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Influence of Microplastics on the Root-Soil Interfacial Migration of Polycyclic Aromatic Hydrocarbons in Soil: Insights from Particle Size, pH, and Dissolved Organic Matter

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Abstract:

The co-contamination of microplastics (MPs) and polycyclic aromatic hydrocarbons (PAHs) in agricultural soils has emerged as a critical environmental concern. However, the mechanistic understanding of MP-mediated PAH migration at the root–soil interface under varying environmental conditions remains limited, constraining accurate ecological risk assessment. In this study, polyethylene (PE) and polystyrene (PS) MPs were selected as model particles, and pot experiments were conducted with Chinese pak choi to systematically investigate the effects of MP particle size, soil pH, and dissolved organic matter on the root–soil interfacial migration of PAHs. The bioaccumulation and translocation capacity of PAHs in pak choi and the associated health risks were comprehensively evaluated. The results demonstrated that both PE and PS MPs reduced PAH uptake by pak choi, with PS MPs exhibiting a more pronounced inhibitory effect. Under varying pH conditions, total PAH concentrations in pak choi cultivated in PS

MPs-amended soils decreased by 70.6%–87.1% relative to the control, whereas reductions in PE MP treatments ranged from 11.9% to 53.1%. The particle size of MPs exerted a non-monotonic influence on PAH phytoavailability: the lowest PAH accumulation in pak choi was observed at 50 μm (PS: 4805.2 $ng \cdot kg^{-1}$; PE: 5324.4 $ng \cdot kg^{-1}$), whereas elevated accumulation at 0.8 μm. Soil pH modulated MP adsorption capacity by altering surface charge characteristics: PS MPs exhibited maximum PAH sorption at pH 7 corresponding to minimal plant uptake, whereas PE MPs showed optimal sorption at pH 5. The influence of DOM was MP-type dependent: DOM enhanced PAH solubility and plant availability in control and PE MP treatments, whereas in PS MPs-amended soils, DOM and PS MPs synergistically strengthened PAH immobilization via π–π interactions, thereby suppressing PAH translocation into pak choi. Health risk assessment revealed that PS MPs treatment reduced the total PAH concentration and the BaP-equivalent toxicity (TEQBaP) of pak choi relative to the controls. This indicates that PS MPs attenuated the toxicological burden associated with PAH accumulation under the experimental conditions. These findings highlight the critical importance of considering MP polymer type, particle size distribution, and interactive environmental factors in assessing PAH ecological risks in agricultural systems.

Keywords: Microplastics; Root-soil interface; Migration behavior; Polycyclic aromatic hydrocarbons; Health risk

1. Introduction

The large-scale application of agricultural plastic film has significantly enhanced crop yields and agricultural economic returns; however, the issue of plastic film residue has become increasingly severe. Owing to the high stability of plastic materials, they can persist in the natural environment for centuries before complete degradation; moreover, through prolonged weathering, ultraviolet radiation and mechanical abrasion, large plastic debris is further fragmented into MPs (Singh et al. 2021). MPs are generally

defined as plastic particles or fragments with a size smaller than 5 mm, characterised by a large specific surface area and strong hydrophobicity, which enable their long-term occurrence in soil and their function as effective carriers for various persistent organic pollutants (Ihenetu et al. 2025). The sources of MPs in agricultural soils are diverse, including plastic film residue, sewage sludge application, surface water irrigation, and atmospheric deposition (Tang 2023). Once introduced into soil, MPs not only alter the physicochemical properties and structure of the soil, but also, owing to their strong adsorption affinity, significantly affect the environmental fate and ecological risks of coexisting organic pollutants (Chen et al. 2024; Wahl et al. 2021). PAHs are a group of ubiquitous persistent organic pollutants in soil environments, exhibiting carcinogenic, teratogenic, and mutagenic effects, and can enter the food chain through plant uptake, thus posing potential threats to human health. The transport behaviour of PAHs at the root–soil interface is particularly critical for their plant uptake and accumulation (Zhao et al. 2020; Zhao et al. 2026). Studies have demonstrated that MPs can act as a more important “sink” for PAHs than soil organic matter, exhibiting strong sorption capacity for PAHs and thereby significantly influencing their transport, distribution, and ultimate fate in soil (Li et al. 2025; Luo et al. 2026). Wang and Wang (2018) compared the sorption capacity of PE MPs and natural clay for phenanthrene using partition coefficients (Kd), confirming that the hydrophobic surface of MPs endows them with a sorption capacity one to two orders of magnitude higher than that of natural sediments, revealing that MPs may substantially prolong the residence time of PAHs in the environment. Furthermore, ageing processes can further modify the surface physicochemical properties of MPs. Wang et al. (2024) found that aged MPs, owing to increased surface roughness and specific surface area, exhibited a sorption capacity for high-molecular-weight PAHs up to three times higher than that of pristine plastics. These studies have revealed the potential risk of MPs as carriers of PAHs; however, most investigations remain confined to static sorption experiments in single media (e.g., aqueous environments), with insufficient attention to the dynamic processes occurring in soil, a complex multiphase system. The surface physicochemical properties of MPs are key determinants of their PAH sorption behaviour. Zhang et al. (2024) reported competitive sorption between MPs and DOM, where the presence of DOM significantly

reduced the sorption capacity of MPs for PAHs. Li et al. (2025) systematically investigated the effects of pH and DOM on MP-mediated PAH transport, pointing out that MP-enriched soils enhance the environmental persistence of PAHs through pH- and DOM-mediated mechanisms. In addition, He et al. (2025) found that low-polarity MPs such as polypropylene (PP) exhibit predominantly hydrophobic interactions for phenanthrene sorption, whereas high-polarity MPs such as polyvinyl chloride (PVC) enhance sorption through synergistic π–π conjugation and hydrogen bonding. The interactions among multiple factors, including MP type, particle size and environmental conditions, render the sorption behaviour of the MP–PAH complex system highly complex.

