

Polypropylene microplastics alter the cadmium adsorption capacity on different soil solid fractions

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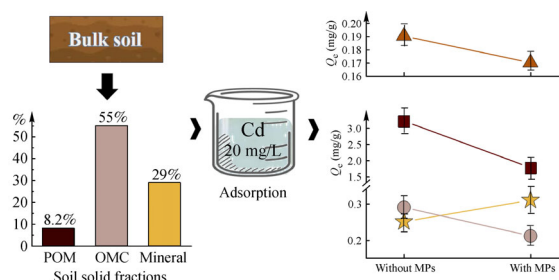
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HIGHLIGHTS

- PP-MPs reduced the adsorption capacity of the bulk soil for Cd in aqueous medium.
- The responses of the POM, OMC and mineral fractions to PP-MPs were different.
- PP-MPs reduced the adsorption of POM and OMC fractions to Cd.
- PP-MPs increased the adsorption of mineral fraction to Cd.
- Effect of MPs on soil adsorption may be controlled by proportion of POM, OMC and mineral fractions.

GRAPHIC ABSTRACT



ABSTRACT

Microplastics (MPs) are widely present in a variety of environmental media and have attracted more and more attention worldwide. However, the effect of MPs on the interaction between heavy metals and soil, especially in soil solid fraction level, is not well understood. In this study, batch experiments were performed to investigate the adsorption characteristics of Cd in bulk soil and three soil solid fractions (i.e. particulate organo matter (POM), organic-mineral compounds (OMC), and mineral) with or without polypropylene (PP) MPs. The results showed that the addition of PP-MPs reduced the Cd adsorption capacity of the bulk soil in aqueous solution, and the effects varied with PP-MPs dose and aging degree. Whereas, the responses of the three fractions to PP-MPs were different. In presence of PP-MPs, the POM and OMC fractions showed negative adsorption effects, while the mineral fraction showed positive adsorption. For the bulk soil, POM and OMC fractions, the adsorption isotherm fitted to the Langmuir model better than the Freundlich model, whereas, the Freundlich isotherm model was more fitted for the mineral fraction. Combined with the comprehensive analysis of the partitioning coefficients, XRD and FTIR results, it was found that OMC fraction extremely likely play a leading role in the bulk soil adsorption of Cd in this study. Overall, the effect of MPs on adsorption capacity of the bulk soil for Cd may be determined by the proportion of POM, OMC, and mineral fractions in the soil, but further confirmation is needed.

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ARTICLE INFO

Article history:

Received 18 May 2021

Revised 15 July 2021

Accepted 20 July 2021

Available online 8 September 2021

Keywords:

Polypropylene microplastics
Cadmium
Adsorption
POM
OMC
Mineral

1 Introduction

Nowadays, plastics and plastic products have been widely used in various industries and human daily life. However, because of their overuse and mismanagement, nearly 5000 million metric tons plastic wastes generated between 1950 and 2015 were discharged into landfills or natural environments (Geyer et al., 2017; Huang et al., 2021). These plastic debris were difficult to degrade, and probably

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Special Issue—Microplastic and Nanoplastic Pollution: Characterization, Transport, Fate, and Remediation Strategies (Responsible Editors: Wen Zhang, Melissa Pasquinielli & Yang Li)

to be the most long-lasting anthropogenic pollution in our earth (Khalid et al., 2020). What is more, plastics particles that < 5 mm in size are often overlooked (Hartmann et al., 2019), these small particles called microplastics (MPs) are sourced widely from the uses of manufactured plastic particles (primary MPs), including personal care products, agricultural fertilizers, detergents and cleaning products, as well as paints, and from fragmentation of large plastics into smaller particles (secondary MPs) via ultraviolet radiation, high temperature, weathering and physical abrasion processes (Gewert et al., 2015; Jambeck et al., 2015; Scudo et al., 2017; Kabir et al., 2021; Sun et al., 2022).

MPs have been reported in soils on a global scale, including Asia, Europe, North America, Africa, and Oceania (Yang et al., 2021), and their abundances vary from 870 particles/kg in home garden soil (Huerta Lwanga et al., 2017) to 42960 particles/kg in cropped areas (Zhang and Liu, 2018). The vast majority of MPs in soil were polyethylene (PE) and polypropylene (PP) (Liu et al., 2018; Deng et al., 2020; Zhou et al., 2019). The persistence, ubiquity, variety, and abundance of MPs are a serious environmental risk to the soil (Khalid et al., 2020). Plenty of evidence revealed that, accumulation of different types of MPs may influence soil physical properties, including soil bulk density, soil aggregation, pore size distribution, hydraulic conductivity, water holding capacity, soil water evaporation, evapotranspiration and desiccation (de Souza Machado et al., 2018; 2019; Wan et al., 2019; Mbachu et al., 2021). Besides, they was reported to affect the geochemical environments of the soil through altering pH and dissolved organic matter (DOM) (Rillig, 2018; Yang et al., 2018; Zhou et al., 2021), the influence was reported to vary with concentration, size, type and shape of the plastic particles (Boots et al., 2019; Qi et al., 2020; Yu et al., 2020; Zhou et al., 2021).

Meanwhile, heavy metal pollution has been considered as another soil pollutants for long time (Cabrera et al., 1998; Sari and Tuzen, 2014; Altunay et al., 2021), in which the proportion of cadmium (Cd) pollution increases most significantly (Shang et al., 2018). Cd concentration was reported to exceed the standard by 19.4% in China, with the largest influence range (Zhuang, 2015). In general, the adsorption behavior of heavy metals was affected by soil properties, such as pH, soil organic matter content (SOM), cation exchange capacity (CEC), clay minerals and iron and manganese oxides (Lair et al., 2007; Park et al., 2011; Bolan et al., 2014; Zhou et al., 2018; Yang et al., 2020). Among them, soil solid fractions including SOM and soil minerals are the major adsorbent controlling the partitioning of heavy metals between soil solid and solution (Shi et al., 2018; Komy et al., 2014; Qu et al., 2019), which affect the immobilization of heavy metal in soils. Soil solid organic matter is usually divided into two fractions via physical fractionation of soil particle sizes, i.e. particulate organic matter (POM) and organo-mineral complexes (OMC). Previous studies have shown POM fraction has

high enrichment capacity for heavy metals via directly complexation and chelation with them in soil (Balabane and van Oort, 2002; Zhang and Ke, 2004; Labanowski et al., 2007). For instance, in lightly polluted arable soils, concentration of Cu, Zn, Pb and Cd in POM fraction was 3-8, 1-7 and 5-11 times as much as bulk soil (Balabane and van Oort, 2002). Besides, OMC fraction can also impact the mobility and bioavailability of heavy metals in soils by surface adsorption and precipitation (Qu et al., 2019).

