

## CRITICAL REVIEW

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# Combined interactions and ecotoxicological effects of micro/nanoplastics and organic pollutants in soil–plant systems: a critical overview

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Micro/nanoplastics (MNPs) are widespread and developing environmental pollutants that can interact synergistically with organic pollutants (OPs) in terrestrial ecosystems, posing potential threats to the soil–plant ecosystem. This comprehensive review delves into the profound understanding of interactions between MNPs and OPs in the soil–plant system and their integrated impact on the soil–plant environment. The mechanisms of adsorption between OPs and MNPs primarily include hydrophobic interactions,  $\pi$ – $\pi$  stacking, hydrogen bonding, pore filling, electrostatic forces, and van der Waals forces. Critical parameters influencing the adsorption behavior of MNPs to OPs encompass the physicochemical properties of the MNPs, the features of the OPs, and the inherent properties of the soil–plant system. The synergistic effects of MNPs and OPs may alter harmful impacts on the soil–plant system by influencing plant growth and development, physiological responses, and photosynthesis. Implementing source control measures, conducting in-depth technical analyses, and enforcing policy implementation are crucial steps towards preventing MNPs and OPs contamination in soil–plant systems. This study provides a basis for evaluating the possible threats posed by the co-occurrence of MNPs and OPs, providing valuable insights into their implications for organisms ranging from humans to entire ecosystems.

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### Environmental significance

The review provides a critical review of the interaction of micro/nanoplastics and organic pollutants, particularly from the combined effects in soil–plant systems. It provides insights into the adsorption mechanisms and influencing factors of micro/nanoplastics and organic pollutants. It is discussed that the synergistic effects of MNPs and OPs may alter harmful impacts on the soil–plant system by influencing plant growth and development, physiological responses, and photosynthesis. These assessments will furnish decision-makers with a scientific foundation to devise targeted governance initiatives, thereby effectively mitigating the dual pollution issue of MNPs and OPs.

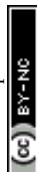
## 1. Introduction

Plastic particles measuring less than 5 mm in diameter are referred to as microplastics (MPs), whereas those measuring less than 100 nm are termed nanoplastics (NPs).<sup>1</sup> In contrast to MPs, NPs possess superior permeability, enabling them to infiltrate live cells more effectively, which may result in more potent and intricate toxicological effects.<sup>2</sup> Plastic pollution has become a significant issue for the global environment.<sup>3</sup> By 2050, it is anticipated that 12 billion metric tons (Mt) of plastic garbage would be either land filled or released into natural habitats worldwide.<sup>4</sup> The extensive prevalence of micro/nanoplastics (MNPs) throughout all environmental subzones

and their nutrient transfer could jeopardize ecosystems and public health.<sup>5,6</sup> Current research has established that MNPs exhibit developmental toxicity, reproductive toxicity, cytotoxicity, immunotoxicity, neurotoxicity, and phytotoxicity.<sup>7–9</sup> Moreover, MNPs can endanger human health by adsorbing related pollutants and infiltrating the food chain.<sup>10–12</sup>

Organic pollutants (OPs) constitute a category of synthetic compounds that endure in the environment for long periods due to their resistance to degradation and ability to be transported over long distances, frequently persisting for many years before degradation.<sup>13,14</sup> Due to their considerable hydrophobicity and enlarged surface area,<sup>15</sup> MNPs demonstrate a pronounced capacity to absorb OPs, augmenting their dissemination and modifying their environmental behavior and trajectory.<sup>5</sup> A multitude of studies has explored the adsorption mechanism of OPs by MNPs and analyzed many influencing elements, including MNPs particle size,<sup>16</sup> the structures of MNPs and OPs,<sup>17</sup> and environmental conditions<sup>18</sup> affecting

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adsorption behavior. The synergistic harmful effects of MNPs and OPs have garnered significant attention.<sup>19,20</sup> The disintegration of MNPs may result in the re-release of adsorbed contaminants, perpetuating a continuous cycle of harm to terrestrial and aquatic ecosystems.<sup>21,22</sup>

The levels of occurrence and abundance of MNPs in aquatic environments have been documented,<sup>23</sup> and MNPs and OPs interactions in aquatic environments can move along the food chain from lower to higher trophic levels, with a variety of toxic effects on organisms at those trophic levels.<sup>24,25</sup> Indeed, as an important source of nutrients for humans and animals, the soil-plant system is also used for the transfer and transformation of soil contaminants,<sup>26</sup> and MNPs and OPs may alter soil physicochemical properties,<sup>27</sup> enzyme activities<sup>28</sup> and microbial community structure,<sup>29</sup> thereby affecting crop photosynthetic parameters, chlorophyll content and resistance to oxidative stress.<sup>30,31</sup> However, the lack of relevant scientific literature on terrestrial systems means that understanding the interactions and ecotoxic effects of MNPs and OPs in soil-plant systems is limited.

Therefore, this paper presents a comprehensive overview of the current research on the interactions and toxic effects of MNPs and OPs in soil-plant systems both domestically and internationally. The review also focuses on the coexistence

levels, adsorption mechanisms, influencing factors, and joint toxic effects of MNPs and OPs in soil-plant systems. Furthermore, this paper looks forward to future developments in research on this topic, with the aim of providing valuable references for assessing environmental risks and controlling pollution related to the coexistence and mechanisms of MNPs and OPs.

## 2. MNPs and OPs in soil-plant systems

The primary sources of MNPs in soil comprise the application of municipal sludge, landfill of plastic waste, application of organic fertilizers, residual decomposition of agricultural films, deposition of atmospheric MNPs, surface runoff and carry-over of agricultural irrigation water.<sup>32–34</sup> Soil MNPs can be conveyed to plant stems and leaves, potentially infiltrating the food chain and posing health hazards.<sup>35</sup> The majority of organic compounds identified in MNPs are persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), phthalates (PAEs), and pharmaceuticals and personal care products (PPCPs).<sup>35,36</sup> The concentration of OPs associated with MNPs differs significantly across various regions, with adsorption concentrations of these OPs in MNPs ranging from  $\mu\text{g g}^{-1}$  to  $\text{pg g}^{-1}$ .<sup>37–39</sup> This research summarizes the incidence of MNPs and OPs in the soil-plant system, as well as their coexistence levels, based on a literature survey of important domestic and international studies.