As "emerging pollutant carriers", MPs may exacerbate the ecological risks to the soil–plant system through their synergistic transport with PAHs (Ali et al. 2024). Wang et al. (2023) explored the environmental behaviour of MPs in agricultural systems and their combined risks to crops, first proposing that the rhizosphere interface is a critical zone for the synergistic transport of MPs and PAHs, and emphasising that organic acids exuded by roots can promote PAH desorption by altering the surface charge of MPs, thereby enhancing crop exposure risk. Lu et al. (2025), using hydroponic experiments, investigated the transport and combined toxicity of micro- and nano-plastics with PAHs in ryegrass, finding that the presence of MPs significantly reduced the effective concentration of PAHs in aqueous solution and consequently decreased PAH content in plant tissues, with competitive inhibition mechanisms governing the translocation of MPs and PAHs within plants. Dynamic changes in the rhizosphere environment, such as pH fluctuations, significantly regulate the stability of MP–PAH complexes. Bhagat et al. (2021) noted that the interactions between MPs and PAHs are markedly modulated by environmental pH and ionic strength. Although these studies have greatly advanced our understanding of MP–PAH interactions, existing work has primarily focused on sorption–desorption kinetics, combined toxicity, and transport patterns of MPs and PAHs in single media such as water or sediments. For soil, a highly heterogeneous multiphase system, systematic studies are still lacking on how the spatial heterogeneity of MPs

drives PAH transport at the root–soil interface, the multi-factor coupling mechanisms, and the implications for agricultural product safety. In particular, how the interactions among MP type (e.g., PE and PS), particle size, and environmental factors (pH, DOM concentration) collectively regulate PAH transport in the rhizosphere and plant accumulation remains to be explored in depth.

To this end, given the current status of combined MP and PAH contamination in agricultural soils, the present study selected pak choi as the test plant and conducted pot simulation experiments with PE MPs, PS MPs and typical PAHs as target pollutants, systematically investigating the transport behaviour of PAHs at the root–soil interface under different pH, DOM concentration and MP particle size conditions. The aims are to elucidate the multi-factor coupling mechanisms by which MPs regulate PAH transport at the root–soil interface, to clarify the importance of interactions among MP type, particle size and environmental factors in ecological risk assessment, and to provide a theoretical basis and key parameters for the safe management of agricultural products under combined MP and PAH contamination, thereby contributing to the achievement of healthy soil management goals in farmlands.

2. Materials and methods

2.1. Materials and chemicals

The experimental soil was collected from agricultural land in the northern suburb of Shenyang, Liaoning Province (42°4′ N, 123°31′ E). For fields under different utilization regimes, a total of 10 sampling points were established in a random manner. At each point, the surface soil layer (3–5 cm) was collected in equal volumes using a spade, and the subsamples were thoroughly mixed to form a composite sample, which was then bagged and recorded. Upon return to the laboratory, the soils were air-dried in the shade and subsequently passed through a 1-mm stainless steel sieve before storage. The physicochemical properties of the soil samples are summarised in Table S1.

PE and PS MPs with diameters of (0.80 ± 0.12), (50 ± 2.5), (200.0 ± 5.3), (500.0 ± 6.5) and (1000 ± 3.5) μm were purchased from Shanghai Guanbu Electromechanical

Technology Co., Ltd. The 16-component PAH mixed standard was acquired from Pestanal, Sigma-Aldrich (USA). Dichloromethane, n-hexane, calcium oxide powder, glacial acetic acid, and humic acid (HA), all of analytical reagent grade, were obtained from Beijing Chemical Reagent Company, while acetonitrile of chromatographic grade was supplied by Thermo Fisher Scientific (USA). The experimental pots were made of polyvinyl chloride (PVC), with a volume of 2 L. The plant used in the experiment was pak choi, and its seeds were obtained from Shenyang Qianyuan Horticulture and Flowers Co., Ltd. (Shenyang, China).

2.2. Experimental instruments and equipment

The RE52-99 rotary evaporator was obtained from Shanghai Yarong Biochemical Instrument Factory; the solid-phase extraction apparatus was sourced from Merck Supelco (USA); and the high-performance liquid chromatograph (HPLC, Agilent 1100) was acquired from Agilent Technologies Inc., USA.

2.3. Pot experiments

The pot experiment was conducted in a greenhouse at the College of Environmental Sciences, Shenyang University, using pak choi as the test plant. Preparation of PAH-contaminated soil: A 2 L beaker was charged with 100 mL of acetone, into which 1 mL of a 16 PAH mixture (0.1 $mg \cdot mL^{-1}$) was added and thoroughly mixed. Subsequently, 1000 g of soil was slowly poured into the beaker, and the soil was homogenised thoroughly with the acetone solution containing the PAHs, resulting in a contaminated soil with a final PAH concentration of 0.1 $mg \cdot kg^{-1}$.

The experimental design comprised 20 MPs treatments, including five PE MPs size treatments, five PS MPs size treatments (with particle sizes of 0.8, 50, 200, 500, and 1000 μm) and two control (CK) treatments; three pH treatments (pH 5, pH 7, and pH 11); and five dissolved organic matter (DOM) concentration treatments (0, 5, 10, 20, and 40 $mg \cdot L^{-1}$, with 0 $mg \cdot L^{-1}$ as the control). Each treatment was set up in triplicate. The

preparation of soils for the different treatments and the detailed procedures of the pot experiment were as follows (see supplementary material of Text S1).

2.4. Detection and Analysis of PAHs

PAHs were determined using a high-performance liquid chromatograph (HPLC, Agilent 1100, Agilent Technology Co., Ltd., USA). The mobile phase consisted of water and acetonitrile in a volume ratio of 60:40, delivered at a flow rate of 1 $mL \cdot min^{-1}$. The detector wavelength was programmed as follows: 280 nm from 0 to 10.6 min, 246 nm from 10.7 to 11.6 min, 250 nm from 11.7 to 12.6 min, 280 nm from 12.7 to 13.4 min, 320 nm from 13.5 to 15.4 min, 265 nm from 15.5 to 17.9 min, 290 nm from 18.0 to 21.4 min, and 290 nm from 21.5 to 30.0 min. Qualitative analysis was performed by matching chromatographic peak retention times, while quantification was carried out using the external standard method. The concentration range of the PAH standard solutions was 50–2000 $ng \cdot mL^{-1}$. Each sample was measured three times (Li et al. 2024).