MPs such as PE or PP are mostly composed of Carbon (Zhou et al., 2021), once incorporated in soil, MPs may gradually be immobilized, binding with soil minerals or organic compounds through biotic and abiotic processes (Zhou et al., 2021). Studies have shown that the presence of MPs not only affect soil microenvironments, but also affect the metal mobility and availability in soils (Yu et al., 2020). In a recent study, high-density PE-MPs decreased soil adsorption capacity but increased desorption of Cd (Zhang et al., 2020). Nevertheless, in another study, MPs was declared to reduce bioavailability of heavy metals from available mobile fractions to stable organic forms (Yu et al., 2020). By far, the possible mechanism are ascribed to the interaction between MPs and heavy metals, as well as the changed physical and chemical properties of the soil induced by MPs (Yu et al., 2020; Zhang et al., 2020). Few studies have considered how the interaction changed between soil solid fraction and heavy metals caused by the presence of MPs.

This study, therefore, was set up to assess the adsorption between soil solid fraction and Cd in the absence/presence of MPs. We separated the bulk soil into three fractions: POM, OMC and mineral, and chose PP-MPs as research object. Batch experiments were employed to test the hypotheses that the addition of MPs to soil solid fraction would alter their adsorption to Cd, and further influence the adsorption capacity of bulk soil. We also investigated the influences of MPs dosage and aging degree of MPs on Cd adsorption. We tried to study the effects of MPs on soil adsorption of heavy metals from the perspective of soil solid fraction, in order to further understand how MPs change soil adsorption capacity.

2 Materials and methods

2.1 MPs and reagents

PP-MPs were purchased from the Zhangmutou Tesulang Chemical Co., Ltd. (Dongguan, China), with size less than 100 μm . The aged PP-MPs were prepared via virgin PP-MPs exposed to both natural light (8:00–20:00 in the daytime, Beijing times) and ultraviolet lamp (20:00–8:00 in the evening, Beijing times, UVA-365-400 nm band) for 3 months. All MPs samples were cleaned with ultra-pure water, dried in oven at 50°C, and then stored for use.

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd., China, analytical grade) was used to prepare stock solution with 100 mg/L Cd. Work solutions with desired Cd concentrations were prepared by diluting the stock solution with distilled water.

2.2 Soil collection and preparation

The forest surface soil (0–20 cm) was sampled from Wuhan, Hubei Province. After removal of large roots, residues and gravel, the soil sample was homogenized, air-dried, passed through 2 mm sieves and stored prior to use.

100 g soil sample was dispersed in a 500 mL beaker with 300 ml of distilled water in the presence of glass beads (Labanowski et al., 2007). After oscillating at $25 \pm 1^\circ\text{C}$ for 24 h (240 r/min), the suspension was screened through a 53 μm sieve and divided into two particle size fractions, namely 2000–53 μm and $< 53 \mu\text{m}$. The $< 53 \mu\text{m}$ OMC were obtained by centrifugation. The light POM and dense mineral fractions were separated from the 2000–53 μm fraction by the method of repeated suspension with distilled water (Zhou et al., 2018). POM fraction was obtained through repeatedly supernatant filtration and the precipitate was mineral fraction. Then the separated soil fractions were dried below 45°C , weighed and ground. The corresponding weight of POM, mineral and OMC fractions in bulk soil were 81.9, 289.9, and 550.5 g/kg, respectively.

2.3 Adsorption experiments

For kinetics experiments, 25 g bulk soil and corresponding proportions of soil fractions (POM, OMC and mineral) with virgin PP-MPs (0%, 10%, w/w) were placed into a series of 500 mL conical flasks with an initial Cd concentration of 20 mg/L. 0.005 mol/L KNO_3 was used as the background electrolyte. All samples were performed at room temperature ($25 \pm 1^\circ\text{C}$) on a hermostatic oscillator at 160 r/min. The contact time is an important factor in determining the adsorption process (Awual et al., 2019b), to obtain the reaction equilibrium time, the solution was sampled and filtered at 5, 30, 60, 120, 240, 360, 540 and 1440 min, respectively. The concentration of Cd was determined by the atomic adsorption spectrometry (AAS, ZEE nit-700P, Analytik Jena AG, Germany).

In the adsorption isotherm experiments, the initial concentrations of Cd were 5, 10, 20, 30 and 50 mg/L, respectively, other procedures were the same with the kinetics experiment. The adsorption isotherm experiment time was set for 360 min to reach equilibrium.

To investigate the adsorption capacity of soil solid fractions for Cd in different MPs dosage and aging degree, 2 g bulk soil and corresponding proportions of soil fractions (POM, OMC and mineral) were added into 50 mL centrifuge tube. Concentration gradient of 0%, 2% and 10%, as well as virgin and aged MPs were chosen,

respectively. KNO_3 of 0.005 mol/L was used as the background electrolyte, and 40 mL $\text{Cd}(\text{NO}_3)_2$ solution (20 mg/L) was added into tubes. Other procedures were the same with adsorption isotherm experiments.

2.4 Characterization of MPs

Diffraction intensity data and the crystal structure of the MPs samples were obtained using X-ray diffraction (XRD) (Model: D8 ADVANCE, Make: BRUCKNER, Germany) over a 2θ range of 5° – 50° at a scan rate of $2^\circ/\text{min}$. The X-ray beam was at a voltage of 40 kV and a current of 40 mA.

