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Antagonistic effect of polystyrene nanoplastics on cadmium toxicity to maize (*Zea mays* L.)

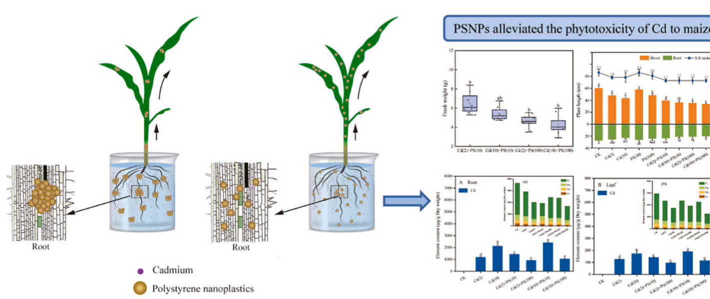
Luya Wang [a,b,1], Bigui Lin [b,d,1], Lin Wu [b,d], Pan Pan [b,d], Beibei Liu [b,d,*], Ruilong Li [c,**]

[a] College of Ecology and Environment, Hainan University, Haikou, 570228, PR China
[b] Environmental and Plant Protection Institute, Chinese Academy of Tropical Agricultural Sciences, Hainan Danzhou Tropical Agro-ecosystem National Observation and Research Station, Key Laboratory of Low-carbon Green Agriculture in Tropical Region of China, Ministry of Agriculture and Rural Affairs, Danzhou, 571737, PR China
[c] School of Marine Sciences, Guangxi University, Nanning, 530004, PR China
[d] Hainan Key Laboratory of Tropical Eco-Circuling Agriculture, Haikou, 571101, PR China

HIGHLIGHTS

- High level polystyrene nanoplastics (PSNPs) brought toxicity to maize.
- PSNPs were transported from roots to leaves by vascular bundles.
- PSNPs alleviated the phytotoxicity of Cd to maize by antagonistic effect.
- PSNPs could act as a container for Cd bioaccumulation.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanoplastics (NPs) (<1 μm) have gradually attracted worldwide attention owing to their widespread occurrence, distribution, and ecosystem risks. Few studies have explored the interaction between NPs and heavy metals in crops. In this study, we investigated the influence of polystyrene nanoplastics (PSNPs; 10 mg/L and 100 mg/L) and cadmium (2 mg/L and 10 mg/L) on the physiological and biochemical indices of maize plants, grown in Hoagland solution with contaminants, for 14 days. The fresh weight and growth of the maize plants were significantly reduced after exposure to high concentrations of PSNPs and Cd ($p < 0.05$). Specifically, the fresh weight decreased by 30.3% and 32.5% in the PSNPs and Cd treatment, respectively. Root length and shoot length decreased by 11.7% and 20.0%, and by 16.3% and 27.8%, in the PSNPs and Cd treatment, respectively. However, there were no significant effects on the fresh weight and growth of maize plants as Cd levels increased from 2 to 10 mg/L in the presence of PSNPs. Polystyrene nanoplastics alleviated the phytotoxicity of Cd in maize. Scanning electron microscopy (SEM) showed that PSNPs and Cd could enter maize roots and were transported upwards to the leaves through the vascular bundle. The activities of peroxidase (POD) and catalase (CAT) in maize leaves increased significantly under high concentrations of PSNPs, whereas superoxide dismutase (SOD) activity decreased ($p < 0.05$). The differences in SOD activity may be related to the absence of microelements

* Corresponding author. Institute of Environment and Plant Protection, Chinese Academy of Tropical Agricultural Sciences, Haikou, 571101, PR China.
** Corresponding author.
E-mail addresses: liubeibei1110@126.com (B. Liu), liruilong@gxu.edu.cn (R. Li).
[1] Co-first author: No. 4 Xueyuan Road, Longhua District, Haikou, Hainan 571101, PR China. linbigui@163.com

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such as Zn, Fe, and Mn. This study provides a scientific basis for further exploration of the combined toxicological effects of heavy metals and NPs on the environment.

1. Introduction

Microplastics (MPs) and nanoplastics (NPs) pollution is an environmental issue worldwide due to their adverse effects on organisms, community structure, and ecosystem function (Lian et al., 2021; Sun et al., 2021). Microplastics and/or NPs are ubiquitous, mainly distributed in terrestrial ecosystems, where the number of plastic particles is estimated to be 4 to 23 times greater than that in the ocean (Dong et al., 2020; Horton et al., 2017). The quantity of plastic particles varies from 10 to 12,560 items/kg in agricultural soils worldwide (Gong et al., 2021).

The toxic and biological effects of NPs are more complex and difficult to address than those of MPs. Nanoplastics have a larger specific surface area and stronger ability to penetrate different biological barriers, increasing their chemical and biological interactions with organisms or contaminants (Gaylarde et al., 2021). Increased bio-chemical interactions also lead to changes in the uptake, transport, and toxicity of NPs (Peng et al., 2020). Plants can take up NPs, even at a very early growth stage. When their diameters are smaller than those of the cell wall pore (3.5–5.0 nm), NPs can penetrate the wall facilitated by the mucous enveloping the root cap (Li et al., 2020a). Nanoparticles can cross the root xylem vessels through the apoplastic spaces of the apical region, which promote their rapid transport in the roots. Alternatively, NPs can enter epidermal cells through endocytosis (Bandmann et al., 2012). Li et al. (2020b) found that lettuce and wheat absorbed 0.2 μm NPs, and Sun et al. (2020) used two fluorescently labelled NPs to verify their absorption in plants. Therefore, it is not accidental for plants to absorb NPs, and they can be present in vegetables and crops. (Huang et al., 2021). Nanoplastics that enter cells accumulate in plants according to their surface charge. Compared with negatively charged NPs, positively charged NPs inhibit photosynthesis and stimulate antioxidant system activity more fully (Sun et al., 2021). Moreover, NPs reduce disease resistance in plants (Huang et al., 2021), and to this end Jiang et al. (2019) indicated that polystyrene nanoplastics (PSNPs) caused more severe oxidative damage and genotoxicity in *Vicia faba*.

Physical interactions, including dispersion, electrostatic interactions, and intermolecular hydrogen bonding, were dominant in the plastic particle absorption process (Liu et al., 2018). For example, oxytetracycline is adsorbed by plastic particles through a hydrogen-bonding mechanism on the plastic surface (Zhang et al., 2018). Cortés-Arriagada (2021) suggested that the external surface of polyethylene terephthalate nanoplastics is nucleophilic, allowing mass transfer, intraparticle diffusion, and the formation of stable compounds through internal and external surface adsorption. Specifically, internal surface absorption is dominated by dispersion effects, while external surface absorption was by electrostatic energies (Cortés-Arriagada, 2021; Gaylarde et al., 2021).