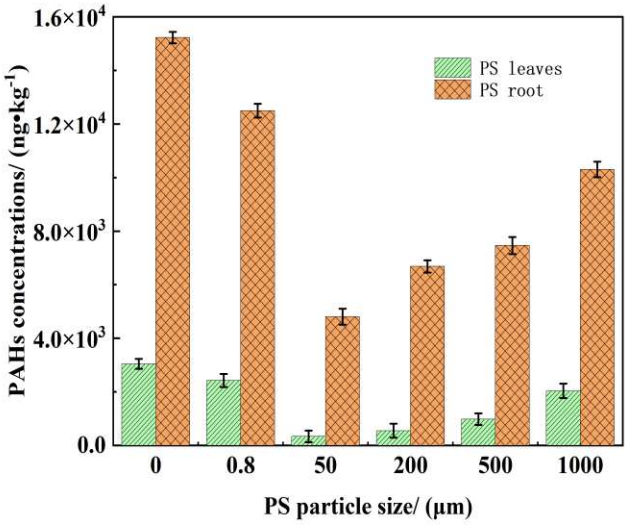
3. Results

3.1. MP particle size modulates the bioaccumulation and translocation of PAHs in pak choi grown in MPs-amended soils

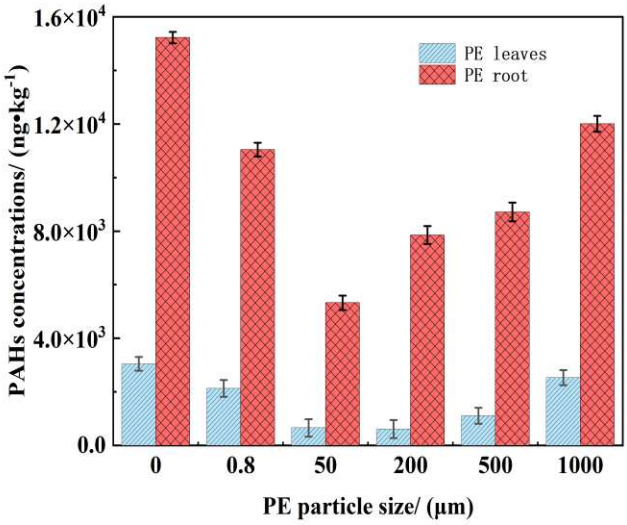
3.1.1 Uptake and Distribution of PAHs by Pak Choi in MPs-Amended Soils under Different MP Particle Sizes

Analysis of PAH contents in the roots and leaves of pak choi under different MP particle sizes (Figures 1 and 2) showed that, across all particle size treatments, the PAH contents in roots were higher than those in leaves. With increasing MP particle size, the PAH contents in both roots and leaves in the two MP-amended soils exhibited a trend of a significant decrease followed by a gradual increase; however, the magnitude of change in root PAH content was substantial, whereas that in leaf PAH content was relatively moderate. The lowest PAH contents in both roots and leaves were observed at the particle size of 50 μm in both MP-amended soils. Compared with the CK soil, the addition of

MPs of different particle sizes reduced the PAH contents in roots and leaves. However, relative to the PS MPs-amended soil, the PAH contents in roots and leaves in the PE MPs-amended soil decreased more markedly at particle sizes <50 μm, while they increased more markedly at particle sizes between 50 and 1000 μm.



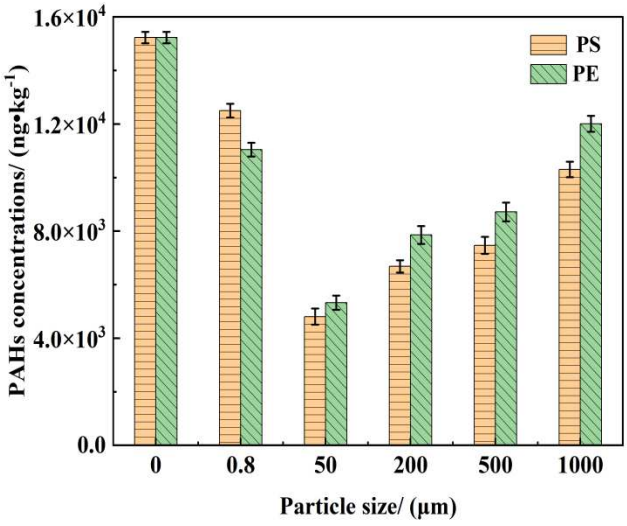
a) PS



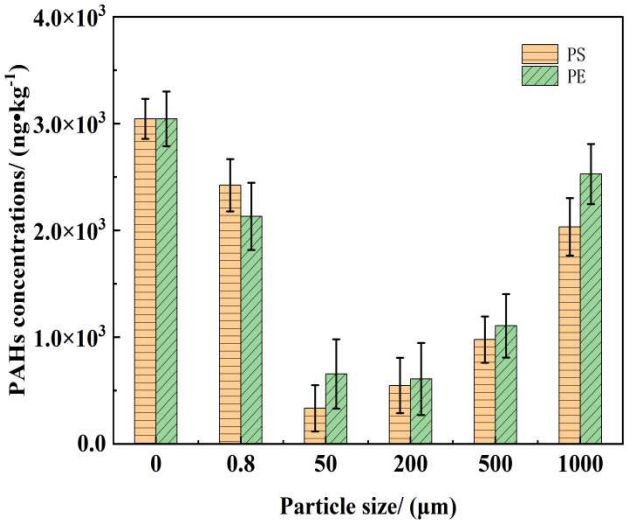
b) PE

Fig. 1 Concentrations of PAHs in roots and leaves of pak choi under different particle sizes of MPs