### 2.1 MNPs pollution

Research indicates that MNPs are globally present in soil (Table 1), including regions such as Africa, Europe, Asia, North America, and Oceania.<sup>40</sup> The concentrations of MNPs in croplands and pastures in Chile's Región Metropolitana were found to average  $306 \pm 360$  and  $184 \pm 266$  items per kg, respectively.<sup>41</sup> A comparable amount of MPs ( $1270 \pm 150$  pieces per kg) has been documented in a tidal freshwater wetland situated in Kenilworth Park and Aquatic Gardens in Washington, D.C.,



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Table 1 Status of MNPs pollution in soil

| Country/area    | Soil type            | Composition                | Shape                                                     | Size (mm) | Abundance                         | References |
|-----------------|----------------------|----------------------------|-----------------------------------------------------------|-----------|-----------------------------------|------------|
| Shandong, China | Coast line soil      | PE, PP, PS, PEU            | Pellets, foams, fragments, flakes, films, fibers, sponges | <1        | 1.314–14 712.5 N kg <sup>-1</sup> | 44         |
| Zhejiang, China | Farmland             | PP, PE, PA, PES, PVC       | Films, fragment, fiber                                    | <3        | 263–571 pieces per kg             | 45         |
| Shaanxi, China  | Farmland             | PS, PE, PP, HDPE, PVC, PET | Film, fiber, fragment and pellet                          | <5        | 1430–3410 particles per kg        | 47         |
| Yunnan, China   | Farmland/forest land | PE                         | Fiber, fragment, film                                     | <10       | 7100–42 960 particles per kg      | 48         |
| Shanghai, China | Paddy field          | PE, PP                     | Microfibers                                               | <1        | 10.3 ± 2.2 items per kg           | 49         |
| Hubei, China    | Vegetable field      | PA, PP                     | Fibers and microbeads                                     | <0.2      | 320–12 560 items per kg           | 50         |
| Xinjiang, China | Farmland             | PE                         | Fragment                                                  | <5        | 80.3–1075.6 pieces per kg         | 51         |
| Guangxi, China  | Farmland             | PP, PE, PET                | Fragment, fibers                                          | <5        | 5–545.9 items per kg              | 52         |
| Chile           | Farmland             | PE, PVC, PS                | Fibers                                                    | <5        | 600–10 400 pieces per kg          | 53         |
| Mauritius       | Farmland             | PP, PA, PE, PS             | Fibers                                                    | <5        | 73.3–433.3 particles per kg       | 54         |
| Iran            | Farmland             | PE                         | Fragment                                                  | <1        | 67–400 particles per kg           | 55         |
| Swiss           | Floodplain soil      | PS, PA, PVC, PA            | —                                                         | <0.5      | 55.5–593 particles per kg         | 56         |
| America         | Park green soil      | PE, PS                     | Fibers                                                    | <5        | 334–3068 pieces per kg            | 42         |
| Korea           | Farmland             | PE                         | Fragment, sheet, fiber                                    | 0.2–0.3   | 160 ± 93 items per kg             | 57         |
| Germany         | Farmland             | PE, PS                     | Film, fragment                                            | <5        | 0.34 ± 0.36 particles per kg      | 58         |

USA.<sup>42</sup> Nizzetto<sup>43</sup> estimated the discharge of 430 000 tons of MNPs from sludge into farmland soils in Europe and 300 000 tons in North America. In Shandong Province, China, coastal soil samples analysis revealed MNP concentrations ranging from 1.3 to 14 712.5 items per kg.<sup>44</sup> Significant contamination of MNPs, averaging  $9.8 \times 10^3$  items per kg, was detected in soil samples from 100 locations across 10 counties in Yunnan Province. This contamination is linked to extensive plastic mulch.<sup>45</sup> MNPs can be assimilated by plants and disseminated across many organs. Jiang<sup>46</sup> found that polystyrene (PS) plastic particles measuring less than 0.2  $\mu\text{m}$  can translocate to broad bean leaves. Furthermore, PS particles as little as 0.1  $\mu\text{m}$  can infiltrate the root tip of broad bean plants, while 5  $\mu\text{m}$  PS particles have minimal capacity to penetrate the root tip.

## 2.2 OPs pollution

Various OPs are also widely present in the environment of soil-plant systems. The average concentrations of perfluoroalkyl acids (PFAAs) diminish in the subsequent sequence across several continents: North America precedes Asia, followed by Africa, Europe, Oceania, and South America. It is important to note that the soils in North America exhibit notably elevated concentrations of PFHpA, which may be linked to the extensive production and use of PFAAs in North American countries in the past.<sup>59</sup> The spatial study results reveal higher average concentrations of OCPs in the soils of North and Central China relative to other regions of the country.<sup>60</sup> Polycyclic aromatic hydrocarbons (PAHs) have been identified in several agricultural soil samples. The total PAH readings varied from below the detection limit to 27 580 ng g<sup>-1</sup>, with a mean of  $772 \pm 895$  ng g<sup>-1</sup> ( $n = 40$ ). The concentration of carcinogenic PAHs ranged from below the detection limit to 7940 ng g<sup>-1</sup>, with a mean of  $464 \pm 889$  ng g<sup>-1</sup> ( $n = 17$ ).<sup>60</sup> The noncancer risk linked to PCBs was substantially heightened in agricultural soils located in the Yangtze River Delta, with a hazard index of 44.0 for children and 24.7 for adults.<sup>61</sup> Sun<sup>62</sup> studied the content of PAEs in soil and vegetables in economically developed areas of the Yangtze River Delta, and found that the average content of PAEs in vegetables could reach 601 ng g<sup>-1</sup>, and bis(2-ethylhexyl)phthalate (DEHP) was the main content. Some studies collected farmland vegetables in Jilin Province and determined that the average PAHs content reached 171.3 ng g<sup>-1</sup>,<sup>63</sup> which may be related to locally developed industrial production. The average content of PAHs in vegetable samples near the e-waste dismantling area can reach 284 ng g<sup>-1</sup>.<sup>64</sup> OPs pollution resulting from industrial emissions has emerged as the primary risk factor for the soil-plant system. The migratory pathway of “atmospheric deposition – soil adsorption – crop enrichment” ultimately results in considerable health risks.