The functional groups on the surface of the MPs were identified by Fourier-transform infrared spectroscopy (FTIR) (Model: Nexus470, Make: Thermo Nicolet Corporation, America), which recorded the spectra between 4000 cm^{-1} and 400 cm^{-1} with a resolution of 4 cm^{-1} in transmission mode. Each sample was mixed with KBr powder, ground, pressed, and put into FTIR instrument for determination. The spectrogram was the average of 30 scans.

The scanning electron microscopy (SEM, Model: Hitachi S-4800, Make: Hitachi, Japan) was used to determine the surface morphology and structure of the virgin and aged MPs.

2.5 Data analysis and quality control

Adsorption capacity was expressed by calculating the adsorption amount of Cd by MPs unit mass at time t (Q_t , mg/g) and at equilibrium (Q_e , mg/g). The adsorption kinetics were modeled by the pseudo-first order model, the pseudo-second order model, as well as the Elovich model. To reveal the adsorption mechanism, Langmuir and Freundlich isotherm models were used to fit the adsorption data. In addition, the partitioning coefficients (K_d) was also calculated.

To ensure the quality and accuracy of data, blank tests and standard solutions were included with each batch experiment. All adsorption experiments were conducted in triplicate and results were reported as mean with standard deviations. The charts and data were generated using OriginPro 2018.

3 Results

3.1 Adsorption kinetics

For the adsorption process, the amount of Cd^{2+} absorbed by soil samples at a certain moment (Q_t) is calculated as follows:

$$Q_t = \frac{(C_0 - C_t) \times V_0}{m}, \quad (1)$$

where Q_t is the amount of Cd^{2+} absorbed by soil fractions at a certain moment (mg/g); C_0 is the initial concentration of Cd^{2+} in the solution (mg/L); C_t is the concentration of Cd^{2+} at a certain moment in the solution (mg/L); V_0 is the initial added solution volume (L); m is the weight of the dried soil or soil fractions (g).

Both bulk soil and three soil fractions showed rapid increased adsorption capacity on Cd at the beginning of the reaction. After 30 min, Cd concentration increased slowly with time until equilibrium at around 360 min (Fig. 1). Therefore, in order to ensure the adsorption balance, the subsequent adsorption time was set at 360 min. The process of Cd adsorption by soil and MPs was divided into two stages: fast adsorption stage and slow adsorption stage. The adsorption rate of Cd in soil fractions reached about 80% of the equilibrium adsorption capacity during the first 0.5 h. The equilibrium adsorption capacity of bulk soil, POM, OMC and mineral fractions without the added MPs were 0.199, 3.207, 0.286 and 0.248 mg/g, respectively, followed the order of $\text{POM} > \text{OMC} > \text{mineral} > \text{bulk soil}$. However, when exposed to 10% PP-MPs, the adsorption capacity of bulk soil, POM and OMC fractions on Cd decreased. Among them, the influence of MPs on POM is the most significant, followed by OMC (Figs. 1 (a)–1(c)). By contrast, MPs slightly increased the adsorption capacity of mineral fraction on Cd

(Fig. 1 (d)).

To describe the Cd adsorption process in different soil samples, the pseudo-first order model (Eq. (2)), the pseudo-second order model (Eq. (3)), and the Elovich model (Eq. (4)) were used to analyze the adsorption process.

$$Q_t = Q_e(1 - e^{-K_1 t}), \quad (2)$$

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}, \quad (3)$$

$$Q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) = A + K_t \ln t, \quad (4)$$

where Q_e is the adsorption amount of solid phase at adsorption equilibrium (mg/g); K_1 (min^{-1}) and K_2 (min^{-1}) are the pseudo-first and the pseudo-second order equilibrium rate constants, respectively; t is the contact time (min); A is the reaction initial diffusion rate constant (mg/g); K_t is the reaction rate constant ($\text{mg} \cdot \text{g} / \text{min}^{0.5}$); α and β are the Elovich model parameters.

Both the pseudo-first order model and the pseudo-second order model cannot simulate the experimental data. The Elovich model was the optimum. The related parameters are listed in Table 1, where A is the diffusion

