphates, and that ash combined with H^+ in the soil increases the soil pH, which is consistent with the findings of the present study (Table 2). Correlation analyses revealed that the soil concentrations of bioavailable Cd were strongly negative correlated with the pH (Figure 5). In addition, in this study, the soil pH increased slightly with the increasing concentrations of applied ZnO nanoparticles. Shi et al. found that the soil pH increased with the application of copper oxide (CuO) NPs, and that the response varied with time, the NP dose, and the soil type [47], which is similar to the pattern observed in this study. The application of nanoscale zero-valent iron to the soil was able to increase the pH of a soil solution [48]. In this study, the foliar spraying resulted in the deposition of ZnO NPs in the topsoil layer, thereby slightly increasing the soil pH, which could explain the slightly higher soil pH observed under the combined application of ZnO NPs and biochar as compared with that under the ZnO NP treatment alone. Hence, the application of bamboo biochar can effectively fix and passivate the Cd in soil, and it can reduce its accumulation in grains. Therefore, the foliar supply of nutrients and the soil application of biochar is an effective agronomic strategy.

5. Conclusions

The foliar spraying of ZnO NPs improved the growth, biomass, chlorophyll content, and Zn concentration of maize, while reducing the oxidative stress and Cd concentrations. The application of 100 $mg \cdot L^{-1}$ of ZnO NPs had the greatest effect on the plant growth. These results indicate that a suitable application of ZnO NPs can reduce the toxicity and absorption of Cd in maize, while fortifying maize grains with Zn. The combined application of ZnO NPs and bamboo biochar significantly reduced the Cd toxicity in the maize, increased the Zn concentration, and improved the leaf antioxidant system to combat the soil Cd-induced stress. Therefore, the combined application of ZnO NPs and bamboo biochar to leaves can improve the growth and the tolerance to Cd-induced stress in maize. In addition, a more comprehensive assessment of soil remediation technologies will be conducted in the future, which will provide an important theoretical basis for future research on salinity and other soil contaminants following sewage fertilization.

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References

1. Mahmood, A.; Mahmoud, A.H.; El-Abedein, A.I.Z.; Ashraf, A.; Almunqedhi, B.M. A comparative study of metals concentration in agricultural soil and vegetables irrigated by wastewater and tube well water. *J. King Saud Univ. Sci.* **2020**, *32*, 1861–1864. [CrossRef]
2. Murtaza, G.; Javed, W.; Hussain, A.; Wahid, A.; Murtaza, B.; Owens, G. Metal uptake via phosphate fertilizer and city sewage in cereal and legume crops in Pakistan. *Environ. Sci. Pollut. Res.* **2015**, *22*, 9136–9147. [CrossRef]
3. Babak, B.; Madjid, D.; Miklas, S. Response of vegetables to cadmium-enriched soil. *Water* **2014**, *6*, 1246–1256.
4. Chen, H.; Teng, Y.; Lu, S.; Wang, Y.Y.; Wang, J.S. Contamination features and health risks of soil heavy metals in China. *Sci. Total Environ.* **2015**, *512*, 143–153. [CrossRef] [PubMed]
5. Yin, D.; Wang, X.; Peng, B.; Tan, C.; Ma, L.Q. Effect of biochar and Fe-biochar on Cd and As mobility and transfer in soil-rice system. *Chemosphere* **2017**, *186*, 928–937. [CrossRef] [PubMed]
6. Ali, B.; Gill, R.A.; Yang, S.; Gill, M.B.; Farooq, M.A.; Liu, D.; Daud, M.K.; Ali, S.; Zhou, W. Regulation of cadmium-induced proteomic and metabolic changes by 5- aminolevulinic acid in leaves of *Brassica napus* L. *PLoS ONE* **2015**, *10*, e0123328. [CrossRef]