Note: The treatment labeled "0" denotes the control treatment without added MPs and is not a particle-size level. Bars represent means; error bars represent standard deviations (SD) of three independent biological replicates (n=3)



a）Root



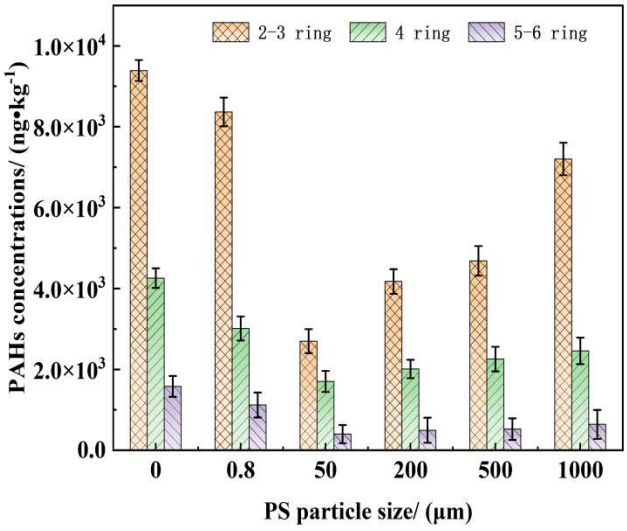
b) Leaves

Fig. 2 Concentration of PAHs in the roots and leaves of pak choi under different particle sizes of MPs

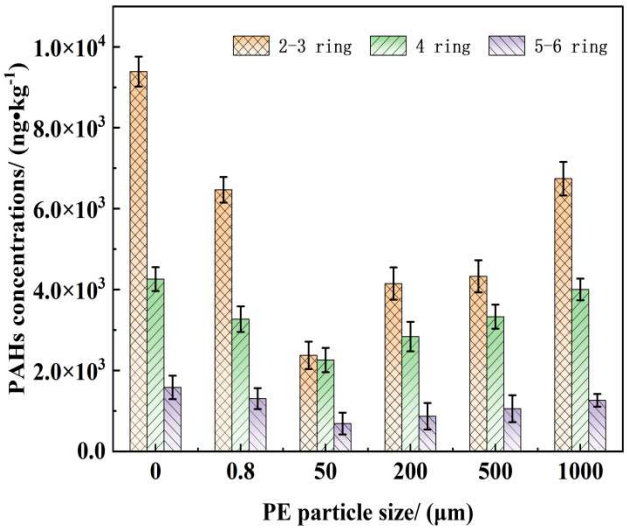
Note: The treatment labeled "0" denotes the control treatment without added MPs and is not a particle-size level. Bars represent means; error bars represent SD of three independent biological replicates (n=3)

Figure 3 presents the uptake concentrations of PAHs and their ring-class fractions by pak choi under different MP particle sizes. As shown in Figure 3, with increasing MP particle size, the uptake concentrations of soil PAHs and their fractions in pak choi exhibited a trend of initial decrease followed by an increase in both MP-amended soils. The lowest concentrations of total PAHs and fractions were observed at the particle size of 50 μm, ranging from 401.1 to 2699.9 ng·kg^{-1} (total PAHs: 4805.2 ng·kg^{-1}) in the PS

MPs-amended soil and from 689.2 to 2377.4 ng·kg^{-1} (total PAHs: 5324.4 ng·kg^{-1}) in the PE MPs-amended soil. With increasing particle size, the decrease in the uptake concentration of low-ring PAHs was relatively more pronounced in the PE MPs-amended soil, whereas in the PS MPs-amended soil, the decreases in medium- and high-ring PAH uptake concentrations were relatively larger.



a）PS



b）PE

Fig. 3 Concentrations of PAHs and their compositions in pak choi under different MPs particle size

Note: The treatment labeled “0” denotes the control treatment without added MPs and is not a particle-size level. Bars represent means; error bars represent SD of three independent biological replicates (n=3)

3.1.2 Bioconcentration and translocation factors of PAHs in pak choi under different MP particle sizes

The calculated BCFs and TFs of PAHs in pak choi under different particle sizes are presented in Table S2. As shown in the table, the addition of PE MPs and PS MPs of different sizes reduced the bioconcentration factors (BCFs) and translocation factors (TFs) of PAHs in pak choi. At the MP particle size of 50 μm, the BCFs and TFs were lowest in both PE MPs- and PS MPs-amended soils, and they increased with either an increase or a decrease in the MP particle size. However, compared with the PE MPs-amended soil, the PS MPs-amended soil at 50 μm exhibited lower BCFs but higher TFs for PAHs in pak choi.

3.2. Soil pH modulates the bioaccumulation and translocation of PAHs in pak choi grown in MPs-amended soils

3.2.1 Uptake and distribution of PAHs by pak choi in MPs-amended soils under different pH conditions

Figure 4 illustrates the uptake of PAHs and their ring-class fractions by pak choi under different pH conditions. As shown in Figure 4, pH exerted a marked influence on the uptake of soil PAHs by pak choi. In the CK soil, the uptake of total PAHs and of high-, medium-, and low-ring PAHs by pak choi was lowest at pH 7. When the pH was lowered, the uptake of total PAHs and of high- and medium-ring PAHs increased, whereas that of low-ring PAHs remained unchanged. In contrast, raising the pH resulted in a pronounced increase in low-ring PAH uptake, while the uptake of high- and medium-ring PAHs showed little variation. Across the different pH treatments in the CK soil, the uptake of total PAHs followed the order pH 7 < pH 5 < pH 11; for medium- and high-ring PAHs, the order was pH 11 < pH 7 < pH 5; and for low-ring PAHs, the order was pH 7 = pH 5 < pH 11. (see supplementary material of Text S2)

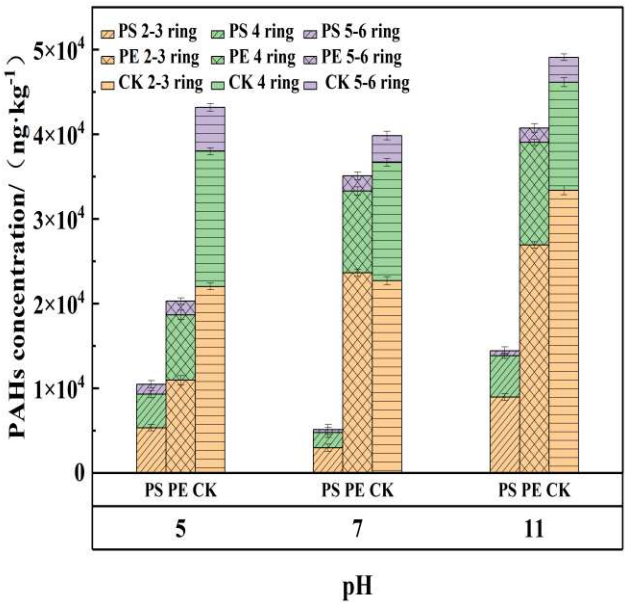


Fig. 4 Uptake of PAHs and their components in soil by pak choi under different pH conditions