## 2.3 MNPs and OPs co-pollution

OPs identified in MNPs particles are classified into two categories: (1) endogenetic OPs inherent to the plastic, including polymer monomers and additives,<sup>65</sup> and (2) exogenetic OPs prevalent in the external environment.<sup>13</sup> There is a paucity of research on the coexistence of MNPs and OPs in soil-plant



systems.<sup>27,30</sup> Lu *et al.* explored the cooccurrence of MNPs and OPs in agricultural soils situated in the suburbs of Fuzhou city.<sup>28</sup> The findings suggest that MPs with larger particle sizes were subject to more substantial weathering. Moreover, MPs acquired from soil with an extended vegetable cultivation history exhibited higher levels of antibiotics. The findings indicate that alterations in root exudate composition do not impact the desorption capability of polyethylene terephthalate (PET) with regard to PAHs contaminants. Additionally, PET particles serve as a carrier to convey PAHs from various sources to the rhizosphere. These conclusions are drawn from research conducted by Abbasi.<sup>29</sup> Wang<sup>66</sup> investigated the impact of MPs and PAHs on the growth of rice (*Oryza sativa* L.). The adsorption of polycyclic aromatic hydrocarbons by low-concentration microplastics mitigated the inhibitory effects on lipid peroxidation, antioxidant enzyme activity, and photosynthesis, thereby diminishing toxicity to rice seedlings. Elevated concentrations of MP and PAH synergistically augment the toxicity of PAH, consequently impairing plant photosynthesis. These investigations have demonstrated the detrimental consequences caused by the simultaneous presence of contaminants in the soil-plant system.

### 3. Sorption processes and influencing factors between MNPs and OPs

Macromolecular polymers known as MNPs display small particle sizes and hydrophobic features. They have the ability to transport OPs, and in this way, MNPs can disperse within the environment. As a result, pollutants can be affected in terms of their distribution.<sup>67,68</sup> Soil MNPs adsorb OPs by multiple methods, including hydrophobic interactions, surface sorption (electrostatic interactions, van der Waals forces, hydrogen bonding and  $\pi$ - $\pi$  interactions), and pore filling (Fig. 1).

While MNPs exhibit a high sorption capacity for hydrophobic OPs, their sorption ability is comparatively low for hydrophilic OPs.<sup>69</sup> The existence of oxygen-containing functional groups such as -OH, -COOH and C=O may heighten the polarity of MNPs particle surfaces, ultimately diminishing their capacity for adsorbing weakly polar organic matter.<sup>36</sup> This organic matter adheres to MNPs surfaces; in doing so, it takes up a fraction of the adsorption sites, leading to a decrease in the particle adsorption potential for other materials.

#### 3.1 Sorption mechanisms

**3.1.1 Hydrophobic interaction.** The predominance of hydrophobic MPs, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), PS, and PET, facilitates the adsorption of hydrophobic OPs such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), PAHs, and PCBs. The adsorption of hydrophobic organic pollutants onto MNPs is primarily governed by hydrophobic interaction mechanisms. Consequently, hydrophobic interactions serve as the principal sorption mechanism for these OPs.<sup>17,70</sup> The nonpolar, semicrystalline, and rubbery polymers PE and PP demonstrate a greater sorption affinity for hydrophobic organic molecules like phenanthrene, mostly due to the dominance of hydrophobic interactions in the sorption process.<sup>71</sup> The adsorption efficiency of PE towards diflufenzuron, carbendazim, malathion, dipterex, and difenoconazole exhibited a linear dependence on their corresponding octanol-water partition coefficients ( $\log K_{ow}$ ), as quantified in Wang's study.<sup>68</sup> Experimental investigations demonstrated that the sorption capacity of polyamide microplastics (PA-MPs) for endocrine-disrupting compounds (EDCs) scaled with increasing contaminant hydrophobicity (quantified by  $\log K_{ow}$ ), revealing hydrophobic interactions as the dominant governing mechanism in these adsorption systems.<sup>72</sup> Furthermore, hydrophobic interaction noticeably affected the sorption of OPs including

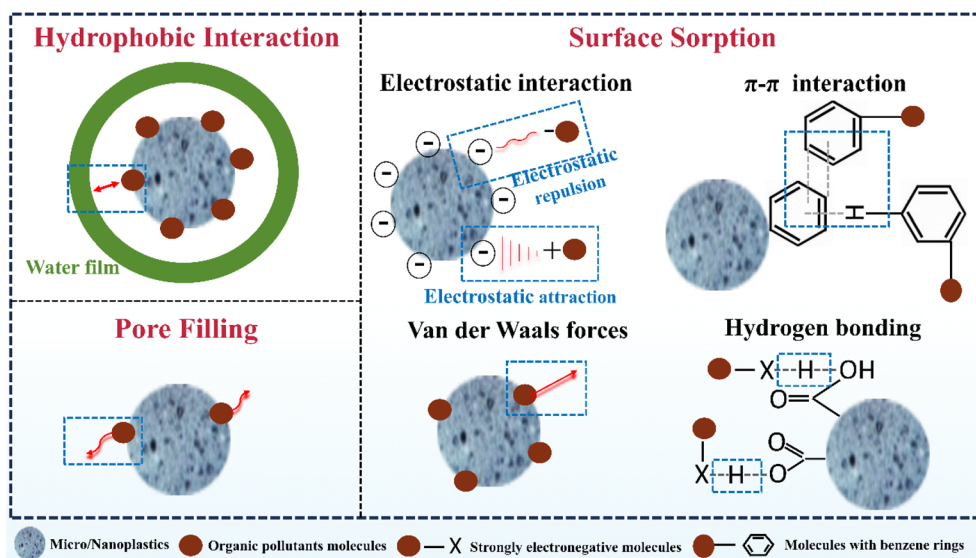


Fig. 1 Schematic representation of the primary interaction between MNPs and OPs.





perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (PFOSA), sulfamethoxazole (SMX), propranolol (PRP) and sertraline (SER) on MNPs.<sup>73,74</sup>

**3.1.2 Surface sorption.** Surface adsorption denotes the physicochemical mechanism whereby solid-liquid interfaces capture dissolved OPs and colloidal materials *via* interfacial interactions, which are quantitatively affected by surface properties (e.g., functional groups, specific surface area) and solution chemistry.<sup>75,76</sup> The mechanistic framework governing these sorption phenomena is primarily mediated through four fundamental pathways: electrostatic attraction, van der Waals forces, hydrogen bonding, and  $\pi$ - $\pi$  electron coupling. Generally, MNPs with a greater surface area exhibit enhanced adsorption capabilities.<sup>77</sup> Prior studies suggest that the functional groups of MNPs and OPs may influence sorption *via* hydrogen bonding interactions.<sup>36</sup> The hydroxyl, carboxyl, and amino groups on the surface of polyamide (PA) function as hydrogen donors, whereas the O or N atoms of amide groups in hydrophilic organic molecules serve as hydrogen acceptors.<sup>78</sup> Vibrational spectroscopy analysis revealed marked attenuation of O-H/N-H stretching vibrations ( $3400\text{--}3700\text{ cm}^{-1}$ ) following polyamide (PA) exposure to polar organic adsorbates, providing spectroscopic evidence for interfacial hydrogen-bond formation between surface functional groups and target analytes.<sup>79</sup> Yu<sup>80</sup> evidenced hydrogen bonding between two electronegative atoms in tetracycline, PE, PVC, and PS. Likewise, the adsorption of anionic atorvastatin (pH 6.5) on negatively charged aged PS MPs,<sup>18,81</sup> further substantiated the significance of hydrogen bonds in augmenting the interaction.