Globally, agroecosystem contamination with heavy metals is a universal phenomenon. Microplastics and nanoplastics are deemed to be loaded with heavy metals through physical adsorption, which may have a strong influence on plant growth and development, as well as on the benign cycle of agroecosystems (Wang et al., 2022). Dong et al. (2020) found that MPs increased arsenic toxicity in rice seedlings; similarly, the absorption and toxicity of Ni and Zn in plants increased in the presence of MPs (Bhagat et al., 2021). Wang et al. (2021) suggested that MPs alleviated the phytotoxicity of Cd to *Vallisneria natans* (Lour.) Hara; however, MPs had no effect on Cu toxicity in marine microalgae *Tetraselmis chuii* (Davarpanah and Guilhermino, 2015). Therefore, it was demonstrated that co-contamination with different heavy metals and MPs would also have different effects.

Cadmium is one of the key heavy metals that can impair plant growth and biomass (Lian et al., 2020b); in addition, the long-term consumption of Cd-rich foods results in cancer (Deng et al., 2021). The co-contamination of MPs and Cd in plants has been well studied (Abbasi et al., 2020; Zong et al., 2021), and it was found that MPs alleviated the phytotoxicity of Cd to plants, but MPs-Cd co-contamination has a greater inhibitory influence on plant growth than single contamination. Given the size of MPs, they are unlikely to translocate to aboveground tissues across the root stomas and are most likely to accumulate at the root surface, forming compounds with root mucilage (Urbina et al., 2020). The co-contamination compounds of MPs and Cd may be concentrated in the plant roots; however, the environmental fate of NPs that adsorb Cd is not yet clearly understood. Owing to the smaller particle size, NPs could carry Cd from roots to shoots, which could allow Cd to spread faster through the plant.

Maize is a widely cultivated crop in China. It is an important feed source for animal husbandry and the breeding industry, and is also an indispensable raw material for the chemical industry. Therefore, we selected maize as our test plant to evaluate the effects of PSNPs and Cd on growth responses, element accumulation, and antioxidant defenses in maize. This study is expected to provide new insights for further elucidation of the toxic and biological effects of NPs and Cd on crops, and has certain reference significance for the ecological risk assessment of NPs in the environment.

2. Materials and methods

2.1. Characterization of polystyrene nanoplastics

Polystyrene nanoplastics were obtained from the Beijing Zhongkeleiming Daojin Technology Co. Ltd (Beijing, China). These PSNPs had smooth spheres with no surface dissociative functional groups, and an average diameter of approximately 25 nm. A Zeta PALS instrument (Brookhaven Instruments Corporation, USA) was used to measure the zeta potential of the PSNPs in ultra-pure water. The PSNPs were negatively charged, with their absolute values ranging from −31 mV to −16 mV.

2.2. Cultivation of maize plants

Maize (*Zea mays* L.) seeds were disinfected with sodium hypochlorite (2%, v/v) and thoroughly rinsed with deionized water after disinfection for 30 min. Subsequently, maize seeds were soaked in distilled water and settled in the dark at 25 °C to germinate synchronously. After budding, healthy maize seedlings were transferred to the nursery substrates filled with nutrient soil for seven days of preculture. Subsequently, as a treatment group, nine homogeneous maize seedlings were transplanted into 3 L of Hoagland solution containing Cd and/or PSNPs. The concentrations of PSNPs and Cd were 10 mg/L and 100 mg/L, and 2 mg/L and 10 mg/L, respectively. The concentrations of PSNPs (10 mg/L) and Cd (2 mg/L) were used because Lian et al. (2020a) found they had an inhibitory effect on plants. Concentrations of PSNPs (100 mg/L) and Cd (10 mg/L) were also selected to explore the impact of high concentrations on plants. The experiment consisted of 10 treatments: a control; four single groups (different concentrations of Cd or PSNPs); four combined groups (different concentrations of Cd and PSNPs), and one additional group that was static for five days in advance (2 mg/L Cd and 10 mg/L PSNPs) as in Lian et al. (2020b). Plants were cultivated under natural light at 25 °C for 14 days, the nutrient solution was replenished every three days, and the physiological indices of the plants were investigated after 14 days of growth.

2.3. Scanning electron microscope

To gain insights into the loci and translocation of PSNPs in the maize seedling stage, we visualized the morphological and quantitative changes in PSNPs in maize seedling roots and leaves. Scanning electron microscopy (SEM) (TM4000, JEOL, Japan) was performed using the method described by Sun et al. (2021). Roots and leaf samples were ground to a powder with liquid nitrogen, covered with gold for 60 s, and observed under a SEM.

2.4. Determination of cadmium and mineral elements

Freeze-dried root and leaf powder (0.2 g) was digested in a microwave with 6 mL concentrated HNO_3 acid (MARS6, CEM, USA). After digestion, the sample volume was fixed at 50 mL, with 10 mL being used for determination. The concentrations of Cd and other mineral elements in the solution were determined using inductively coupled plasma mass spectrometry (ICP-MS) (PE NexION, PerkinElmer, USA).

2.5. Determination of antioxidant enzymes and malondialdehyde content

Maize leaves (0.2 g) were ground to a powder with liquid nitrogen and homogenized in 2 mL of PBS buffer. The homogenates were centrifuged for 30 min to obtain supernatants, which were used as crude enzyme extracts for enzyme activity determination. The activities of peroxidase (POD), superoxide dismutase (SOD), and catalase (CAT), as well as the malondialdehyde (MDA) content in maize leaves, were determined using the method described by Lian et al. (2020b). Leaves (0.2 g) were homogenized in 2 mL of 0.1% (w/v) trichloroacetic acid (TCA) and centrifuged for 20 min. The supernatant was mixed with 0.5% (w/v) thiobarbituric acid (TBA), heated in a water bath for 30 min, refrigerated to room temperature, and centrifuged again under the same conditions. Absorbance at 532 and 600 nm was recorded.

2.6. Statistical analysis

All experiments were replicated at least three times, and data are expressed as mean ± standard deviation (SD). Data were processed using SPSS 26 and Origin 2018 software. A one-way ANOVA was used to analyze significant differences ($p < 0.05$) among the data sets, followed by Duncan's post-hoc test.