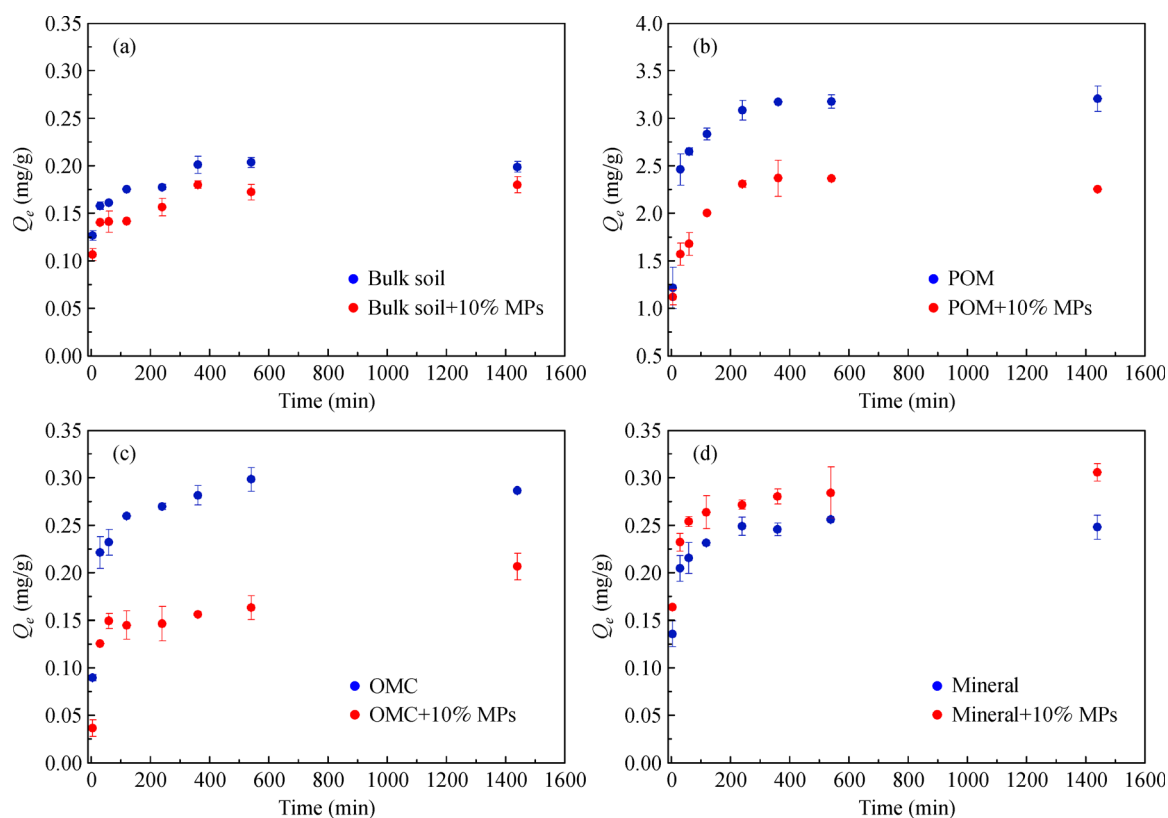


Fig. 1 The experimental kinetics data for Cd adsorption onto bulk soil and three soil fractions [(a) bulk soil; (b) POM; (c) OMC; and (d) mineral].

Table 1 Kinetic parameters of Cd adsorption by the bulk soil and three soil fractions obtained from the Elovich model before and after adding MPs

| Parameter | Bulk soil | | POM | | OMC | | Mineral | |
|-----------|-----------|-------|-------|-------|-------|-------|---------|-------|
| | - | + | - | + | - | + | - | + |
| α | 27.31 | 10.05 | 7.12 | 6.42 | 0.31 | 0.05 | 8.80 | 10.45 |
| β | 70.85 | 75.33 | 2.89 | 4.15 | 29.08 | 40.02 | 48.87 | 42.61 |
| A | 0.107 | 0.088 | 1.047 | 0.791 | 0.075 | 0.020 | 0.124 | 0.143 |
| K_t | 0.014 | 0.013 | 0.346 | 0.241 | 0.034 | 0.025 | 0.020 | 0.023 |
| R^2 | 0.923 | 0.910 | 0.867 | 0.886 | 0.848 | 0.866 | 0.863 | 0.941 |

Note: +, - represent with MPs and without MPs, respectively.

rate constant, reflecting the initial rate of the reaction. K_t is the reaction rate constant, which is positively correlated with the reaction rate. For bulk soil, POM and OMC fractions, both A and K_t decreased after addition of MPs, indicating that the presence of MPs reduced the initial reaction rate and overall adsorption rate of the soil to Cd. Moreover, POM fraction showed the highest A and K_t , while OMC fraction had the closest K_t to the bulk soil and mineral fraction had the closest A to the bulk soil.

The average adsorption rate (V_{average}), fast adsorption rate (V_{fast}) and slow adsorption rate (V_{slow}) of Cd were calculated based on the adsorption curve of fast and slow adsorption stages for bulk soil and three soil fractions, in the absence/presence of MPs (Zhang et al., 2000) (Table 2). Coexistence of MPs reduced the V_{average} , V_{fast} , and V_{slow} of bulk soil and soil fractions, except mineral fraction. Besides, the V_{average} and V_{fast} of OMC fraction decreased significantly when MPs were present.

Table 2 The average, fast and slow reaction rate [mg/(L·min)] of Cd adsorption by the bulk soil and three soil fractions before and after adding MPs

| Soil fraction | V_{average} | V_{fast} | V_{slow} |
|---------------------|----------------------|-------------------|-------------------|
| Bulk soil | 0.032 | 0.293 | 0.009 |
| Bulk soil + 10% MPs | 0.029 | 0.290 | 0.006 |
| POM | 0.032 | 0.296 | 0.009 |
| POM + 10% MPs | 0.031 | 0.276 | 0.008 |
| OMC | 0.021 | 0.202 | 0.008 |
| OMC + 10% MPs | 0.012 | 0.189 | 0.007 |
| Mineral | 0.010 | 0.098 | 0.002 |
| Mineral + 10% MPs | 0.018 | 0.163 | 0.005 |

3.2 Adsorption equilibrium

3.2.1 Adsorption isotherms

Two most commonly used adsorption isotherm equations, Langmuir and Freundlich isotherm models were applied to fit the experimental data. Their mathematical expressions are written as follows:

Langmuir isotherm model:

$$Q_e = \frac{Q_m \times C_e}{\frac{1}{b} + C_e} \quad (5)$$

Freundlich isotherm model:

$$Q_e = K_F \times C_e^{\frac{1}{n}}, \quad (6)$$

where Q_e is the adsorption amount of solid phase at adsorption equilibrium (mg/g); C_e is the concentration of adsorbate in the liquid phase at adsorption equilibrium (mg/L); Q_m is the maximum adsorption capacity of different soil fractions (mg/g); b is the Langmuir parameter; K_F and n are the Freundlich equation characteristic parameters.

Figure 2 and Table 3 illustrates the fitting results of the equilibrium data of Cd adsorption on bulk soil and three soil fractions in the absence/presence of PP-MPs. For bulk soil, POM and OMC fractions, the Langmuir isotherm model ($R^2 > 0.91$) fitted better than the Freundlich isotherm model. However, for mineral fraction, the Freundlich model was the best fitted ($R^2 > 0.93$). It can be seen that, the addition of PP-MPs reduced the adsorption capacity of Cd by bulk soil and soil fractions, except for mineral fraction. Besides, the Q_m value of POM fraction was always the highest whether PP-MPs existed or not, likewise, the influence of PP-MPs on POM was the most significant among all soil samples. Additionally, the values of b were lower than 1, which indicated that the adsorption of Cd on all soil samples were due to preferential adsorption (Zhang et al., 2000). Finally, according to the parameters of Freundlich equation, the $1/n$ values of the bulk soil and OMC fraction were very similar before and after the addition of MPs, suggesting the important role of OMC fraction in the process of Cd adsorbed by soil.