Electrostatic interactions are essential for the adsorption of charged OPs onto the surface of MNPs. These interactions transpire when both MNPs and OPs possess electric charges. Electrostatic sorption transpires due to opposing electric charges, whereas electrostatic repulsion results from identical electric charges.<sup>67</sup> Razanajatovo<sup>73</sup> found that negative charge on the surface of PE, in conjunction with the positive charge of serum exosomes and plasma-derived proteins, enhanced their sorption to PE. PA, PS, PVC, and PP demonstrated higher polarity than PE and PET. Polar functional groups inherent in polymeric matrices ( $-\text{CO}-\text{NH}-$  [PA], aromatic moieties [PS],  $-\text{Cl}$  [PVC],  $-\text{CH}_3$  [PP]) elevate interfacial binding affinity with polar contaminants *via* synergistic dipole-dipole and dipole-induced dipole coupling mechanisms.<sup>82</sup> Electrostatic repulsion, rather than attraction, limits the interaction between medicines and MPs.<sup>83</sup> At pH 6.8, the sorption of SMX onto PE was hindered due to the negative charge of both substances.

van der Waals forces constitute low-intensity intermolecular interactions arising from transient electron cloud asymmetries and dipole alignments between atomic/molecular entities. The adsorption of hydrophilic SMX onto PE may be ascribed to van der Waals interactions.<sup>83</sup> Hüffer demonstrated that aliphatic and aromatic adsorbates can solely adhere to aliphatic PE through the particular van der Waals force. This was observed for seven adsorbates in total.<sup>84</sup>

The predominant mechanism between PS and aromatic compounds was proposed to be  $\pi$ - $\pi$  interaction. The nanoparticles nano-PS and  $\text{C}_{60}$  exhibited considerably greater

sorption as a result of surface aromatic  $\pi$ - $\pi$  interactions, whereby  $\log K_d$  values spanned as high as 11.2 for  $\text{C}_{60}$ .<sup>85</sup> Compounds containing aromatic rings, such as benzene derivatives, are known to adsorb onto PS. Antibiotics such as ciprofloxacin, sulfadiazine, and trimethoprim also adsorb onto MPs made of both PS and PE. Additionally, PS has been found to adsorb ibuprofen.<sup>17</sup>

**3.1.3 Pore filling.** MNPs possess pores of diverse dimensions, facilitating the penetration and trapping of OPs within their nanoscale cavities. These pores are diminutive and can capture small molecular-sized organophosphates. The pore-filling process entails the entry of pollutants that subsequently become ensnared in the minute pores of MNPs.<sup>86</sup>

Zhang analyzed the sorption characteristics of the broad-spectrum antibiotic oxytetracycline (OTC) on both pristine and weathered PS. The  $1/n$  readings reveal nonlinear adsorption of OTC on both varieties of PS foam, as seen by the Freundlich  $1/n$  value significantly diverging from 1. The nonlinearity indicates the participation of pore-filling processes in the adsorption process.<sup>39</sup> The pore diameter of MNPs (PE, PP, PS, PVC) is less than that of tylosin molecules, preventing their penetration into the pore interior. Kinetic profiling revealed an order-of-magnitude reduction in intra-particle diffusion rates during tertiary adsorption phases relative to secondary-stage surface migration dynamics.<sup>87</sup>

## 3.2 Factors influencing the sorption

**3.2.1 Properties of MNPs.** The composition and attributes of MNPs, such as type, size, crystallinity, glass transition temperature, and degree of age, are critical factors influencing the adsorption of OPs (Fig. 2). The structural characteristics of functional groups and the surface physicochemical properties of different MNPs types vary considerably, resulting in unique adsorption patterns for OPs.

Particle size reduction mediates geometric amplification of surface-to-volume ratios and active site density, enhancing interfacial adsorption potentials through surface-to-volume ratio scaling. Comparative studies demonstrated 1–2 order-of-magnitude enhancement in sorption capacities for NPs relative to MPs, attributed to geometric surface area amplification and quantum confinement effects.<sup>85</sup> Researching the effects of weathering on the environmental behavior of MNPs revealed that weathering induces the fragmentation of MNPs into smaller particles. As a result, these fragments may demonstrate improved sorption capabilities for contaminants due to the increase in specific surface area (SSA).<sup>18</sup> Surface characterization protocols reveal weathering-induced augmentation of SSA in MNPs, with contaminant adsorption affinities of environmentally transformed MNPs demonstrating proportional dependence ( $r^2 > 0.85$ ) on SSA elevation, establishing surface area modulation as a critical aging-governed adsorption determinant.<sup>18,39</sup> Wang<sup>16</sup> reported that the sorption characteristics of phenanthrene and nitrobenzene exhibited alterations with reduction in particle size to the nanoscale range. The sorption capacity for phenanthrene and nitrobenzene was lowered due to the aggregation of nano-PS. Yu<sup>80</sup> discovered that the adsorption



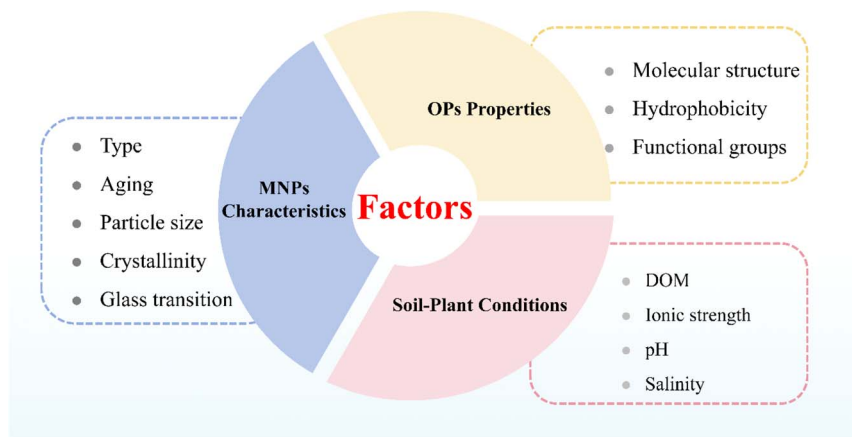


Fig. 2 Factors influencing the adsorption of MNPs and OPs.

of tetracycline on PE particles increased as particle size decreased, attributable to differences in particle size and specific surface area. Nevertheless, it was observed that the equilibrium adsorption capacity of PE-125  $\mu\text{m}$  particles was relatively diminished. The underlying mechanism for this phenomenon is believed to be associated with hydrogen bonding.