3. Results

3.1. Fresh weight and growth of maize plants

The fresh weight of maize plants decreased after exposure to Cd or PSNPs alone, decreasing by 23.9% and 19.2% on average, respectively (Fig. 1A). In particular, the fresh weight decreased by 30.3% with the addition of 100 mg/L PSNPs. This addition decreased the fresh weight relative to the fresh weight without PSNPs addition. However, no significant decrease in the fresh weight of maize plants was found with an increase in Cd concentration from 2 mg/L to 10 mg/L in the presence of equal concentrations of PSNPs (Fig. 1B). The root and shoot lengths of maize plants were significantly inhibited by 10 mg/L Cd or 100 mg/L PSNPs ($p < 0.05$). The inhibition ratios of root length and shoot length reached 16.3% and 11.7%, and 27.8% and 20.0%, respectively (Fig. 2). When the Cd concentration increased from 2 mg/L to 10 mg/L, root and

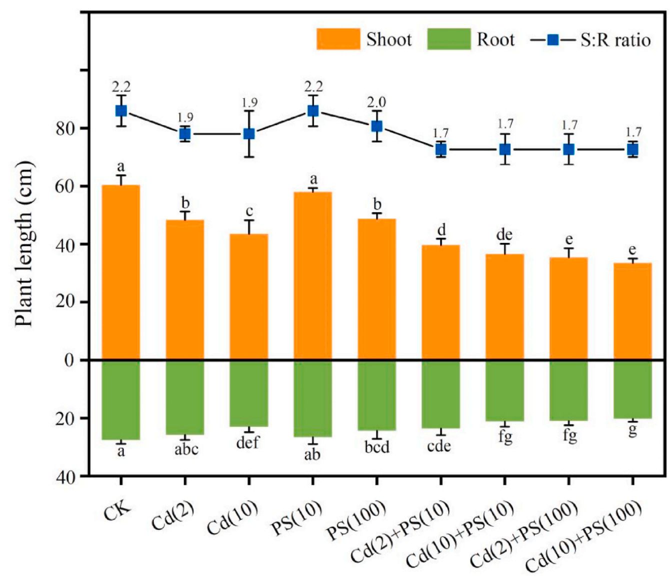

Fig. 2. Length of maize roots and shoots among the different treatment groups. Values are the mean values and SD error bars. Different letters indicate significant differences in results; the same letters indicate non-significant differences in results ($p < 0.05$). CK: Control; Cd(2): 2 mg/L Cd; Cd(10): 10 mg/L Cd; PS(10): 10 mg/L PSNPs; PS(100): 100 mg/L PSNPs.

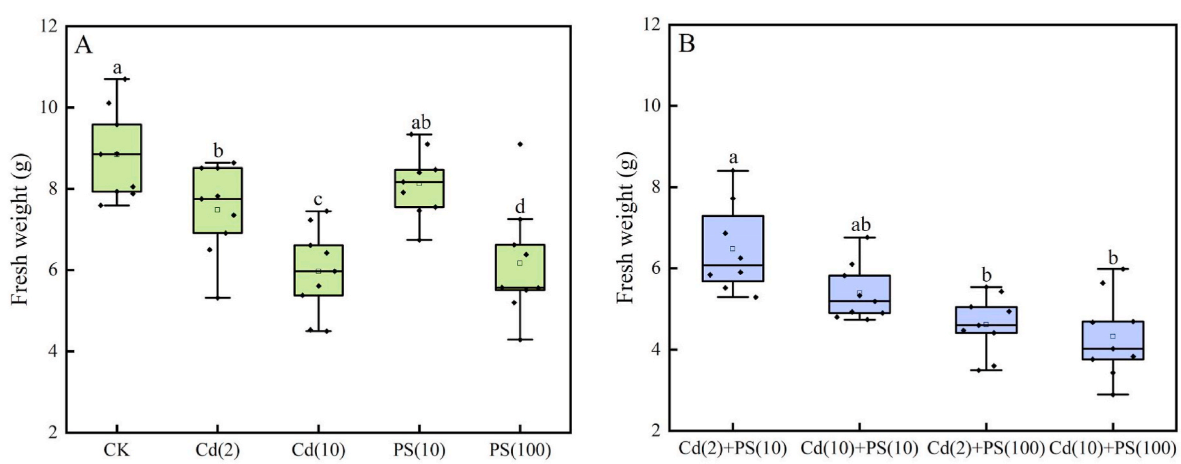

Fig. 1. Responses of fresh weight of maize seedlings to polystyrene nanoplastics (PSNPs) and Cd exposure levels, including single groups (A) and combined groups (B). Boxplots exhibited the max, upper quartile, median, lower quartile, min, mean, and whiskers showed the range of variation. Different letters indicate significant differences in results; the same letters indicate non-significant differences in results ($p < 0.05$). CK: Control; Cd(2): 2 mg/L Cd; Cd(10): 10 mg/L Cd; PS(10): 10 mg/L PSNPs; PS(100): 100 mg/L PSNPs.

shoot lengths did not decrease significantly in the presence of equal concentrations of PSNPs. The S:R ratio decreased slightly and was approximately 1.7.

3.2. Cadmium and mineral nutrient element accumulation in maize plants

The Cd and mineral nutrient element contents were measured in maize roots and leaves across all treatments. The Cd content in the roots was much higher than that in the leaves (Fig. 3A and B). In maize roots, the Cd content was 1204.4 ± 9.8 μg/g after exposure to 2 mg/L Cd, and 1440.1 ± 9.0 μg/g after exposure to Cd-PSNPs combined (2 mg/L Cd + 10 mg/L PSNPs), which increased significantly by 19.6% compared with 2 mg/L Cd ($p < 0.05$). After exposure to Cd-PSNPs combined (2 mg/L Cd + 100 mg/L PSNPs), the Cd content was 608.7 ± 2.7 μg/g, which decreased significantly by 49.5% compared with the experiment using 2 mg/L Cd alone ($p < 0.05$).

Similarly, in maize leaves, the Cd content was 128.7 ± 1.7 μg/g after exposure to 2 mg/L Cd, and 143.4 ± 3.2 μg/g after exposure to Cd-PSNPs combined (2 mg/L Cd + 10 mg/L PSNPs), which increased significantly by 11.4% compared with exposure to 2 mg/L Cd alone ($p < 0.05$). After exposure to Cd-PSNPs combined (2 mg/L Cd + 100 mg/L PSNPs), the Cd content was 90.3 ± 1.5 μg/g, which decreased significantly by 29.8% compared with exposure to 2 mg/L Cd alone ($p < 0.05$). When the Cd concentration was 10 mg/L, the pattern was consistent with that at 2 mg/L.

In addition, the mineral nutrient content in the maize roots was also higher than that in the leaves (Fig. 3A and B). As the concentration of Cd increased, the mineral nutrient element content decreased. Notably, the mineral nutrient element content in the plants decreased significantly when 100 mg/L PSNPs was added ($p < 0.05$).

3.3. The loci and translocation of PSNPs in maize plants

Maize roots are densely packed with rounded pores, whereas the leaves have elongated tubular channels (Fig. 4A and B). In maize roots, PSNPs were found in stomas, whereas in the leaves, they were in the vascular bundle. Specifically, the distribution of PSNPs in the roots and leaves was relatively dispersed after the 10 mg/L PSNPs treatment (Fig. 4C and D). However, PSNPs aggregated in the maize roots and leaves after treatment with 100 mg/L PSNPs (Fig. 4E and F).