Note: Bars represent means; error bars represent SD of three independent biological replicates (n=3)

3.2.2 Bioconcentration and translocation factors of PAHs in pak choi under different pH conditions

To elucidate the effects of MPs on the bioconcentration and translocation of soil PAHs by pak choi under different pH conditions, the BCFs and TFs were calculated for the three soil types across the pH treatments, and the results are presented in Table S3. Under all pH conditions, the BCFs of PAHs in pak choi followed the order: CK soil > PE MPs-amended soil > PS MPs-amended soil. In the CK and PS MPs-amended soils, the BCFs followed the order pH 11 > pH 5 > pH 7, whereas in the PE MPs-amended soil, the order was pH 11 > pH 7 > pH 5. In contrast, the TFs of PAHs followed the order PS MPs-amended soil > CK soil > PE MPs-amended soil. Across all three soil types, the TFs consistently followed the order pH 11 > pH 5 > pH 7.

3.3. DOM modulates the bioaccumulation and translocation of PAHs in pak choi grown in MPs-amended soils

3.3.1 Uptake and distribution of PAHs by pak choi in MPs-amended soils under different DOM concentrations

Figure S3 presents the concentrations of PAHs and their ring-class fractions taken up by pak choi under different DOM concentrations. As shown, the uptake concentrations of PAHs varied with DOM concentration. With increasing DOM concentration, the uptake concentrations in the CK and PE MPs-amended soils increased for total PAHs and all ring classes, with particularly pronounced increases at DOM concentrations of 20 and 40 $mg \cdot L^{-1}$. In contrast, in the PS MPs-amended soil, the uptake concentrations of total PAHs and of each ring class decreased markedly with increasing DOM, and the decreases were substantially larger at 20 and 40 $mg \cdot L^{-1}$. Compared with the CK soil, the uptake concentrations in both MP-amended soils were lower across all DOM concentrations. Specifically, in the PE MPs-amended soil, the reductions relative to the CK soil were 25.1%–44.4% for total PAHs, 46.4%–77.6% for low-ring PAHs, 22.0%–54.3% for medium-ring PAHs, and 24.5%–42.7% for high-ring PAHs. In the PS MPs-amended soil, the corresponding reductions were 49.0%–97.5%, 59.4%–96.8%, 49.1%–98.4%, and 61.9%–97.6%, respectively.

Analysis of PAH contents in the roots and leaves of pak choi in the three soil types under different DOM concentrations (Figures S4 and S5) revealed that the PAH contents varied with DOM concentration. With increasing DOM concentration, the PAH concentrations in both roots and leaves increased in the CK and PE MPs-amended soils, with particularly pronounced increases at DOM concentrations of 20 and 40 $mg \cdot L^{-1}$. In contrast, in the PS MPs-amended soil, the PAH concentrations in roots and leaves decreased with increasing DOM, and the decreases were substantially larger at 20 and 40 $mg \cdot L^{-1}$. Compared with the CK soil, the PAH concentrations in roots and leaves were

297 lower in both MP-amended soils across all DOM concentrations, with the reductions
298 being more substantial in the PS MPs-amended soil.

299 *3.3.2 Bioconcentration and translocation factors of PAHs in pak choi under different*
300 *DOM concentrations*

301 The BCFs and TFs of PAHs in pak choi in the three soil types under different DOM
302 concentrations were calculated, and the results are presented in Table S4. As shown in
303 Table S4, with increasing DOM concentration, the BCFs in the CK and PE
304 MPs-amended soils increased, whereas those in the PS MPs-amended soil decreased. The
305 BCFs were less than unity in all three soils, following the order CK soil > PE
306 MPs-amended soil > PS MPs-amended soil. The TFs were also below unity across the
307 three soils under all DOM concentrations, and the TFs followed the order CK soil > PS
308 MPs-amended soil > PE MPs-amended soil. In all three soils, the TFs decreased with
309 increasing soil DOM concentration.

310 **4. Discussion**

311 ***4.1. Effect of MP particle size on the transport behaviour of PAHs at the root–soil***
312 ***interface***

313 PAHs in soil can enter plants via the root system and subsequently undergo
314 translocation and accumulation within plant tissues, processes that are closely governed
315 by soil composition and properties (Nazir et al. 2025; Xia et al. 2023). The experimental
316 results showed that, under varying pH and DOM concentrations, the PAH concentrations
317 in pak choi grown in PE MPs and PS MPs-amended soils were reduced, with marked
318 decreases observed in the uptake of low-, medium- and high-ring PAHs. Compared with
319 the CK soil, the bioconcentration factors of PAHs in pak choi were substantially lower in
320 both MPs-amended treatments, indicating that the addition of PE and PS MPs reduced the
321 mobility of soil PAHs and their components, thereby decreasing the bioconcentration
322 potential of PAHs in pak choi (Ma et al. 2016; Wang et al. 2025). The high-ring PAH

contents in pak choi grown in PE and PS MPs-amended soils were lower than those of medium- and low-ring PAHs. Compared with the CK soil, the reduction in high-ring PAH contents was greater than that of low-ring PAHs in both MPs-amended treatments, suggesting that MPs addition exerted a stronger inhibitory effect on the uptake of high-ring PAHs than on that of low-ring PAHs by pak choi. This phenomenon is primarily attributable to the structural properties of PAHs. Low-ring PAHs possess relatively lower molecular weights and hydrophobicities, whereas high-ring PAHs, with their higher molecular weights and greater hydrophobicity, are more readily associated with soil MPs (Ghosal et al. 2016).