3.2.2 The partitioning coefficients

The partitioning coefficients (K_d) were calculated by Eq. (7):

$$K_d = \frac{C_{\text{ads}}}{C_e} = \frac{M_{\text{total}} - M_{\text{MPS}}}{\frac{m}{C_e}}, \quad (7)$$

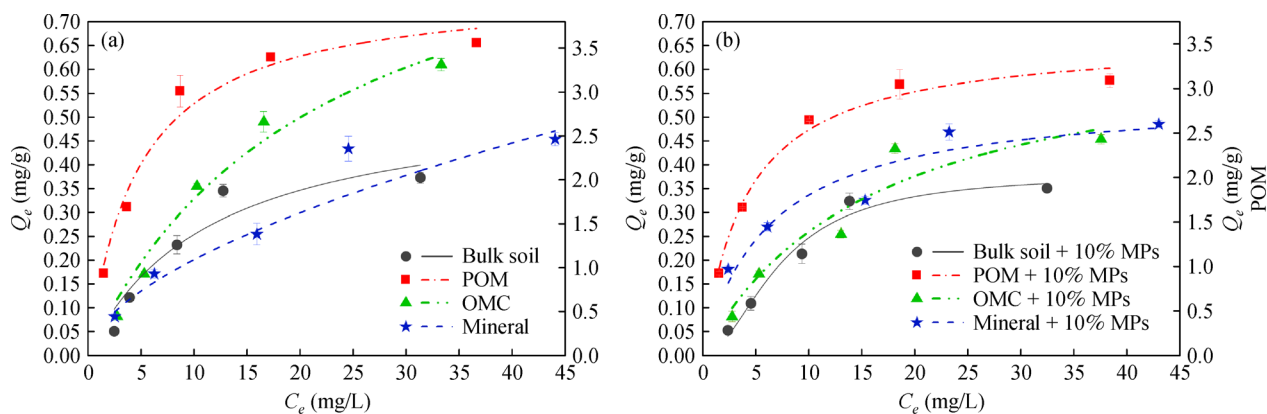


Fig. 2 The isotherm models of Cd on bulk soil and three soil fractions (POM, OMC, and mineral) before (a) and after (b) adding PP-MPs. (bulk soil, POM and OMC fractions fit by the Langmuir isotherm model; mineral fraction fit by Freundlich isotherm model; The left Y-axis are bulk soil, OMC, and mineral fraction; The right Y axis is POM).

Table 3 The Langmuir and Freundlich isotherm models parameter values of Cd adsorption by the bulk soil and three soil fractions before and after adding MPs

| Soil fraction | Langmuir model | | | Freundlich model | | |
|---------------------|----------------|------------|-------|------------------|-------|-------|
| | Q_m (mg/g) | b (L/mg) | R^2 | K_F | $1/n$ | R^2 |
| Bulk soil | 0.545 | 0.087 | 0.916 | 0.073 | 0.503 | 0.826 |
| Bulk soil + 10% MPs | 0.527 | 0.075 | 0.927 | 0.062 | 0.523 | 0.850 |
| POM | 4.190 | 0.216 | 0.973 | 1.212 | 0.326 | 0.852 |
| POM + 10% MPs | 3.566 | 0.246 | 0.986 | 1.137 | 0.301 | 0.869 |
| OMC | 1.040 | 0.046 | 0.975 | 0.075 | 0.616 | 0.934 |
| OMC + 10% MPs | 0.680 | 0.062 | 0.917 | 0.073 | 0.526 | 0.869 |
| Mineral | 0.427 | 0.225 | 0.859 | 0.139 | 0.290 | 0.943 |
| Mineral + 10% MPs | 0.546 | 0.160 | 0.907 | 0.142 | 0.338 | 0.927 |

Note: Q_m and b were derived from the plot of C_e/Q_e against C_e (Awual et al., 2019a).

where C_{ads} and C_e are the metal amount adsorbed per unit mass of soil (mg/g) and the final concentration of solutions (mg/L); M_{total} is the total adsorption quantity of soil fractions and MPs at adsorption equilibrium (mg); M_{MPs} is the adsorption quantity of MPs at adsorption equilibrium (mg); m is the mass of soil fractions (g).

K_d can represent the capacity of soil to adsorb and retain heavy metal ions. The higher the K_d value, the greater the affinity of heavy metal ions to soil solid phase. K_d values of bulk soil and three soil fractions under different initial Cd concentration are presented in Table 4. The addition of MPs reduced the adsorption of Cd in bulk soil, POM and OMC fraction systems, except for mineral, which is in accordance with the result from adsorption isotherms. Moreover, the K_d values of bulk soil and OMC were close whether MPs were added or not.

3.3 Characterization

3.3.1 SEM analysis

The surface of virgin and aged PP-MPs was characterized

by SEM technique (Fig. 3). Virgin MPs particles were uniform in size around 50 μm , with relatively smooth surface. By contrast, aged PP-MPs appeared to be irregular pellets or clumps, and bonding and agglomeration occurred among plastic particles, resulting in uneven and rough bulges.