3.4. Antioxidant enzyme activity and MDA content

Peroxidase (POD), catalase (CAT), and superoxide dismutase (SOD) enzyme activities, and the malondialdehyde (MDA) content of maize leaves were both affected by Cd and PSNPs (Fig. 5A, B, C, and D). Peroxidase enzyme activity in maize leaves increased significantly after exposure to Cd or PSNPs alone, and more than doubled after exposure to 10 mg/L Cd; therefore, POD enzyme activity was more strongly affected by Cd than by PSNPs. Catalase enzyme activity in maize leaves increased significantly with increasing Cd concentrations ($p < 0.05$), and the addition of PSNPs increased CAT enzyme activity in maize leaves relative to those without PSNPs. However, there was no difference between the 10 mg/L and 100 mg/L PSNPs treatment groups. Superoxide dismutase enzyme activity in maize leaves increased slightly when maize plants were exposed to Cd or 10 mg/L PSNPs alone, but there was no significant difference among the different treatments ($p < 0.05$). Surprisingly, SOD enzyme activity was significantly reduced when 100 mg/L PSNPs were added. For example, the activities of POD and CAT in maize leaves increased by 32.9% and 28.6%, respectively, after exposure to 100 mg/L PSNPs alone, whereas SOD activity decreased by 9.6%. The MDA content in maize leaves exhibited a slightly increasing trend with increasing pollutant concentrations. In the presence of PSNPs and 10 mg/L Cd, MDA increased significantly compared to the control, by 41.8% and 47.7%, respectively.

4. Discussion

4.1. Inhibition effects under PSNPs exposure

This study indicated that high concentrations of PSNPs (100 mg/L) had a remarkable inhibitory effect on the fresh weight, root length, and shoot length of maize plants in the Cd-free microcosm (Figs. 1A and 2). This inhibition may be related to the aggregation of PSNPs in the maize plants (Fig. 4E and F). A similar phenomenon was observed in other studies in which NPs aggregated in microalgae (Li et al., 2015), directly affecting their bioavailability and toxicity. Aggregated NPs would cover the cell surface, suppress nutrient utilization and exchange, and result in substantial cell apoptosis such as contraction, rupture, and separation (Wu et al., 2019; Yang et al., 2021). The excessive accumulation of reactive oxygen species (ROS) resulting from PSNPs destroys chloroplast structure, inhibits photosynthetic activity, and leads to a decline in chlorophyll content (Lian et al., 2021). The most severe form of oxidative stress is DNA damage (Yang et al., 2021) which directly interferes

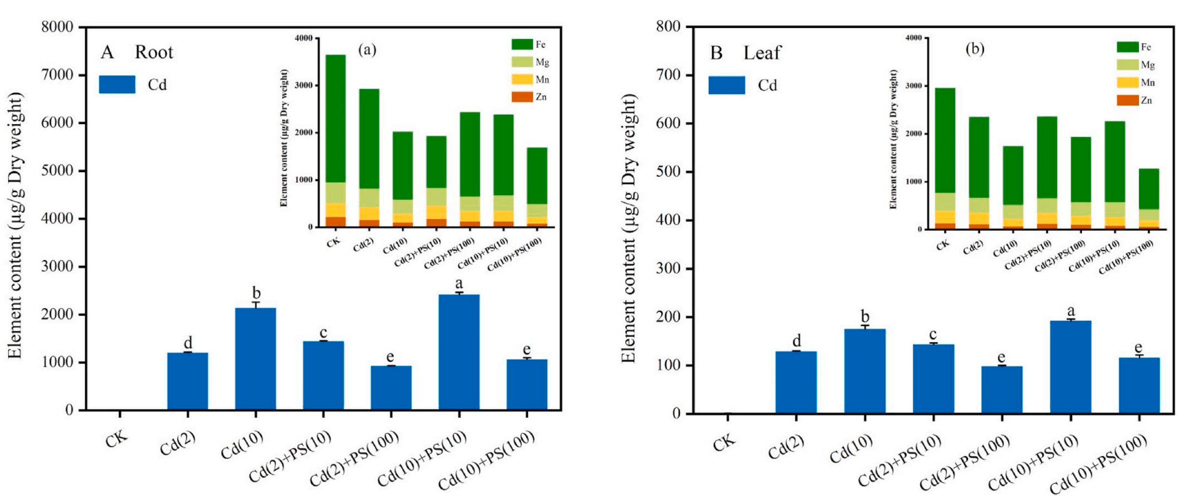

Fig. 3. Content of Cd and other mineral nutrient elements in maize roots (A, a) and leaves (B, b) among the different treatment groups. Values are the mean values and SD error bars. Different letters indicate significant differences in results; the same letters indicate non-significant differences in results ($p < 0.05$). CK: Control; Cd (2): 2 mg/L Cd; Cd(10): 10 mg/L Cd; PS(10): 10 mg/L PSNPs; PS(100): 100 mg/L PSNPs.