As a contributing factor to the sorption of OPs, various MNPs types exhibit distinct adsorption properties towards OPs. Guo investigated the sorption properties of tylosin on four different MNPs. The primary mechanisms governing the sorption of tylosin onto MNPs comprised electrostatic interactions, surface complexation, and hydrophobic interactions.<sup>87</sup> Additionally, the sorption capacity of tylosin onto the MNPs exhibited a descending trend as follows: PE < PP < PS < PVC. The sorption behavior of sulfamethazine (SMT) onto various MNPs types revealed that the sequence of interaction energies between SMT and MNPs was as follows: PA-SMT exhibited the highest energy, followed by PET-SMT, PE-SMT, PVC-SMT, PS-SMT, and PP-SMT. The sorption capacity exhibited a robust association with the interaction energies between MNPs and SMT.<sup>88</sup> The tetracycline adsorption isotherm data were analyzed using the Linear and Freundlich models. Among the various particle sizes, PE (125  $\mu\text{m}$ ) demonstrated the greatest equilibrium adsorption capacity, whilst PVC (74  $\mu\text{m}$ ) exhibited the least adsorption, aligning with prior research findings.<sup>80</sup>

Crystallinity describes the structure of polymers and is a significant factor influencing their adsorption behavior.<sup>70</sup> Typically denotes the ratio of polymer crystals, articulated as a mass fraction or volume fraction, generally below 90%. According to the law of molecular chain arrangement, polymers can be divided into crystalline, semicrystalline and amorphous states. The discernible reduction in crystallinity and hydrophobicity, coupled with an elevation in the carboxyl index of PE-MPs-16, enhanced the sorption efficacy. This indicates that hydrophobic partitioning, electrostatic attraction, and hydrogen bonding each contribute uniquely to the capture of tetracyclines and crystal violet.<sup>89</sup> Guo<sup>37</sup> discovered that the sorption coefficients of PE for phenanthrene, lindane, and

naphthalene increased as crystallinity decreased, when normalized by organic carbon content.

The glass transition temperature ( $T_g$ ) is an intrinsic characteristic of amorphous polymer materials, and its value is directly correlated with the mobility of molecular chains. Polybutylene succinate (PBS) and polylactic acid (PLA) are compostable polymers. PBS demonstrates a rubbery polymer characteristic at its glass transition temperature, while PLA reveals a glassy polymer nature. The molecular architecture of the glassy polymer (PLA) is highly cross-linked, restricting the mobility of OPs; hence, PBS has a greater fipronil adsorption capability than PLA.<sup>90</sup>

MNPs that persist in the environment for extended periods undergo considerable alterations in their characteristics due to the combined effects of physical, chemical, and microbial processes, which subsequently influence the interactions between coexisting contaminants and MNPs. Research indicated that as environmental aging progresses, MNPs undergo further fragmentation, resulting in reduced particle size, increased surface cracking, enhanced specific surface area, the formation of new functional groups, and a marked increase in the adsorption capacity for pollutants such as PAHs, PCBs, pesticides, antibiotics, and heavy metals.<sup>67,70</sup> Tests indicated that weathered PS had an average pore diameter of  $5.1 \pm 0.2$  nm, while the original PS displayed a pore diameter of  $39.3 \pm 0.5$  nm. This indicated that weathering resulted in the creation of many tiny pores, hence augmenting the SSA of PS from  $2.0 \pm 0.1$  to  $7.9 \pm 0.2$   $\text{m}^2 \text{g}^{-1}$ .<sup>91</sup> Furthermore, as MNPs mature, specific chemical bonds, including C-H and C-C, experience oxidation reactions. Consequently, this oxidation introduces oxygenated functional groups that augment their hydrophilicity and reinforce hydrogen bonding between MPs and OPs in aquatic environments, thereby improving their adsorption capacity for hydrophilic OPs.<sup>92</sup> Wu<sup>75</sup> conducted a study to investigate the impact of various aging treatments, such as exposure to seawater and ultraviolet radiation, both individually and in combination, on the ability of MPs to adsorb 2,2',4,4'-tetrabromodiphenyl ether (BDE-47). Their findings revealed



that aged PS exhibited a lower capacity for BDE-47 adsorption compared to its original state.

**3.2.2 Properties of OPs.** The adsorption of various OPs onto MNPs varies. The adsorption affinity of PE for PCBs, PAHs, perfluorinated compounds (PFCs), and antimicrobial OPs diminished in succession, with the average  $K_d$  value varying by seven orders of magnitude within the same aquatic environment.<sup>16</sup> PS demonstrates a strong attraction for OPs with several chlorine substituents, resulting in effective adsorption.

Generally, the molecular structure and hydrophobicity of OPs are important factors in determining the degree of adsorption on MNPs. OPs with strong hydrophobicity easily adsorb MNPs, which is closely related to the  $K_{ow}$  of OPs. Nonpolar organic compounds with  $\log K_{ow}$  values over 2 are classified as hydrophobic organic pollutants (HOCs), and those exhibiting greater hydrophobicity demonstrate increased adsorption affinity to MNPs. Comparative hydrophobicity assessments revealed low-polarity polymers (PE, PP, PS) demonstrated significantly higher 17 $\beta$ -estradiol adsorption affinities relative to polar substrates (PVC, polycarbonate [PC], polymethyl methacrylate [PMMA], PA), attributable to hydrophobic partitioning dominance in nonpolar polymer matrices.<sup>92</sup> The functional groups of the contaminants may influence their sorption behavior. MNPs exhibit a higher affinity for adsorption of organic contaminants with benzene ring configurations. Wang<sup>74</sup> demonstrated that the varying sorption levels of PFOS and PFOSA on PE can be ascribed to their distinct functional groups.

The ionic strength and the presence of coexisting ions are typically critical factors influencing the adsorption of OPs. Elevated ionic strength typically compresses the double electric layer, diminishes electrostatic repulsion, and may enhance adsorption *via* hydrophobic interactions or van der Waals forces, particularly for nonionic organic pollutants. Moreover, coexisting cations (*e.g.*,  $Ca^{2+}$ ,  $Mg^{2+}$ ) may compete with OPs for negatively charged adsorption sites (such as organic carboxyl groups and clay mineral interlayers), thereby hindering adsorption. Anions may influence the adsorption of positively charged OPs. The presence of MNPs may create new ion exchange sites or alter the ionic environment of the solution.