The addition of MPs of different particle sizes reduced PAH contents in both roots and leaves of pak choi. At a particle size of 50 μm, the PAH contents in roots and leaves were the lowest in both PS and PE MPs-amended treatments, and the bioconcentration factors and translocation factors were also minimised, indicating that at this particle size, the bioavailability of soil PAHs was relatively low and the accumulation and translocation capacity of pak choi was weakest. This is likely due to stronger sorption of PAHs onto MPs particles of this specific size, which is consistent with the results of sorption experiments using MPs of different sizes. These experiments demonstrated that soils amended with 50 μm MPs exhibited higher PAH sorption than those amended with either smaller or larger MPs. Larger MP particles have a smaller specific surface area and therefore a lower sorption capacity for contaminants such as PAHs; however, when particles are excessively small, they tend to aggregate, reducing the effective contact area between MPs and PAHs and consequently decreasing sorption capacity and sorbed amounts (Hataley et al. 2022). At a particle size of 0.8 μm for both PS and PE, the tendency of particles to aggregate reduces the effective surface area accessible for PAH sorption, thereby weakening the competitive suppression of root uptake relative to 50 μm. Lu et al. (2025) demonstrated that MPs significantly reduced the effective concentrations of PAHs in hydroponic solutions, thereby decreasing PAH contents in plant tissues;

moreover, competitive inhibition occurred between MPs and PAHs during plant translocation, and the inhibition of PAH translocation by MPs was more pronounced with decreasing particle size.

Furthermore, the reduction in PAH concentrations in roots and leaves was more pronounced in the PS MPs-amended treatment than in the PE MPs-amended treatment. Compared with the PS treatment, the PE treatment exhibited a more marked decrease in root and leaf PAH contents at particle sizes below 50 μm, whereas a more pronounced increase was observed at particle sizes between 50 and 1000 μm. This differential effect, dependent on polymer type, can be explained by the distinct physicochemical properties of PE and PS. PE is a rubbery polymer, with a glass transition temperature well below room temperature, possessing greater free volume and more flexible polymer chains, which facilitates the partitioning of PAHs into the polymer bulk (Wang et al. 2019). In contrast, PS is a glassy polymer with a denser chain structure; however, the presence of phenyl groups in PS enables π–π interactions with the aromatic rings of PAHs, thereby enhancing the surface sorption of PAHs onto PS (Agboola and Benson 2021).

4.2. Effect of MPs on the transport behaviour of PAHs at the root–soil interface under different pH conditions

Soil pH is a key environmental factor regulating the mobility and bioavailability of PAHs in soil. The results of the present study demonstrated that, across the three soil types, the uptake concentrations of PAHs by pak choi exhibited systematic variations with pH, confirming the important regulatory role of pH on the transport behaviour of PAHs at the root–soil interface. In the PS MPs-amended soil, the concentrations of total PAHs and their fractions in pak choi were lowest at pH 7, and the bioconcentration and translocation factors were also minimal at this pH; at pH 5 or 11, however, both the PAH concentrations and the corresponding bioconcentration and translocation factors increased. This indicates that under neutral conditions, the PAH concentration in the soil solution of the PS MPs-amended soil was low and bioavailability was reduced, resulting

in diminished accumulation and translocation capacities of pak choi; under acidic or alkaline conditions, the PAH concentration in the soil solution increased, bioavailability was enhanced, and the plant's accumulation and translocation capacities correspondingly increased. Vujić et al. (2023) found that the maximum adsorption of most organic contaminants onto MPs occurred near pH 7.

These findings are in close agreement with the present results, namely that at pH 7, the adsorption of PAHs onto PS MPs was strongest, leading to a decrease in PAH concentration in the soil solution and consequently reduced bioavailability and plant uptake. This adsorption behaviour is closely related to the surface charge properties of PS MPs: at pH 7, which is close to the point of zero charge of PS MPs, the adsorption of PAHs onto PS MPs was maximal, resulting in a lower PAH concentration in the soil solution, reduced bioavailability, and decreased uptake by pak choi. When the pH was below this value, the PS surface carried a positive charge, while above this value it carried a negative charge; at pH 11, the negative surface charge of PS MPs increased, generating stronger electrostatic repulsion with negatively charged or ionisable PAH molecules, thereby reducing the adsorption capacity of PS MPs for PAHs.

In the PE MPs-amended soil, the uptake of PAHs by pak choi was lowest at pH 5, and increased as the pH rose to 7 and 11. This pH-dependent pattern was different from that observed in the PS treatment, and may be attributable to differences in the surface physicochemical properties of the two types of MPs. Li et al. (2024) demonstrated that the adsorption of BaA and BaP onto PE MPs reached a maximum at pH 5.0. The point of zero charge of PE is approximately 4.96, and pH 5 is close to this value, at which the net surface charge of PE approaches zero, favouring PAH adsorption onto PE surfaces through hydrophobic partitioning and π–π interactions. As the pH increased to 7 and 11, the negative surface charge of PE MPs gradually increased, enhancing electrostatic repulsion with PAH molecules and decreasing the adsorption capacity; consequently, the

PAH concentration in the soil solution became relatively higher, bioavailability gradually increased, and PAH uptake by pak choi correspondingly rose.

Notably, across the different pH treatments, the uptake of low-ring PAHs (2–3 rings) by pak choi consistently accounted for a high proportion (54%–67% of total PAHs) and exhibited substantial variation, whereas the uptake of high-ring PAHs (5–6 rings) was the lowest (4%–8%) and showed little variation, indicating that soil pH had a negligible effect on the transport of high-ring PAHs at the root–soil interface. This phenomenon is closely related to the physicochemical properties of PAHs. High-ring PAHs possess higher octanol–water partition coefficients and greater hydrophobicity, making them more prone to association with MPs and soil organic matter. Wei et al. (2020) found that three- and four-ring PAHs are more readily taken up by plants than five- and six-ring PAHs. Furthermore, the water solubility of high-ring PAHs is extremely low, and their concentrations in soil solution are inherently limited; combined with their adsorption and immobilisation by MPs and soil organic matter, the regulatory effect of pH changes on the bioavailability of high-ring PAHs is substantially attenuated.