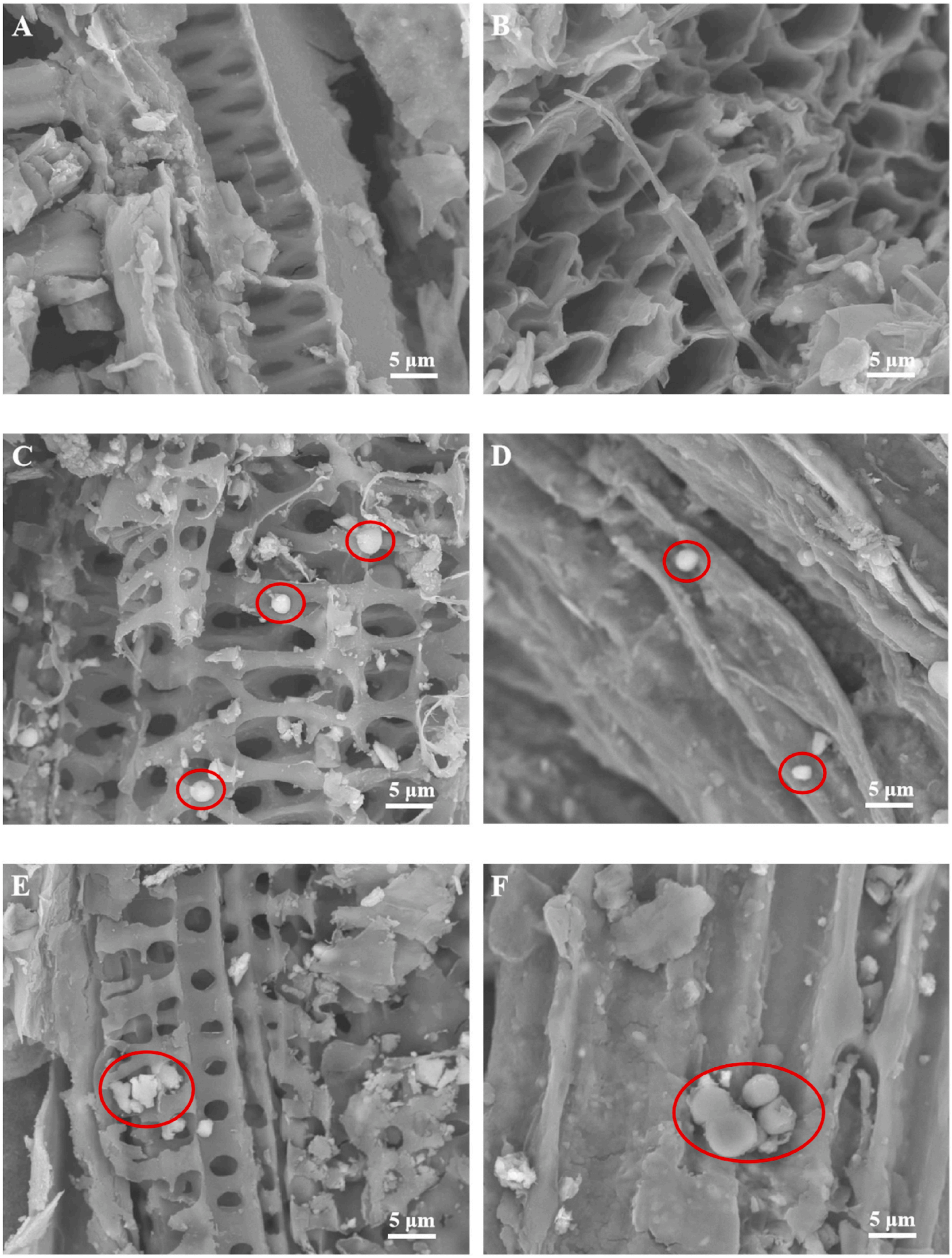

Fig. 4. SEM images of PSNPs distribution on root and leaf surfaces after 14 days of exposure. The left column shows the roots and the right column shows the leaves. CK (A, B); 10 mg/L PSNPs treatment (C, D); 100 mg/L PSNPs treatment (E, F). The red circle represents the PSNPs.

with DNA synthesis, repair, and photosynthesis in maize. Disordered photosynthesis seems to be responsible for the decrease in the maize S:R ratio; however, soluble sugar, the main product of photosynthesis, is highly sensitive to external stress, which affects the supply of carbohydrates from source to end (Li et al., 2020c). In general, plant biomass declines when the energy consumed by the decomposition of soluble sugars exceeds the energy accumulated by the substrate (Li et al., 2020c).

Low concentrations of PSNPs (10 mg/L) inhibited the fresh weight, root length, and stem length of maize, but this was not significant, which may be explained by the plant's detoxification mechanisms. Plants detoxify by accommodating intracellular osmotic pressure, degrading

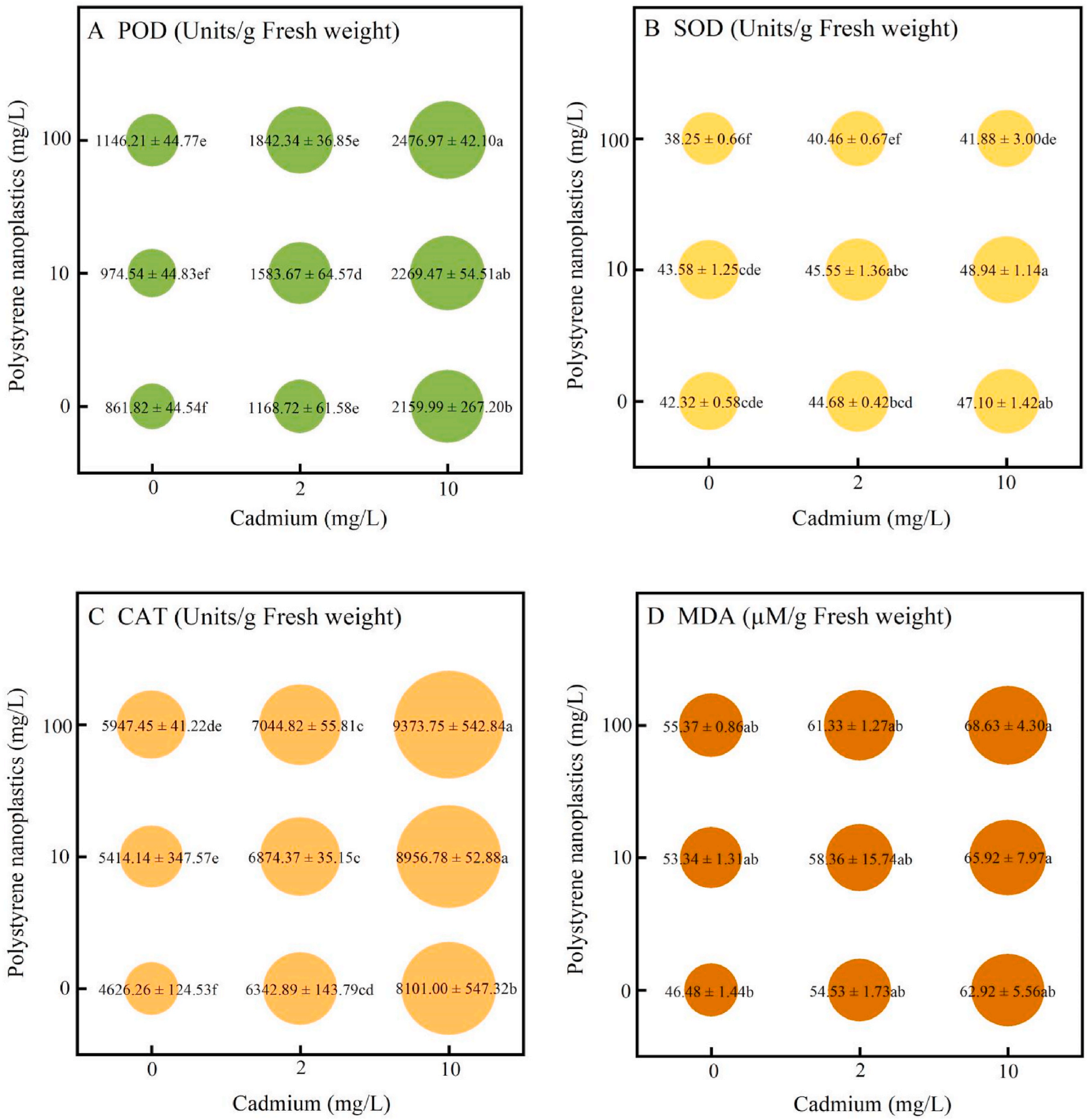

Fig. 5. POD (A), SOD (B), and CAT (C) activity and MDA content (D) in maize leaves after exposure to Cd or PSNPs. In the bubble plot, the areas of the circles represent mean ± SD. Different letters indicate significant differences in results; the same letters indicate non-significant differences in results ($p < 0.05$).

impaired proteins and organs, and promoting cell proliferation (Yang et al., 2021). In conclusion, plants can withstand the harmful effects of low concentrations of PSNPs.