**3.2.3 Soil-plant system conditions.** Various soil environmental factors (*e.g.*, pH, salinity, ionic strength, dissolved organic matter, *etc.*) significantly influence the adsorption of OPs on MNPs. The interplay among the OPs'  $pK_a$ , the solution's pH, and the MNPs'  $pH_{pzc}$  governs the electrostatic attraction and repulsion interactions, potentially influencing the adsorption process between the OPs and the MNPs.<sup>73</sup>

The pH influences the electrostatic interactions between MNPs and OPs by altering their surface charges. The increase in pH will make ionizable OPs negatively charged and show electrostatic adsorption or repulsion with MNPs. These factors will ultimately affect the sorption effect of MNPs on OPs. MPs can alter the pH of soils,<sup>93</sup> which may, in turn, influence the sorption of OTC to soil. Li<sup>94</sup> determined the pH values of soil OTC solution, soil with 5% PA MNPs OTC solution, and soil with 10% PA MNPs OTC solution to be  $7.11 \pm 0.04$ ,  $7.20 \pm 0.03$ , and  $7.32 \pm 0.04$ , respectively. The pH of the reaction systems

evidently rose with the introduction of PA, and the pH elevation correlated with the quantity of PA added. In contrast, Du<sup>89</sup> found that the influence of pH on the  $q_e$  of PE was minimal in the soil environment, exhibiting insignificant variation in adsorption to tetracyclines and crystal violet. This may result from the strong affinity of PE-MPs for soil, elevated alkalinity, substantial dose, and nuanced interaction with soil organic matter, in contrast to the aquatic environment.

The adsorption of OPs by MNPs is influenced by salinity variables, which can alter the intensity of electrostatic interactions in the adsorption process and the extent of ion exchange. Ions in the soil may compete with OPs for adsorption sites on MNPs, hence influencing the adsorption of OPs by these particles. Yu<sup>95</sup> indicated that the equilibrium adsorption capacity of SMX in solution progressively increased with the concentrations of NaCl and  $CaCl_2$ . Elevated sodium ion concentration was demonstrated to impede the adsorption of ionic PFOS on PE and PP. Concurrently, the concentration of sodium ions did not influence the adsorption of either perfluorinated chemical onto PVC.<sup>74</sup> The elevation of salinity enhances the adsorption of organic pollutants onto microplastics in most instances. Guo<sup>88</sup> discovered that with rising salinity,  $Na^+$  competes with antibiotics for adsorption on the surfaces of MNPs by creating hydrogen bonds.

Dissolved organic matter (DOM) is prevalent in soil, with humic acid and fulvic acid as prominent representatives. They possess numerous binding sites for OPs, hence directly influencing the adsorption behavior of these pollutants on MNPs. Xu<sup>83</sup> discovered that increased fulvic acid levels ( $20 \text{ mg L}^{-1}$ ) competitively hindered tetracycline sorption on three MNPs, resulting in over 90% reduction in adsorption. Wu<sup>96</sup> revealed that dissolved organic matter (modeled by Aldrich HA) competitively inhibited the adsorption of endocrine disruptors – 4-methylbenzylidene camphor, 17 $\alpha$ -ethinyl estradiol, and triclosan (TCS) through preferential  $\pi$ - $\pi$  interactions. Seidensticker<sup>97</sup> investigated the desorption of phenanthrene and tonalide from PE within a DOM gradient of 0 to  $1000 \text{ mg L}^{-1}$ , concluding that desorption rates escalated with elevated DOM concentrations.

## 4. Toxic effects of MNPs and OPs in soil-plant systems

As previously observed, MNPs and OPs may negatively impact the soil-plant system, leading to the accumulation and transference of pollutants in soil and vegetation. Altering the physical and chemical qualities of soil will negatively impact plant development and physiological responses. Recent studies have extensively documented the ecotoxicity of MNPs and OPs to plants (Table 2), often assessed using growth indicators such as seed germination rate, root length, physiological responses, and photosynthetic activity (Fig. 3).

### 4.1 Effects of the combined toxicity of MNPs and OPs on plant growth

The germination rate of plant seeds serves as a crucial metric for assessing the hazardous impact of MNPs on flora, as both MNPs





Table 2 Toxic effects of MNPs and OPs in soil – plant systems

| Specie                                  | Shape                                             | Organic pollutants                                    | Combined effect                                                                                                                                                                                                                                          | References |
|-----------------------------------------|---------------------------------------------------|-------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <i>Micracystis aeruginosa</i>           | Polystyrene cationic amino-modified nanoparticles | Glyphosate                                            | Combined exposure displayed antagonism against <i>M. aeruginosa</i> growth suppression                                                                                                                                                                   | 44         |
| Lettuce                                 | Polyethylene microplastic                         | Di- <i>n</i> -butyl phthalate                         | MP exposure induces growth inhibition, photosynthetic disruption, and antioxidant system impairment in lettuce                                                                                                                                           | 102        |
| Microalgae <i>Chlorella pyrenoidosa</i> | Polystyrene microplastics                         | Dibutyl phthalate                                     | DBP/PS co-exposure disrupted key cellular parameters (volume, morphology, chlorophyll fluorescence) in microalgae                                                                                                                                        | 103        |
| Nonylphenol                             | PE, PA, PS                                        | Microalgae <i>Chlorella pyrenoidosa</i>               | MPs/NPs alone caused algal growth suppression and oxidative stress, while co-exposure demonstrated an antagonistic relationship through different routes                                                                                                 | 104        |
| Freshwater microalgae                   | PET, PLA, POM, PS                                 | Macrolide antibiotics azithromycin and clarithromycin | Antibiotic-containing MPs significantly impaired cyanobacterial biomass production and chlorophyll synthesis through metabolic disruption                                                                                                                | 117        |
| Wheat seedlings                         | PE                                                | Phenanthrene                                          | PE-MPs independently disrupt wheat photosynthesis by ROS buildup; concurrent exposure to phenanthrene synergistically exacerbates photodamage <i>via</i> intensified oxidative cascades                                                                  | 10         |
| Soybean                                 | PS                                                | Phenanthrene                                          | Heightened genotoxic stress and oxidative cascades in roots treated with micron-sized microplastics                                                                                                                                                      | 99         |
| Wheat                                   | Polystyrene nanoplastic                           | Polycyclic aromatic hydrocarbons                      | Co-exposure to ANT and FLU exhibited heightened phytotoxicity, characterized by growth retardation, water loss, stomatal dysfunction, and reactive oxygen species buildup, alongside photoinhibition due to diminished photosynthetic electron transport | 118        |
| Cherry radish                           | PA, PP, PVC                                       | Oxytetracycline                                       | Co-exposure to OTC and PVC alleviated PVC-induced phytotoxicity in cherry radish, notably safeguarding leaf proliferation and shoot biomass through improved antioxidative regulation                                                                    | 107        |
| Rice                                    | Polystyrene nanoplastics                          | Phenanthrene                                          | Phe and PS co-exposure impaired rice development while augmenting ROS-scavenging capacity                                                                                                                                                                | 119        |
| Dandelion                               | Polystyrene nanoplastics                          | Dibutyl phthalate                                     | Co-exposure to polystyrene nanoparticles and dibutyl phthalate markedly impacted dandelion development, elicited oxidative stress, modified antioxidant levels, and impaired photosynthetic characteristics and chlorophyll fluorescence                 | 114        |