4.3. Effect of MPs on the transport behaviour of PAHs at the root–soil interface under different DOM concentrations

DOM can act as a carrier to enhance the mobility of PAHs in soil, thereby increasing the potential for PAH transport to deeper soil layers and groundwater. With increasing DOM concentration, the uptake concentrations of PAHs and their fractions by pak choi in the CK and PE MPs-amended soils increased, and the bioconcentration factors also increased. This observation aligns with recent studies demonstrating that DOM inhibits PAH adsorption by soil substrates while simultaneously increasing their bioavailability. Zhao et al. (2024) reported that plant-derived DOM enhanced the uptake and transport of PAHs by wetland plants, with benzo[a]pyrene bioavailability increasing by 1.88–2.00 times upon DOM addition. The increased DOM concentration in our CK and PE MPs-amended treatments likely enhanced PAH solubilization in the soil solution, thereby

promoting root uptake and subsequent translocation to aerial tissues. In contrast, in the PS MPs-amended soil, the PAH uptake concentrations by pak choi decreased markedly with increasing DOM, and the bioconcentration factors also declined, indicating that high DOM concentrations substantially reduced PAH bioavailability, lowered the uptake capacity of pak choi, and inhibited PAH accumulation in the PS MPs-amended soil. This divergent response suggests that, under high DOM levels, PS MPs and DOM exerted a stronger adsorption effect on PAHs, effectively sequestering them from the soil solution and reducing their bioavailability.

Under near-neutral soil conditions, PS MPs and DOM exhibited strong adsorption of hydrophobic organic contaminants such as PAHs, mainly through π–π interactions. This observation is supported by the finding that the aromatic structures within DOM promoted the adsorption of PAHs through π–π interactions. Trujillo et al. (2026) further confirmed, using the Dubinin–Radushkevich model, that PAH sorption to PS involves chemisorption contributions primarily through π–π interactions. Additionally, hydrophobic interaction and pore-filling have been identified as the main sorption mechanisms for PAHs on PS. When DOM is present, its aromatic moieties can be sorbed by PS MPs through π–π interactions, competing with PAHs for available adsorption sites on the PS surface. This competitive adsorption effectively reduces the partitioning of PAHs onto PS MPs and may further suppress PAH desorption from the PS–DOM complex, thereby lowering the free dissolved concentration of PAHs in the soil solution.

In the PE MPs-amended soil, however, the molecular structure of PE MPs differed from that of PS; PE MPs lacked benzene rings and exhibited weak polarity, and their interaction with PAHs was primarily via hydrophobic partitioning, resulting in a lower adsorption capacity for PAHs. The adsorption of phenanthrene and fluoranthene onto PE has been shown to be primarily associated with hydrophobic interactions and monolayer chemisorption. Moreover, the addition of HA increased the solubility of PAHs, thereby inhibiting their adsorption onto PE MPs surfaces, which led to a reduction in PAH

457 adsorption by the PE MPs-amended soil and consequently enhanced the transport of
458 PAHs to pak choi roots and leaves. Zafar et al. (2024) demonstrated that the presence of
459 humic substances significantly reduces the adsorption of phenanthrene onto both pristine
460 and aged PE MPs, with a notable decrease in the partitioning coefficient (K_d) of
461 phenanthrene from 2.60×10^4 to 1.30×10^4 $L \cdot kg^{-1}$ on MPs in the presence of HA.
462 Furthermore, an increase in HA concentration was associated with lower K_d values. This
463 reduction in PAH adsorption onto PE MPs in the presence of DOM, combined with the
464 carrier function of DOM that enhances PAH mobility, collectively explains the observed
465 increase in PAH uptake by pak choi in the PE MPs-amended soil with rising DOM
466 concentration.

467 The contrasting effects of DOM on PAH bioavailability in PS versus PE
468 MPs-amended soils highlight the critical role of MP polymer type in determining the
469 direction and magnitude of DOM's influence on PAH fate at the root–soil interface. In
470 PS-amended soils, the combination of π–π interactions between DOM and the PS surface
471 and competitive adsorption for PAHs leads to reduced PAH bioavailability. In PE
472 MPs-amended soils, the lack of aromatic rings on the polymer surface renders
473 hydrophobic partitioning the dominant interaction mechanism, and the solubilizing effect
474 of DOM on PAHs outweighs any competitive adsorption, ultimately enhancing PAH
475 bioavailability.

476 ***4.4. Health risks of PAH uptake by pak choi from MP-amended soils***

477 The soil–plant system represents one of the major pathways through which PAHs
478 enter the food chain; the uptake and accumulation of soil PAHs by edible crops, such as
479 vegetables, can directly threaten food safety and human health. In the present study,
480 differences were observed in the maximum uptake of PAHs by pak choi shoots under
481 varying pH conditions, DOM concentrations, and MPs particle sizes. In the CK soil, the
482 uptake amounts of PAHs were 8.41–11.5 $ng \cdot g^{-1}$, 6.59–17.9 $ng \cdot g^{-1}$, and 5.05–6.21 $ng \cdot g^{-1}$,
483 respectively; in PE MPs-amended soil, they were 3.76–8.27 $ng \cdot g^{-1}$, 5.02–12.7 $ng \cdot g^{-1}$, and

0.333–2.42 ng·g^{-1}, respectively; and in PS MPs-amended soil, they were 1.03–5.03 ng·g^{-1}, 0.545–4.64 ng·g^{-1}, and 0.608–2.53 ng·g^{-1}, respectively. It should be noted that GB 2762-2025 specifies a maximum level of 5 μg·kg^{-1} for benzo[a]pyrene (BaP) in specific food categories, and does not establish a regulatory limit for the sum of PAHs (ΣPAHs); this BaP limit is therefore not directly applicable to ΣPAHs. Accordingly, the ΣPAHs values reported here are interpreted as a comparative measure of PAH accumulation across treatments rather than as a basis for regulatory compliance assessment. To further account for the marked differences in toxicological potency among individual PAHs, the BaP-equivalent toxicity (TEQBaP) was calculated from the individual PAH concentrations using published toxic equivalency factors (TEFs) (Chebykina et al. 2021), and is used below as the toxicologically weighted indicator for comparing treatments. This pattern is consistent with recent findings that leafy vegetables tend to accumulate higher PAH levels than root and fruit vegetables (Xu et al. 2024; Zhu et al. 2021).