4.2. Polystyrene nanoplastics alleviated the phytotoxicity of Cd to maize

In the microcosm without PSNPs, the fresh weight, root length, and shoot length of maize plants showed a downward trend with increasing Cd concentrations (Figs. 1A and 2). This is because Cd ions entering plants can reduce chlorophyll content and antioxidant enzyme activity and change the permeability of cell membranes, resulting in the inhibition of plant growth and even death (Li et al., 2021). Cadmium replaces magnesium in chlorophyll molecule synthesis, which is one of the reasons for the reduction in chlorophyll content (Grajek et al., 2020). However, the growth of maize plants was not affected by the increase in Cd concentration in the presence of PSNPs (Figs. 1B and 2).

High concentrations of PSNPs (100 mg/L) alleviated the phytotoxicity of Cd in maize, which was associated with a reduction in the uptake of Cd (Fig. 3). The abundant negatively charged PSNPs adsorbed Cd through electrostatic action, leading to a substantial reduction in the cations in the solution. Owing to a decrease in electrostatic repulsion, PSNPs rapidly aggregate and wrap Cd in the polymer (Gaylarde et al., 2021; Ma et al., 2014). The SEM images (Fig. 4) show that PSNPs were distributed in the stomata and vascular bundles. The potential pathway for PSNPs reaching plants is by entering the root system through the stomatal pathway, and then transferring upward through vascular bundles to the leaves under the action of transpirational pull (Wu et al., 2021). The same uptake pathway has also been observed for copper oxide nanoparticle internalization into lettuce and cabbage bodies (Xiong et al., 2017). Therefore, some PSNP polymers carrying Cd accumulate on the root surfaces due to their size, and compete for adsorption sites with Cd^{2+} in solution (Dong et al., 2020).

Nevertheless, there was no aggregation effect at low concentrations of PSNPs (10 mg/L), and the distribution of PSNPs in the maize plant roots and leaves was relatively dispersed (Fig. 4C and D). A possible mechanism of alleviation is that PSNPs act as containers for Cd bioaccumulation (Yang et al., 2014). When Cd-loaded PSNPs enter plants, this leads to a higher Cd content in the PSNP-Cd treatment than in the Cd treatment alone (Fig. 3). Polystyrene nanoplastics form stable compounds with Cd over time through internal and external surface adsorption, reducing the toxicity and fluidity of Cd (Cortés-Arriagada, 2021; Yang et al., 2014); this results in a high Cd content in plants which does not inhibit their growth and development. To verify this, we added a group as follows: the 2 mg/L Cd and 10 mg/L PSNPs were static for five days in advance to allow them to form a stable compound, while the other conditions remained the same. The results showed that as the fresh weight, root length, and shoot length increased, the Cd content showed little change when compared with the Cd-PSNPs combined (2 mg/L Cd and 10 mg/L PSNPs) without being kept static for five days in advance (Fig. 6), as expected.

4.3. Changes to antioxidant enzymes and malondialdehyde content

Plants have highly efficient antioxidant systems that counteract ROS toxicity (Li et al., 2015). Lai and Luo (2019) suggest that the enhanced antioxidant enzyme system in Indian mustard (*Brassica juncea* L.) contributes to the elimination of excess ROS. Except for SOD activity, POD and CAT activities were enhanced in all treatments compared with the control (Fig. 5). These results suggest that Cd and PSNPs directly induce oxidative stress in maize. Discrepancies in enzyme activities are probably dependent on plant habitat, plant species, trace elements of synthase in plants, and experimental dose (Lian et al., 2020b; Wang et al., 2021). The decreased SOD activity might be related to the reduction in Zn, Fe, and Mn content (key microelements for the synthesis of SOD enzymes (Lian et al., 2021) when PSNPs were added at a high concentration (100 mg/L) (Fig. 3). Malondialdehyde is one of the main products of membrane lipid peroxidation and reflects the intensity of membrane lipid peroxidation as well as the degree of damage to the plasma membrane (Shen et al., 2018). A gradual increase in MDA content indicated slight damage to the plant cell membrane, whereas MDA increased significantly in the presence of PSNPs only at 10 mg/L Cd (Fig. 5D). These results demonstrate that Cd did not interact with PSNPs to further aggravate membrane lipid peroxidation damage, unless exposed to 10 mg/L Cd.

5. Conclusion

This study found that both PSNPs and Cd inhibited the growth of maize plants as well as inducing oxidative stress; however, PSNPs alleviated the phytotoxicity of Cd to maize through an antagonistic effect. High-concentration PSNPs (100 mg/L) aggregated and accumulated on the root surfaces, while Cd was wrapped in the PSNPs polymer matrix, which reduced the Cd content of the solution. Low concentrations of PSNPs (10 mg/L) were used as containers for Cd bioaccumulation in maize. The PSNPs formed stable compounds with dissociative Cd through internal and external surface adsorption, reducing the toxicity and fluidity of Cd. Polystyrene nanoplastics and Cd entered the root system through the stomatal pathway and were then transferred upward through vascular bundles to the leaves. Moreover, the activities of POD and CAT in maize leaves increased by 32.9% and 28.6%, respectively, after exposure to 100 mg/L PSNPs alone, whereas SOD activity decreased by 9.6%. The discrepancies in SOD activity may be related to the absence of microelements such as Zn, Fe, and Mn. In conclusion, our study provides a scientific basis for estimating the toxicological effects of NPs and Cd on crops.

Author contributions statement

Wang designed the contents and ideas of this study. Lin calculated the data and analyzed the results. LiuWu, Pan, and Li revised and improved the quality of the research. All authors have reviewed the manuscript