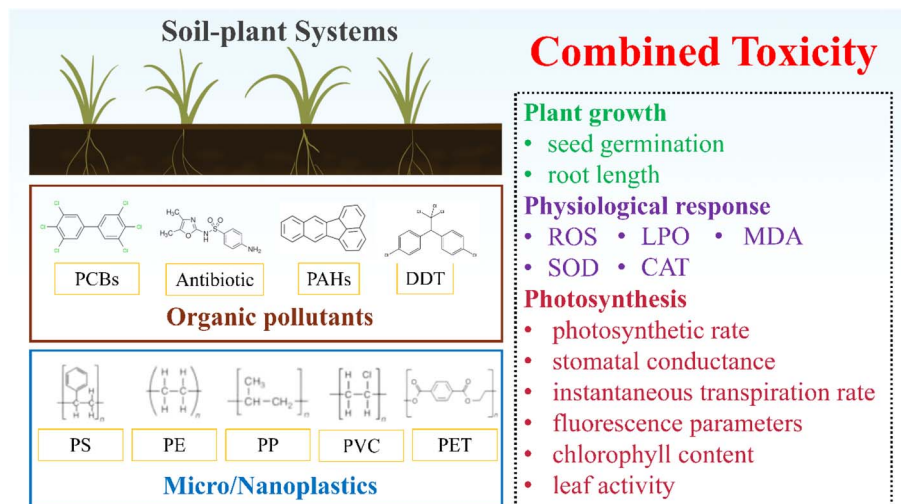


Fig. 3 Ecotoxicological implications of MNPs and OPs interactions in soil–plant systems.

and OPs alter soil structure and diminish seed germination rates. Liu<sup>10</sup> noted a reduction in phenanthrene concentration in wheat roots and leaves corresponding to an increase in PE MPs concentration, indicating that soil-bound PE MPs may adsorb phenanthrene and reduce its absorption by plants. This observation corresponds with the results documented by Wang,<sup>98</sup> which indicated that the accumulation of phenanthrene in wheat soil diminished with the incorporation of PE MPs. The findings from the experiment on soybean seedling absorption of phenanthrene in the presence of PS with varying particle sizes indicate that MNPs hindered the uptake of phenanthrene by both roots and leaves of soybean plants. Moreover, it was observed that when combined with phenanthrene, micrometer-sized MPs exhibited a greater toxic effect on soybean plants than nanometer-sized MNPs.<sup>99</sup>

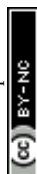
Soybean roots have been discovered to absorb MNPs on their surface within the soil. This interaction may result in competition with phenanthrene for adsorption sites, hence affecting phenanthrene absorption by altering root activity and transpiration.<sup>100,101</sup> In hydroponic settings, the addition of exogenous MNPs intensified the growth inhibition induced by dibutyl phthalate (DBP) in lettuce by aggravating photosynthetic activity.<sup>102</sup> Both DBP and PS were observed to impede microalgal development. At concentrations under  $10 \text{ mg L}^{-1}$ , minimal DBP levels mitigated the inhibitory effects of MNPs on microalgal development, whereas elevated DBP levels exacerbated their detrimental impact.<sup>103</sup> The aggregated evidence on toxicity suggests that MNPs have a positive effect by alleviating the detrimental impacts of nanoparticles on algae. The principal component influencing this effect is the adsorption behavior of MNPs.<sup>104</sup> Rhizosphere microorganisms are posited to participate in the harmful interplay between MNPs and OPs; nevertheless, there is a paucity of studies addressing this issue.<sup>105</sup> Shen<sup>106</sup> found that PS exerted a negligible inhibitory effect on shoot development, with no significant differences seen, while marginally increasing the number of lateral roots and root tips, therefore promoting rice root growth. This discovery corresponds with the

mitigating effects found in cherry radish subjected to a combination of OTC and PVC.<sup>107</sup> The MPs–OPs complex obstructs the stomata on the leaf surface (for instance, PE–MPs adsorbing PAHs and coating the lettuce leaf surface), leading to a 35% reduction in photosynthetic pigments (with carotenoids being the most susceptible), hence directly diminishing biomass accumulation.

#### 4.2 Effects of the combined toxicity of MNPs and OPs on plant physiological responses

In addition to the detrimental consequences of OPs accumulation in plants, new research has demonstrated that MNPs also modify the toxicity of OPs to plants *via* other pathways. Oxidative stress, a common effect of pollutant exposure in plant physiology, can lead to the buildup of reactive oxygen species (ROS), which subsequently degrade biofilm lipids, proteins, and nucleic acids.<sup>108,109</sup> Elevated levels of ROS can cause lipid peroxidation (LPO) damage, resulting in an increase in malondialdehyde (MDA), a consequence of LPO.<sup>110</sup> Plants inherently secrete elevated levels of antioxidant enzymes to mitigate excess ROS as a defense mechanism.<sup>111</sup> Superoxide dismutase (SOD) and catalase (CAT) function as essential cellular antioxidant defense enzymes, constituting the foremost line of protection against oxidative damage induced by ROS.<sup>112</sup>