3.3.2 XRD analysis

To determine the influences of PP-MPs crystallinity on the adsorption behavior of Cd by bulk soil and three soil fractions (POM, OMC, and mineral), the XRD patterns of PP-MPs before and after adsorption were measured (Fig. 4). The diffraction peaks of pure PP are at $2\theta = 14.06^\circ$, 16.92° , 18.64° and 21.94° (Li et al., 2015). The virgin PP-MPs in this study also has the same diffraction peaks. The XRD results showed a similar diffraction peak position and shape between PP-MPs in mineral fraction system and virgin PP-MPs. However, the diffraction peaks of PP-MPs in POM fraction system showed lower intensity compared with the virgin PP-MPs. The PP-MPs in OMC fraction and bulk soil systems exhibited similar XRD

Table 4 Partitioning coefficients K_d (L/g) of Cd in different solid fractions under different initial concentrations

| Cd initial concentration C_0 (mg/L) | K_d (L/g) | | | | | | | |
|--|-------------|-------|-------|-------|-------|-------|---------|-------|
| | Bulk soil | | POM | | OMC | | Mineral | |
| | - | + | - | + | - | + | - | + |
| 5 | 0.021 | 0.017 | 0.616 | 0.512 | 0.029 | 0.017 | 0.068 | 0.048 |
| 10 | 0.031 | 0.022 | 0.462 | 0.413 | 0.032 | 0.03 | 0.041 | 0.033 |
| 20 | 0.028 | 0.021 | 0.345 | 0.248 | 0.034 | 0.015 | 0.018 | 0.017 |
| 30 | 0.027 | 0.022 | 0.197 | 0.160 | 0.030 | 0.023 | 0.015 | 0.019 |
| 50 | 0.012 | 0.010 | 0.097 | 0.076 | 0.018 | 0.012 | 0.009 | 0.011 |

Note: +, - represent with MPs and without MPs, respectively.

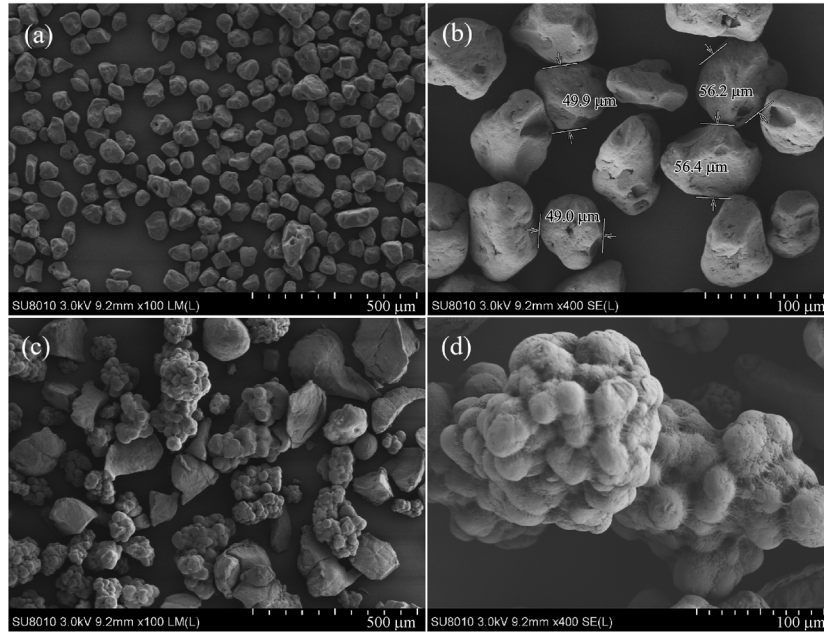


Fig. 3 SEM images of PP-MPs [virgin PP-MPs: (a) magnification: 100 \times , (b) magnification: 400 \times ; aged PP-MPs: (c) magnification: 100 \times , (d) magnification: 400 \times].

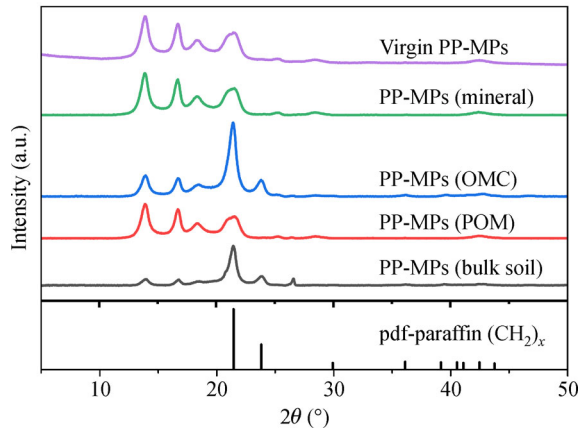


Fig. 4 XRD patterns of virgin PP-MPs (before and after adsorption in bulk soil, POM, OMC and mineral systems) [pdf-paraffin [(CH₂)_x] in the figure is the standard card of paraffin (JCPDS No.40-1995)].

characteristics, their diffraction peaks at 2θ of 21.94° and 23.84° that belonged to the paraffin [(CH₂)_x] were stronger than the virgin PP-MPs.

3.3.3 FTIR analysis

The FTIR spectra of virgin PP-MPs (before and after adsorption in bulk soil and three soil fractions) and aged PP-MPs are presented in Fig. 5. FTIR spectrum of the virgin PP-MPs revealed strong adsorption in the range 2840–3000 cm⁻¹ due to -CH₃ stretching, along with strong bands near 1460 and 1376 cm⁻¹ due to bending adsorptions of -CH₂ and -CH₃ groups, respectively, which are characteristics of PP (Li et al., 2019). There were main changes occurred in the regions of FTIR spectrum of aged PP-MPs characteristic of carbonyl, (1850–1654 cm⁻¹) and hydroxyl, and/or hydroperoxide (3250–3750 cm⁻¹) groups (Chen et al., 2021). For other PP-MPs samples, the

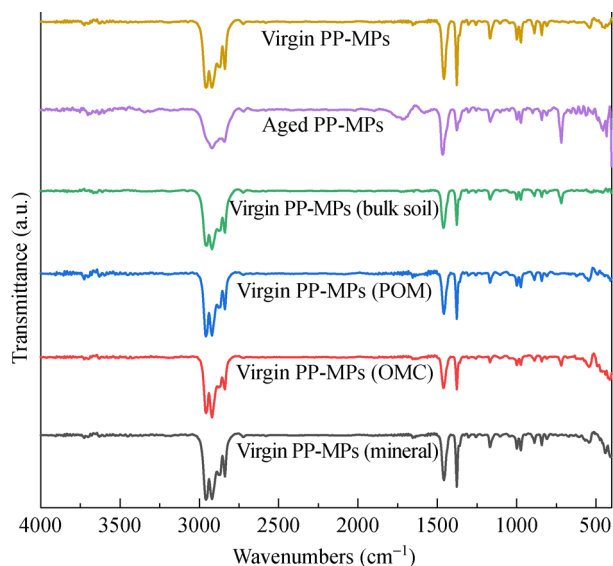


Fig. 5 FTIR spectra of virgin PP-MPs (before and after adsorption in bulk soil, POM, OMC and mineral systems) and aged PP-MPs.

shape and location of adsorption peaks were similar to virgin PP-MPs.