In PE MPs-amended soil, the TEQBaP of pak choi was lower than that in CK soil at low pH but remained elevated at high pH; under varying DOM concentrations, TEQBaP stayed relatively high across all conditions, indicating that the toxicity burden was not consistently attenuated. Under different MPs particle sizes, TEQBaP was comparatively low, suggesting a relatively smaller toxicological burden. In PS MPs-amended soil, TEQBaP was consistently lower than in CK soil across all environmental conditions examined, indicating that the presence of PS MPs may reduce the BaP-equivalent toxicity burden of PAHs accumulated in pak choi. This observation echoes the findings of Lili et al. (2022), who employed ^{14}C isotope labelling and reported that the total accumulation efficiency of pyrene associated with PE MPs in rice seedlings (14.5 ± 0.3%) was lower than that of freely dissolved pyrene (22.4 ± 1.2%), and that MPs sorption reduced the root-to-shoot translocation of pyrene. Given the benzene ring structure of PS MPs, they are capable of stronger sorption of PAHs through π–π interactions, thereby more

effectively sequestering PAHs in the soil solid phase, reducing their freely dissolved concentrations in soil solution, and limiting plant uptake and translocation to edible tissues, thus reducing the TEQBaP burden in pak choi tissues relative to CK.

The health risk assessment in this study highlights the key modulating role of MPs type in the food-chain transfer risk of PAHs. In the MPs-free CK soil, pak choi exhibited the highest ΣPAHs and TEQBaP among all treatments under all conditions, indicating that leafy vegetables cultivated in PAH-contaminated soils carry a comparatively high dietary exposure burden in the absence of MPs. The addition of PE MPs reduced PAH bioavailability to a certain extent, but the effect was less pronounced than that of PS MPs and was strongly influenced by environmental conditions, particularly DOM concentration. Elevated DOM concentrations can compete for hydrophobic sorption sites on PE surfaces and increase PAH water solubility, thereby promoting PAH desorption and plant uptake. In contrast, PS MPs consistently reduced both ΣPAHs and TEQBaP in pak choi relative to CK under all conditions, suggesting that PS MPs may hold potential value as a "pollutant-sequestering medium" for reducing the bioavailability and toxicological burden of PAHs in contaminated soils.

5. Conclusions

This study systematically elucidates the mechanisms by which MPs influence the transport and bioaccumulation of PAHs in the soil–plant system, and clarifies the regulatory roles of MP type, particle size, environmental pH, and DOM concentration in this process. The findings reveal that both PE and PS MPs enhance the adsorption capacity of soil for PAHs through mechanisms including hydrophobic partitioning, π–π conjugation, and electrostatic interactions, thereby reducing the bioavailability of PAHs in soil solution and the bioconcentration factors of PAHs in pak choi. This inhibitory effect is particularly pronounced for high-ring PAHs, attributable to their higher octanol–water partition coefficients and greater hydrophobicity. The effect of MP particle size on PAH phytoavailability is non-linear: at a particle size of 50 μm, the adsorption capacity

of MPs for PAHs is maximal and the PAH content in pak choi is the lowest; however, at 0.8 μm, the PAH content in pak choi increased, this was associated with particle aggregation, which reduced the effective surface area available for PAH sorption and thereby weakened the competitive suppression of root uptake relative to the 50 μm treatment.

Environmental pH modulates the adsorption behaviour of MPs by altering their surface charge properties. For PS MPs, the adsorption capacity for PAHs is strongest and plant uptake is lowest at near-neutral pH (pH 7), which is close to the point of zero charge; for PE MPs, the optimal adsorption pH is 5. Outside these pH ranges, the enhanced negative surface charge increases electrostatic repulsion, weakening adsorption efficiency and consequently elevating PAH bioavailability, with low-ring PAHs showing greater sensitivity to pH changes. The influence of DOM is MP-type dependent: DOM enhances the phytoavailability of PAHs in the control and PE MPs-amended soils through solubilisation, whereas in PS MPs-amended soil, DOM and PS MPs synergistically strengthen PAH adsorption and immobilisation via π–π interactions, thereby inhibiting PAH translocation to pak choi.

Under all examined conditions of pH, DOM concentration, and MP particle size, pak choi grown in MP-free control soil exhibited the highest ΣPAH accumulation and TEQBaP, indicating that leafy vegetables cultivated in PAH-contaminated soils without MPs carry a comparatively high exposure burden. PE MPs attenuated PAH accumulation to some extent, but this effect was less pronounced than that of PS MPs and was strongly condition-dependent, particularly with respect to DOM concentration; elevated DOM can compete for hydrophobic sorption sites on PE surfaces and enhance PAH solubility, thereby promoting desorption and plant uptake. In contrast, PS MPs consistently reduced both ΣPAHs and TEQBaP in pak choi across all examined conditions. This is attributable to the benzene-ring structure of PS MPs, which enhances PAH sorption via π–π interactions, thereby sequestering PAHs in the soil solid phase, lowering freely dissolved

concentrations, and limiting root uptake and translocation to edible tissues. Because the current regulatory limit for benzo[a]pyrene is not directly applicable to ΣPAHs, TEQBaP was used here as a toxicologically weighted comparative indicator rather than as a regulatory compliance metric.

CRediT authorship contribution statement

Qing Luo: Conceptualization, Funding acquisition, Supervision, Writing – review & editing, Methodology. Zhen Li: Writing – original draft, Visualization, Data curation. Xin Li: Investigation, Formal analysis. Ting Sun: Supervision, Visualization, Investigation. Yixuan Zheng: Conceptualization, Data curation. Bo Wu: Investigation, Formal analysis.

Environmental significance statement

MPs and PAHs co-contaminate agricultural soils, threatening food safety. How MPs affect PAH uptake by crops under changing environmental conditions remains unclear. Our study shows that PS MPs consistently reduce PAH accumulation in pak choi below safety limits, whereas PE is less effective. Nanoscale microplastics can act as carriers, potentially increasing PAH transport into plants. Soil pH and DOM further modulate these effects. These findings highlight the need to consider MP type, particle size, and environmental interactions when assessing PAH risks in agriculture, providing evidence for food safety management under emerging MP pollution.

Declaration of competing interest

The authors have no relevant financial or non-financial interests to disclose.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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