In a 7-day hydroponic investigation, Lu<sup>113</sup> examined the toxicological effects of PS nanoparticles (PS 50 nm) at a dosage of  $50 \text{ mg L}^{-1}$  and the herbicide quinolinic acid (QNC) at a concentration of  $5 \text{ mg L}^{-1}$  on rice plants (*Oryza sativa* L.). The results demonstrated that rice development was inhibited by QNC and PS + QNC, resulting in enhanced root compensatory growth and the onset of oxidative stress. Florfenicol (FF) is a prevalent antibiotic that, in conjunction with PS MPs, results in the creation of colloidal agglomerates. This led to alterations in the environmental conduct of FF. The concentration of FF positively influenced membrane permeability, MDA concentration, and the activities of SOD, POD, and CAT. These effects hindered rice development and elicited alterations in the



activity of antioxidant enzymes, such as superoxide dismutase, peroxidase, and catalase.<sup>106</sup>

The simultaneous exposure to PS NPs and DBP markedly affected the growth of dandelion (*Taraxacum officinale*) seedlings, provoking oxidative stress and altering both enzymatic and nonenzymatic antioxidant levels, relative to control and separately treated plants.<sup>114</sup> Martin<sup>115</sup> found that the development of *Zea mays* seedlings grown *in vitro* was negatively impacted by two distinct types of MPs beads (W-MPs and B-MPs), both separately and in conjunction with other environmental contaminants. The results demonstrated that W-MPs, alone and in conjunction with OPs (W-MIX), impeded corn germination and led to a modest elevation of free radicals (ROS/RNS) in the leaf tissues.

### 4.3 Effects of combined toxicity of MNPs and OPs on plant photosynthesis

Photosynthetic pigments, including chlorophyll and carotenoids, are crucial to the photosynthetic process in microalgae. Numerous studies indicate that elevated levels of antibiotics impede the synthesis of chlorophyll and carotenoids in microalgae, resulting in a reduction of photosynthetic pigment content. Nonetheless, certain investigations have indicated that antibiotic stress results in an elevation of photosynthetic pigments. Shen<sup>106</sup> reported that exposure to PS alone suppressed the generation of chlorophyll precursors; however, co-exposure to 1 mg per L FF therapy mitigated the effects of FF. The suppression of chlorophyll precursor production indicates an impediment in chlorophyll's capacity to absorb light energy. The implementation of FF led to a decline in the rates of photosynthesis and respiration, signifying that FF affected the functionality of chloroplasts and mitochondria in immature rice plants, resulting in less oxygen consumption. The study demonstrated that the reduction in chlorophyll concentration suggested that PS or DBP exposure impeded the accumulation of photosynthetic pigments in dandelion. Moreover, the reduction in the photosynthetic performance indices Pn, Gs, and Tr was exacerbated in the presence of both PS and DBP. The presence of these contaminants, whether individually or concurrently, affected the previously described parameters.<sup>114</sup> A similar phenomenon has been observed in previous studies regarding the cumulative toxicity of various pollutants. For example, the simultaneous presence of glyphosate and nanoparticles was found to adversely affect the photosynthetic capacity of *Pseudomonas aeruginosa*.<sup>116</sup>

A recent study investigating the impact of polyethylene on the toxicity of di-*n*-butylphthalate in lettuce indicated that all groups exposed to both micro/nano-plastics and di-*n*-butylphthalate exhibited a decline in photosynthetic rate, stomatal conductance, instantaneous transpiration rate, fluorescence parameters, chlorophyll content, and leaf activity. Furthermore, there was an elevation in intercellular carbon dioxide levels relative to the group administered only di-*n*-butylphthalate.<sup>102</sup> The research findings demonstrated that the incorporation of phenanthrene led to a significant reduction in chlorophyll a and carotenoid levels compared to PE alone. Phenanthrene and increased levels of PE-MPs were observed to affect the photosynthetic process in wheat.<sup>10</sup>

## 5. Environmental implications and future perspectives

MNPs have been widely found in various media worldwide, and MNPs pollution in terrestrial ecosystems has received increasing attention. MNPs can act as carriers of OPs and promote their accumulation and distribution in soil-plant systems. In this paper, the interaction between MNPs and OPs in soil-plant system in recent years was summarized, and their sorption behavior, influencing factors and toxic effects were discussed. However, the terrestrial system is a complex system, and the effects of MNPs and OPs in the soil-plant system still have a series of problems to be further studied.

In the future, we need to focus on the following aspects:

(1) The characteristics and attributes of MNPs, the molecular configuration and hydrophobicity of OPs, along with diverse soil environmental variables (including pH, salinity, ionic strength, dissolved organic matter, *etc.*), substantially influence the interaction between MNPs and OPs. There is a need to identify the sources, distribution and transport pathways and influencing factors of MNPs and OPs in soil-plant systems, especially in agroecosystems, and to further assess the toxicity and health risks of MNPs and OPs to plants.

(2) Most of the current studies are short-term studies under indoor conditions, mostly using primary processed MNPs, whereas MNPs entering the soil have different morphologies and varying degrees of aging, and the concentrations in different soil environments may also vary greatly, as well as the effects of the combined action of MNPs and OPs. In the future, multiscale and long-term experiments should be carried out to better understand the effects of MNPs types, shapes, sizes, dosages, and aging degrees on the ecological effects of soil-plant systems.

(3) Advancements in analytical methodologies are crucial for a fuller understanding of the interactions between MNPs and OPs. Integrating high-resolution microscopy, spectroscopy, and molecular modeling can provide comprehensive insights into the mechanisms and impacts of OP adsorption on MNPs. The integration of machine learning techniques facilitates accurate quantitative identification of MNPs and OPs. Integrating novel methodologies will provide a comprehensive understanding of the mechanisms and effects of OPs sorption on MNPs, resulting in more accurate assessments of environmental concerns.

(4) Enhancing public knowledge on the environmental ramifications of MNP and OP interactions is crucial for fostering sustainable habits and mitigating plastic waste. Mitigation and remediation strategies to reduce MNPs and OPs interactions are implemented through the introduction of appropriate laws and regulations. These measures will help to mitigate the adverse effects of MNPs and OPs pollution.

## Data availability

No new data were generated or analysed as part of this review. All data discussed within the text of the manuscript, included in figures or presented in tables, are sourced from previously published articles, which are cited accordingly. All figures are



referenced accordingly and appropriate permissions have been granted.

## Author contributions

Yu Xie: conceptualization, data curation, methodology, software, visualization, writing – original draft. Yaping Lyu: visualization, writing – review & editing. Samina Irshad: investigation. Xingxin Liu: supervision. Yaqi Jiang: supervision. Yi Sun: software, supervision. Ziqi Zhang: supervision. Haojie Wei: investigation. Huiyi He: data curation, supervision. Changcheng An: data curation Peng Zhang: conceptualization, data curation, investigation, supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

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