3.4 Effect of experimental conditions

3.4.1 Effect of MPs dosage

Three doses (0%, 2% and 10%, w/w) of MPs and 20 mg/L Cd solution were designed to test the effect of MPs dosage on Cd adsorption. As depicted in Fig. 6, the Q_e of Cd in bulk soil, POM and OMC systems decreased gradually with increasing MPs dose. POM adsorption capacity showed a significant decrease from 3.21 to 1.77 mg/g as the dosage of MPs increased from 0 to 10%. Nevertheless, the mineral fraction showed opposite trend.

3.4.2 Effect of aging degree

As exhibited in Fig. 7, whether virgin or aged, the addition of MPs affected the adsorption capacity of bulk soil and three soil fractions. Among them, the effect of MPs on bulk soil, POM and OMC fractions was negative, while the effect on mineral fraction was positive. The POM fraction was affected largely, followed by OMC fraction. Moreover, the effect of virgin MPs on Q_e was stronger than that of aged ones.

4 Discussion

Our study indicated that PP-MPs may decrease the adsorption capacity of Cd by soil in aqueous medium,

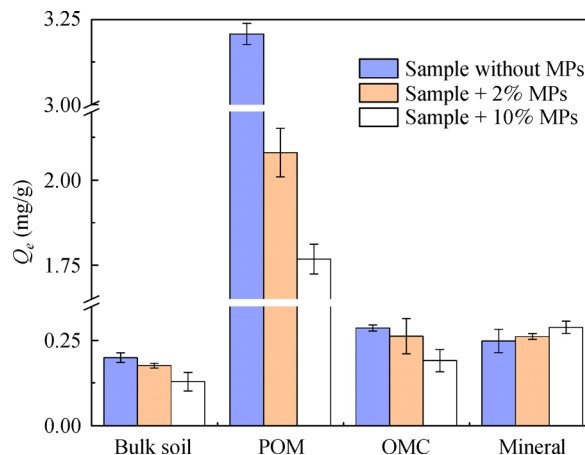


Fig. 6 The effect of MPs dosage on Cd adsorption to bulk soil and three soil fractions (POM, OMC, and mineral).

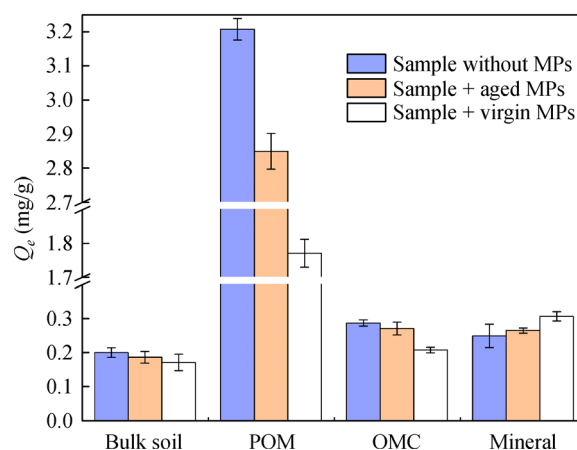


Fig. 7 The effect of virgin and aged PP-MPs on Cd adsorption to bulk soil and three soil fractions (POM, OMC, and mineral).

which is partly in agreement with the result of Zhang et al. (2020). In their study, the existence of HDPE resulted in the soil adsorption for Cd decreased from 0.99 to 0.985 mg/g, and similar decreased trend from 0.37 to 0.35 mg/g was observed in our work. Previous studies suggested that MPs have the ability to adsorb heavy metals (Rios et al., 2007; Holmes et al., 2012; Brennecke et al., 2016), however, their adsorption amount is commonly lower than that of soil (Hodson et al., 2017; Wang et al., 2017; Dobaradaran et al., 2018; Wang et al., 2019; Zhou et al., 2019). A possible explanation is that the soil particulate matter may provide a greater specific surface area than MP particles (Holmes et al., 2012; Holmes et al., 2014; Zhou et al., 2019). Another possible explanation is that soil contains a variety of hydrous oxide minerals and organic matter (Bradl, 2004), these substances possess surface hydroxyl groups (Samiey et al., 2014), which may improve soil adsorption for heavy metals. By contrast, the composition and surface structure of MPs are relatively

simple, its hydrophobic property also limits its adsorption of heavy metals in solution (Hodson et al., 2017).

Our findings further demonstrated differential responses from the adsorption capacity of three soil solid fractions to Cd. POM fraction has the highest equilibrium adsorption capacity for Cd regardless of the presence of MPs, and OMC fraction has a stronger adsorption capacity for Cd than mineral fraction without the added MPs. Here, POM are known to be labile organic components with a rapid turnover (Sebastia et al., 2008). Previous study demonstrated that, due to its functional groups such as -COOH and -OH, POM fractions can be metal enriched in both metal-contaminated and uncontaminated soils through ion exchange and complexation (Guo et al., 2006; Sebastia et al., 2008; Luo et al., 2019). OMC are formed by organic matter combined with minerals in the soil (Quan et al., 2020), which are considered to be long-term soil organic carbon storage (Wen et al., 2019). A recent study revealed that the carboxylic carbon and iron oxides of the OMC served as the binding sites of Cu^{2+} (Tian et al., 2021). However, the adsorption capacity of both POM and OMC fractions to Cd decreased when exposed to MPs, whereas an opposite trend was observed for mineral fraction. Firstly, it can be seen from XRD pattern that there was no significant difference between PP-MPs in POM fraction system and virgin PP-MPs, which indicated that PP-MPs and POM may not bind in aqueous solution, and MPs may reduce the adsorption capacity of POM for Cd by affecting the diffusion of Cd ion in solution (Fig. 4). Secondly, OMC fraction mainly reduced the intensity of PP-MPs diffraction peak and enhanced the diffraction peak representing paraffin $[(\text{CH}_2)_x]$ (Fig. 4), which suggested that the organic matter of OMC fraction adhered to the surface of PP-MPs, thus hindered the adsorption of Cd. Thirdly, PP-MPs in mineral fraction system showed similar XRD pattern and FTIR spectra with virgin PP-MPs, indicating that there was no obvious reaction between mineral fraction and PP-MPs. The adsorption of MPs on minerals is mainly physical adsorption and pore filling (Wu et al., 2015), and MPs can enhance the electronegativity of mineral surface (Yan et al., 2020), which may enhance the adsorption for Cd.