7. Rehman, M.Z.; Rizwan, M.; Ali, S.; Fatima, N.; Yousaf, B.; Naeem, A.; Sabir, M.; Ahmad, H.R.; Ok, Y.S. Contrasting effects of biochar, compost and farm manure on alleviation of nickel toxicity in maize (*Zea mays* L.) in relation to plant growth, photosynthesis and metal uptake. *Ecotoxicol. Environ. Saf.* **2016**, *133*, 218–225. [CrossRef]
8. Wang, L.; Chen, W.; Zhou, W. Assessment of future drought in Southwest China based on CMIP5 multimodel projections. *Adv. Atmos. Sci.* **2014**, *31*, 1035–1050. [CrossRef]
9. Rizwan, M.; Ali, S.; Hussain, A.; Ali, Q.; Shakoor, M.B.; Rehman, M.Z.; Farid, M.; Asma, M. Effect of zinc-lysine on growth, yield and cadmium uptake in wheat (*Triticum aestivum* L.) and health risk assessment. *Chemosphere* **2017**, *187*, 35–42. [CrossRef]
10. Li, Y.; Shen, F.; Guo, H.; Wang, Z.; Yang, G.; Wang, L.; Zhang, Y.; Zeng, Y.; Deng, S. Phytotoxicity assessment on corn stover biochar, derived from fast pyrolysis, based on seed germination, early growth, and potential plant cell damage. *Environ. Sci. Pollut. Res.* **2015**, *22*, 9534–9543. [CrossRef]
11. Roberts, D.A.; Paul, N.A.; Dworjanyn, S.A.; Bird, M.I.; Nys, R.D. Biochar from commercially cultivated seaweed for soil amelioration. *Sci. Rep.* **2015**, *51*, 9665. [CrossRef] [PubMed]
12. Ma, J.Y.; Ni, X.; Huang, Q.Y.; Liu, D.; Ye, Z.Q. Effect of bamboo biochar on reducing grain cadmium content in two contrasting wheat genotypes. *Environ. Sci. Pollut. Res.* **2021**, *28*, 17405–17416. [CrossRef] [PubMed]
13. Liu, Y.X.; Wang, Y.Y.; Lu, H.H.; Lonappan, L.S.; Satinder, K.B.; He, L.L.; Chen, J.Y.; Yang, S.M. Biochar application as a soil amendment for decreasing cadmium availability in soil and accumulation in *Brassica chinensis*. *J. Soils Sediments* **2018**, *18*, 2511–2519. [CrossRef]
14. Kim, H.S.; Kim, K.R.; Kim, H.J.; Yoon, J.H.; Yang, J.E.; Ok, Y.S.; Owens, G.; Kim, K.H. Effect of biochar on heavy metal immobilization and uptake by lettuce (*Lactuca sativa* L.) in agricultural soil. *Environ. Earth Sci.* **2015**, *74*, 1249–1259. [CrossRef]
15. Xu, Z.Y.; Tang, M.; Chen, H.; Ban, Y.H.; Zhang, H.H. Microbial community structure in the rhizosphere of *Sophora viciifolia* grown at a lead and zinc mine of northwest China. *Sci. Total Environ.* **2012**, *435–436*, 453–464. [CrossRef] [PubMed]

16. Irshad, M.A.; Nawaz, R.; Rehman, M.Z.; Imran, M.; Ahmad, M.J.; Ahmad, S.; Inaam, A.; Razzaq, A.; Rizwan, M.; Ali, S. Synthesis and characterization of titanium dioxide nanoparticles by chemical and green methods and their antifungal activities against wheat rust. *Chemosphere* **2020**, *258*, 127352. [CrossRef]
17. Shankar, L.; Raskar, S. Influence of zinc oxide nanoparticles on growth, flowering and seed productivity in onion. *Int. J. Curr. Microbiol. Appl. Sci.* **2014**, *3*, 874–881.
18. Mukherjee, A.; Peralta-Videa, J.R.; Bandyopadhyay, S.; Rico, C.M.; Zhao, L.; Gardea-Torresdey, J.L. Physiological effects of nanoparticulate ZnO in green peas (*Pisum sativum* L.) cultivated in soil. *Metallomics* **2014**, *6*, 132–138. [CrossRef]
19. Rezaei, M.; Abbasi, H. Foliar application of nano-chelate and non-nanochelate of zinc on plant resistance physiological processes in cotton (*Gossipium hirsutum* L.). *Iran. J. Plant Physiol.* **2014**, *4*, 1137–1144.
20. Soliman, A.S.; El-feky, S.A.; Darwish, E. Alleviation of salt stress on *Moringa peregrina* using foliar application of nanofertilizers. *J. Hortic. For.* **2015**, *7*, 36–47.