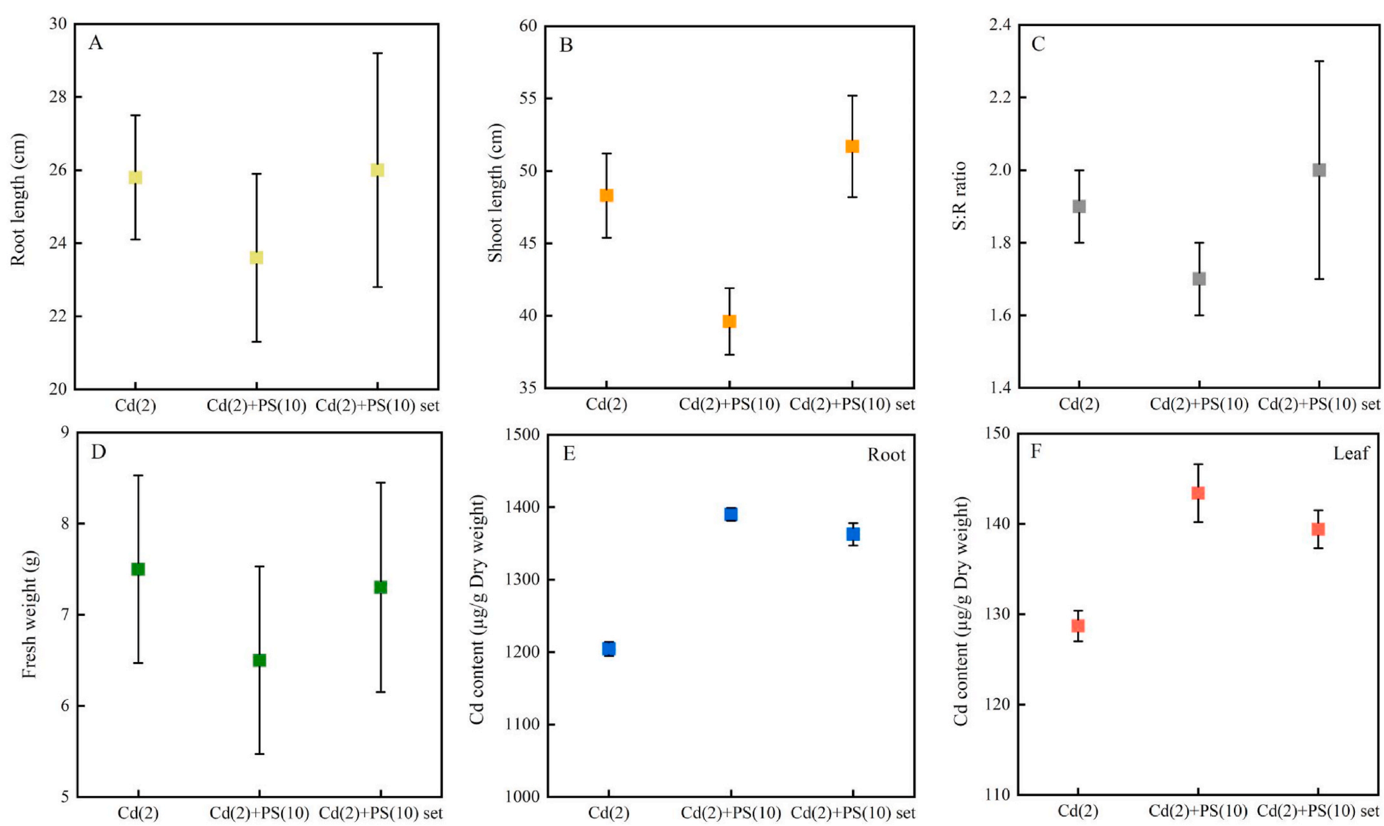

Fig. 6. Effects of adsorption equilibrium on root length (A), shoot length (B), S:R ratio (C), fresh weight (D), Cd content in roots (E), and Cd content in leaves (F) of maize plants. Cd(2):2 mg/L Cd; PS(10):10 mg/L PSNPs; Cd(2)+PS(10) set: one group was static for five days in advance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

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References

Abbasi, S., Moore, F., Keshavarzi, B., Hopke, P.K., Naidu, R., Rahman, M.M., Oleszczuk, P., Karimi, J., 2020. PET-microplastics as a vector for heavy metals in a simulated plant rhizosphere zone. Sci. Total Environ. 744, 140984.

Bandmann, V., Müller, J.D., Köhler, T., Homann, U., 2012. Uptake of fluorescent nano beads into BY2-cells involves clathrin-dependent and clathrin-independent endocytosis. FEBS (Fed. Eur. Biochem. Soc.) Lett. 586 (20), 3626–3632.

Bhagat, J., Nishimura, N., Shimada, Y., 2021. Toxicological interactions of microplastics/nanoplastics and environmental contaminants: current knowledge and future perspectives. J. Hazard Mater. 405, 123913.

Cortés-Arriagada, D., 2021. Elucidating the co-transport of bisphenol A with polyethylene terephthalate (PET) nanoplastics: a theoretical study of the adsorption mechanism. Environ. Pollut. 270, 116192.

Davarpanah, E., Guilhermino, L., 2015. Single and combined effects of microplastics and copper on the population growth of the marine microalgae *Tetraselmis chuii*. Estuar. Coast Shelf Sci. 167, 269–275.

Deng, M., Malik, A., Zhang, Q., Sadeghpour, A., Zhu, Y., Li, Q., 2021. Improving Cd risk managements of rice cropping system by integrating source-soil-rice-human chain for a typical intensive industrial and agricultural region. J. Clean. Prod. 313, 127883.

Dong, Y., Gao, M., Song, Z., Qiu, W., 2020. Microplastic particles increase arsenic toxicity to rice seedlings. Environ. Pollut. 259, 113892.

Gaylarde, C.C., Baptista Neto, J.A., da Fonseca, E.M., 2021. Nanoplastics in aquatic systems-are they more hazardous than microplastics? Environ. Pollut. 272, 115950.

Gong, W., Zhang, W., Jiang, M., Li, S., Liang, G., Bu, Q., Xu, L., Zhu, H., Lu, A., 2021. Species-dependent response of food crops to polystyrene nanoplastics and microplastics. Sci. Total Environ. 796, 148750.

Grajek, H., Rydzyński, D., Piotrowicz-Cieślak, A., Herman, A., Maciejczyk, M., Wieczorek, Z., 2020. Cadmium ion-chlorophyll interaction-Examination of spectral properties and structure of the cadmium-chlorophyll complex and their relevance to photosynthesis inhibition. Chemosphere 261, 127434.

Horton, A.A., Walton, A., Spurgeon, D.J., Lahive, E., Svendsen, C., 2017. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. Sci. Total Environ. 586, 127–141.

Huang, D., Tao, J., Cheng, M., Deng, R., Chen, S., Yin, L., Li, R., 2021. Microplastics and nanoplastics in the environment: macroscopic transport and effects on creatures. J. Hazard Mater. 407, 124399.

Jiang, X., Chen, H., Liao, Y., Ye, Z., Li, M., Klobučar, G., 2019. Ecotoxicity and genotoxicity of polystyrene microplastics on higher plant *Vicia faba*. Environ. Pollut. 250, 831–838.

Lai, J., Luo, X., 2019. High-efficiency antioxidant system, chelating system and stress-responsive genes enhance tolerance to cesium ionotoxicity in Indian mustard (*Brassica juncea* L.). Ecotoxicol. Environ. Saf. 181, 491–498.

Li, J., Hu, L., Zhang, L., Pan, X., Hu, X., 2015. Exogenous spermidine is enhancing tomato tolerance to salinity-alkalinity stress by regulating chloroplast antioxidant system and chlorophyll metabolism. BMC Plant Biol. 15 (1), 303–320.