21. Hussain, A.; Ali, S.; Rizwan, M.; Rehman, M.Z.; Javed, M.R.; Imran, M.; Chatha, S.A.S.; Nazir, R. Zinc oxide nanoparticles alter the wheat physiological response and reduce the cadmium uptake by plants. *Environ. Pollut.* **2018**, *242*, 1518–1526. [CrossRef] [PubMed]
22. Venkatachalam, P.; Jayaraj, M.; Manikandan, R.; Geetha, N.; Rene, E.R.; Sharma, N.C.; Sahi, S.V. Zinc oxide nanoparticles (ZnONPs) alleviate heavy metal-induced toxicity in *Leucaena leucocephala* seedlings: A physiochemical analysis. *Plant Physiol. Biochem.* **2017**, *110*, 59–69. [CrossRef] [PubMed]
23. Bashir, A.; ur Rehman, M.Z.; Hussaini, K.M.; Adrees, M.; Qayyum, M.F.; Sayal, A.U.; Rizwan, M.; Ali, S.; Alsahli, A.A.; Alyemeni, M.N. Combined use of zinc nanoparticles and co-composted biochar enhanced wheat growth and decreased Cd concentration in grains under Cd and drought stress: A field study. *Environ. Technol. Innov.* **2021**, *23*, 101518. [CrossRef]
24. Haripriya, P.; Stella, P.M.; Anusuya, S. Foliar Spray of Zinc Oxide Nanoparticles Improves Salt Tolerance in Finger Millet Crops under Glasshouse Condition. *Sciol Biotechnol.* **2018**, *1*, 20–29.
25. Mallikarjuna, M.G.; Thirunavukkarasu, N.; Hossain, F.; Bhat, J.S.; Jha, S.K.; Rathore, A.; Agrawal, P.K.; Pattanayak, A.; Reddy, S.S.; Gularia, S.K.; et al. Stability performance of inductively coupled plasma mass spectrometry-phenotyped kernel minerals concentration and grain yield in maize in different agro-climatic zones. *PLoS ONE* **2015**, *10*, 0139067.
26. Gupta, H.S.; Hossain, F.; Nepolean, T.; Vignesh, M.; Mallikarjuna, M.G. Understanding genetic and molecular bases of Fe and Zn accumulation towards development of micronutrient-enriched maize. In *Nutrient Use Efficiency: From Basics to Advances*; Rakshit, A., Singh, H., Sen, A., Eds.; Springer India: New Delhi, India, 2015; pp. 255–282.
27. Lichtenthaler, H.K. Chlorophylls and carotenoids-pigments of photosynthetic biomembranes. In *Methods in Enzymology*; Colowick, S.P., Kaplan, N.O., Eds.; Academic Press: San Diego, CA, USA, 1987; Volume 148, pp. 350–382.
28. Dionisio-Sese, M.L.; Tobita, S. Antioxidant responses of rice seedlings to salinity stress. *Plant Sci.* **1998**, *135*, 1–9. [CrossRef]
29. Zou, Q. *Experimental Guidance in Plant Physiology*; China Agricultural Press: Beijing, China, 2000; pp. 161–167.
30. Nakanoy, Y.; Asada, K. Hydrogen peroxide is scavenged by ascorbate-specific peroxidase in spinach chloroplasts. *Plant Cell Physiol.* **1981**, *22*, 867–880.
31. Sharma, P.; Yadav, P.; Ghosh, C.; Singh, B. Heavy Metal Capture from the Suspended Particulate Matter by Morus Alba and Evidence of Foliar Uptake and Translocation of PM Associated Zinc Using Radiotracer (65zn). *Chemosphere* **2020**, *254*, 126863. [CrossRef]
32. Zheljazkov, V.D.; Nielsen, N.E. Effect of Heavy Metals o Peppermint and Cornmint. *Plant Soil* **1996**, *178*, 59–66. [CrossRef]
33. Abbas, T.; Rizwan, M.; Ali, S.; Adrees, M.; Mahmood, A.; Rehman, M.Z.; Ibrahim, M.; Arshad, M.; Qayyum, M.F. Biochar application increased the growth and yield and reduced cadmium in drought stressed wheat grown in an aged contaminated soil. *Ecotoxicol. Environ. Saf.* **2018**, *148*, 825–833. [CrossRef]
34. Bayçu, G.; Gevrek-Kürüm, N.; Moustaka, J.; Csatári, I.; Rognes, S.E.; Moustakas, M. Cadmium-zinc accumulation and photosystem II responses of *Noccaea caerulescens* to Cd and Zn exposure. *Environ. Sci. Pollut. Res.* **2017**, *3*, 2840–2850. [CrossRef] [PubMed]
35. Aujum, S.A.; Tanveer, M.; Hussain, S.; Ullah, E.; Wang, L.C.; Kham, I.; Samad, R.A.; Tung, S.A.; Anam, M.; Shahzad, B. Morpho-physiological growth and yield responses of two contrasting maize cultivars to cadmium exposure. *Clean-Soil Air Water* **2016**, *44*, 29–36.
36. Pullagurala, V.L.R.; Adisa, I.O.; Rawat, S.; Kalagara, S.; Hernandez-Viezcas, J.A.; Peralta-Videa, J.R.; Gardea-Torresdey, J.L. ZnO nanoparticles increase photosynthetic pigments and decrease lipid peroxidation in soil grown cilantro (*Coriandrum sativum*). *Plant Physiol. Biochem.* **2018**, *132*, 120–127. [CrossRef]
37. Dimkpa, C.O.; White, J.C.; Elmer, W.H.; Gardea-Torresdey, J. Nanoparticle and ionic Zn promote nutrient loading of sorghum grain under low NPK fertilization. *J. Agric. Food Chem.* **2017**, *65*, 8552–8559. [CrossRef]
38. Rao, S.; Shekhawat, G.S. Toxicity of ZnO engineered nanoparticles and evaluation of their effect on growth, metabolism and tissue specific accumulation in Brassica juncea. *J. Environ. Chem. Eng.* **2014**, *2*, 105–114. [CrossRef]
39. Huang, G.; Ding, C.; Zhou, Z.; Zhang, T.; Wang, X. A tillering application of zinc fertilizer based on basal stabilization reduces Cd accumulation in rice (*Oryza sativa* L.). *Ecotoxicological Environ. Saf.* **2019**, *167*, 338–344. [CrossRef] [PubMed]
40. Khan, Z.S.; Rizwan, M.; Hafeez, M.; Ali, S.; Javed, M.R.; Adrees, M. The accumulation of cadmium in wheat (*Triticum aestivum*) as influenced by zinc oxide nanoparticles and soil moisture conditions. *Environ. Sci. Pollut. Res.* **2019**, *26*, 19859–19870. [CrossRef]
41. Li, C.; Wang, P.; Lombi, E.; Cheng, M.; Tang, C.; Howard, D.L.; Menzies, N.W.; Kopittke, P.M. Absorption of foliar-applied Zn fertilizers by trichomes in soybean and tomato. *J. Exp. Bot.* **2018**, *69*, 2717–2729. [CrossRef]

42. Read, T.L.; Doolette, C.L.; Li, C.; Schjoerring, J.K.; Kopittke, P.M.; Donner, E.; Lombi, E. Optimising the foliar uptake of zinc oxide nanoparticles: Do leaf surface properties and particle coating affect absorption? *Physiol. Plant* **2020**, *170*, 384–397. [CrossRef]
43. Ditta, A.; Arshad, M. Applications and perspectives of using nanomaterials for sustainable plant nutrition. *Nanotechnol. Rev.* **2016**, *5*, 209–229. [CrossRef]
44. Monreal, C.M.; DeRosa, M.; Mallubhotla, S.C.; Bindraban, P.S.; Dimkpa, C. Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients. *Biol. Fertil. Soils* **2016**, *52*, 423–437. [CrossRef]
45. Seshadri, B.; Bolan, N.S.; Wijesekara, H.; Kunhikrishnan, A.; Thangarajan, R.; Qi, F.; Matheyarasu, R.; Rocco, C.; Mbene, K.; Naidu, R. Phosphorus–cadmium interactions in paddy soils. *Geoderma* **2016**, *270*, 43–59. [CrossRef]
46. Cui, L.Q.; Pan, G.X.; Li, L.Q.; Bian, R.J.; Liu, X.Y.; Yan, J.L.; Quan, G.X.; Ding, C.; Chen, T.M.; Liu, Y.; et al. Continuous immobilization of cadmium and lead in biocharamended contaminated paddy soil: A five-year field experiment. *Ecol. Eng.* **2016**, *93*, 1–8. [CrossRef]
47. Shi, J.; Ye, J.; Fang, H.; Zhang, S.; Xu, C. Effects of Copper Oxide Nanoparticles on Paddy Soil Properties and Compoents. *Nanomater* **2018**, *8*, 839. [CrossRef]
48. Cullen, L.G.; Tilston, E.L.; Mitchell, G.R.; Collins, C.D.; Shaw, L.J. Assessing the impact of nano-and micro-scale zerovalent iron particles on soil microbial activities: Particle reactively interferes with assay conditions and interpretation of genuine microbial effects. *Chemosphere* **2011**, *82*, 1675–1682. [CrossRef]