Li, L., Luo, Y., Li, R., Zhou, Q., Peijnenburg, W.J.G.M., Yin, N., Yang, J., Tu, C., Zhang, Y., 2020a. Effective uptake of submicrometre plastics by crop plants via a crack-entry mode. Nat. Sustain. 3 (11), 929–937.

Li, S., Wang, P., Zhang, C., Zhou, X., Yin, Z., Hu, T., Hu, D., Liu, C., Zhu, L., 2020b. Influence of polystyrene microplastics on the growth, photosynthetic efficiency and aggregation of freshwater microalgae *Chlamydomonas reinhardtii*. Sci. Total Environ. 714, 136767.

Li, Z., Li, R., Li, Q., Zhou, J., Wang, G., 2020c. Physiological response of cucumber (*Cucumis sativus* L.) leaves to polystyrene nanoplastics pollution. Chemosphere 255, 127041.

Li, C., Zhang, T., Feng, P., Li, D., Brestic, M., Liu, Y., Yang, X., 2021. Genetic engineering of glycinebetaine synthesis enhances cadmium tolerance in BADH-transgenic tobacco plants via reducing cadmium uptake and alleviating cadmium stress damage. Environ. Exp. Bot. 191, 104602.

Lian, J., Liu, W., Meng, L., Wu, J., Chao, L., Zeb, A., Sun, Y., 2021. Foliar-applied polystyrene nanoplastics (PSNPs) reduce the growth and nutritional quality of lettuce (*Lactuca sativa* L.). Environ. Pollut. 280, 116978.

Lian, J., Wu, J., Xiong, H., Zeb, A., Yang, T., Su, X., Su, L., Liu, W., 2020a. Impact of polystyrene nanoplastics (PSNPs) on seed germination and seedling growth of wheat (*Triticum aestivum L.*). J. Hazard Mater. 385, 121620.

Lian, J., Wu, J., Zeb, A., Zheng, S., Ma, T., Peng, F., Tang, J., Liu, W., 2020b. Do polystyrene nanoplastics affect the toxicity of cadmium to wheat (*Triticum aestivum L.*)? Environ. Pollut. 263, 114498.

Liu, T., Jiao, C., Peng, X., Chen, Y., Chen, Y., He, C., Liu, R., Wang, H., 2018. Super-strong and tough poly(vinyl alcohol)/poly(acrylic acid) hydrogels reinforced by hydrogen bonding. J. Mater. Chem. B 6 (48), 8105–8114.

Ma, S., Zhou, K., Yang, K., Lin, D., 2014. Heteroagglomeration of oxide nanoparticles with algal cells: effects of particle type, ionic strength and pH. Environ. Sci. Technol. 49 (2), 932–939.

Peng, L., Fu, D., Qi, H., Lan, C.Q., Yu, H., Ge, C., 2020. Micro- and nano-plastics in marine environment: source, distribution and threats-A review. Sci. Total Environ. 698, 134254.

Shen, X., Li, R., Chai, M., Cheng, S., Niu, Z., Qiu, G., 2018. Interactive effects of single, binary and trinary trace metals (lead, zinc and copper) on the physiological responses of *Kandelia obovata* seedlings. Environ. Geochem. Health 41 (1), 135–148.

Sun, H., Lei, C., Xu, J., Li, R., 2021. Foliar uptake and leaf-to-root translocation of nanoplastics with different coating charge in maize plants. J. Hazard Mater. 416, 125854.

Sun, X., Yuan, X., Jia, Y., Feng, L., Zhu, F., Dong, S., Liu, J., Kong, X., Tian, H., Duan, J., Ding, Z., Wang, S., Xing, B., 2020. Differentially charged nanoplastics demonstrate distinct accumulation in *Arabidopsis thaliana*. Nat. Nanotechnol. 15 (9), 755–760.

Urbina, M.A., Correa, F., Aburto, F., Ferrio, J.P., 2020. Adsorption of polyethylene microbeads and physiological effects on hydroponic maize. Sci. Total Environ. 741, 140216.

Wang, H., Ma, L., Zhu, D., Ding, J., Li, G., Jin, B., Shao, Y., Zhang, W., Song, M., Fu, S., 2022. Responses of earthworm *Metaphire vulgaris* gut microbiota to arsenic and nanoplastics contamination. Sci. Total Environ. 806, 150279.

Wang, L., Gao, Y., Jiang, W., Chen, J., Chen, Y., Zhang, X., Wang, G., 2021. Microplastics with cadmium inhibit the growth of *Vallisneria natans* (Lour.) Hara rather than reduce cadmium toxicity. Chemosphere 266, 128979.

Wu, X., Lu, J., Du, M., Xu, X., Beiyuan, J., Sarkar, B., Bolan, N., Xu, W., Xu, S., Chen, X., Wu, F., Wang, H., 2021. Particulate plastics-plant interaction in soil and its implications: a review. Sci. Total Environ. 792, 148337.

Wu, Y., Guo, P., Zhang, X., Zhang, Y., Xie, S., Deng, J., 2019. Effect of microplastics exposure on the photosynthesis system of freshwater algae. J. Hazard Mater. 374, 219–227.

Xiong, T., Dumat, C., Dappe, V., Vezin, H., Schreck, E., Shahid, M., Pierart, A., Sobanska, S., 2017. Copper oxide nanoparticle foliar uptake, phytotoxicity, and consequences for sustainable urban agriculture. Environ. Sci. Technol. 51, 5242–5251.

Yang, W., Wang, Y., Huang, B., Wang, N., Wei, Z., Luo, J., Miao, A., Yang, L., 2014. TiO_2 nanoparticles act as a carrier of Cd bioaccumulation in the ciliate *Tetrahymena thermophila*. Environ. Sci. Technol. 48 (13), 7568–7575.

Yang, W., Gao, P., Li, H., Huang, J., Zhang, Y., Ding, H., Zhang, W., 2021. Mechanism of the inhibition and detoxification effects of the interaction between nanoplastics and microalgae *Chlorella pyrenoidosa*. Sci. Total Environ. 783, 146919.

Zhang, Q., Qu, Q., Lu, T., Ke, M., Zhu, Y., Zhang, M., Zhang, Z., Du, B., Pan, X., Sun, L., Qian, H., 2018. The combined toxicity effect of nanoplastics and glyphosate on *Microcystis aeruginosa* growth. Environ. Pollut. 243, 1106–1112.

Zong, X., Zhang, J., Zhu, J., Zhang, L., Jiang, L., Yin, Y., Guo, H., 2021. Effects of polystyrene microplastic on uptake and toxicity of copper and cadmium in hydroponic wheat seedlings (*Triticum aestivum* L.). Ecotoxicol. Environ. Saf. 217, 112217.