We speculate that the influence of MPs on bulk soil might be controlled by the proportion of POM, OMC and mineral in soils. Although the strong enrichment ability of POM fraction for heavy metals (e.g., Cu, Zn, Pb and Cd) has been confirmed by different studies (Balabane and van Oort, 2002; Zhang, 2006; Besnard et al., 1996), the ratio of POM, OMC and mineral in this study was 1:6.7:3.5, obviously, the OMC fraction was the majority. Additionally, the Cd adsorption amount in POM and OMC fractions had dropped by 0.88 and 2.13 mg, respectively, indicating that the OMC fraction may be responsible for the reduction of soil adsorption capacity by MPs. OMC fraction has been reported the key fraction that determined Cu(II) adsorption in the red soil, where the POM and OMC fractions in soil were 4.39% and 95.6%, respectively (Tian et al., 2021).

Furthermore, the experiments with different MPs content and aging degree showed similar variation trend between OMC and bulk soil (Fig. 6 and Fig. 7).

Zhang et al. (2020) demonstrated MPs dose-dependent effect on soil adsorption. Similar phenomenon was also observed in our study. Compared with 2% dosage, 10% dosage significantly reduced the adsorption of Cd by soil (Fig. 6). The possible reason was ascribed to the agglomeration caused by the accumulation of MPs (Fu et al., 2019), resulting in diffusion inhibition for metal ion. In addition, aged MPs also play key role in metal adsorption. The maximum adsorption capacity of Cd, Pb, Cu, and Zn ions onto the aged MPs was predicted 1–5 times higher than that of the virgin ones in aqueous system (Guo and Wang, 2021). In our study, the addition of MPs decreased soil adsorption, and the effect of aged MPs on soil adsorption of Cd was less than that of virgin MPs. As can be seen from the SEM photograph (Fig. 3), after aging, the MPs particles melt and re-aggregate, forming a large number of bulges on the surface and significantly increasing the roughness, which greatly improved the specific surface area and porosity of aged PP-MPs. Moreover, some oxygen-containing functional groups such as carbonyl, hydroxyl and hydroperoxide groups were observed obviously in the FTIR spectra of aged PP-MPs, which can improve the adsorption capacity for Cd (Mao et al., 2020) (Fig. 5). Therefore, with higher specific surface area and roughness, as well as new oxygen-containing functional groups, the Cd adsorption capacity of aged MPs may be improved relative to virgin MPs.

All experiments in this study were conducted in a solution system, and results showed that the addition of PP-MPs decreased the adsorption capacity of Cd to soil solid fractions. This is in accordance with Zhang et al. (2020) and Li et al. (2021). Nevertheless, in a study from Yu et al. (2020), PE-MPs was declared had decreased the bioavailability of Cu, Cr, and Ni in soil by promoting the transformation of heavy metal speciation from bioavailable to organic bound. This may be partly due to the distinct reaction systems, i.e. in aqueous system or in soil system. Soil contains a variety of inorganic and organic fractions including minerals and organic matters (Bradl, 2004), these fractions may interact with each other. Moreover, the presence of MPs can change soil structure and properties (de Souza Machado et al., 2018), which makes the reaction of MPs and heavy metals in the soil more complicated. Besides, the types, dosage and sizes of MPs, as well as soil types used in these studies also varied, resulting in different performance in soil adsorption.

5 Conclusions

In this study, we investigated the impact of PP-MPs on adsorption behaviors of Cd in soil (bulk soil and soil solid fractions) in aqueous medium. The presence of MPs in soil

reduced the adsorption capacity of the bulk soil for Cd. According to our research, the adsorption capacity of three soil fractions were in the order of POM>OMC>mineral before adding MPs. However, after exposed to MPs, the adsorption ability of POM and OMC fractions decreased, while that of mineral fraction increased. Additionally, the effect of MPs on the adsorption of Cd by soil was related more to the dosage of MPs rather than aging. In conclusion, the effect of MPs on bulk soil might be determined by the proportion of POM, OMC and mineral fractions in soil. Our work provide a further perception regarding the impacts of MPs on adsorption behaviors of Cd in soil. However, only one type of soil was employed in the current study, with stable POM, OMC, and mineral fractions ratio, more research is needed to further figure out the influence of fraction proportion and soil types.

Acknowledgements This work was Supported by the Fundamental Research Funds for the Central Universities, Zhongnan University of Economics and Law (Nos. 2722020JCG065, 2722021BX026 and 202151413).

References

- Altunay N, Hazer B, Tuzen M, Elik A (2021). A new analytical approach for preconcentration, separation and determination of Pb(II) and Cd (II) in real samples using a new adsorbent: Synthesis, characterization and application. *Food Chemistry*, 359: 129923
- Awual M R, Hasan M M, Islam A, Rahman M M, Asiri A M, Khaleque M A, Sheikh M C (2019a). Introducing an amine functionalized novel conjugate material for toxic nitrite detection and adsorption from wastewater. *Journal of Cleaner Production*, 228: 778–785
- Awual M R, Hasan M M, Islam A, Rahman M M, Asiri A M, Khaleque M A, Sheikh M C (2019b). Offering an innovative composited material for effective lead(II) monitoring and removal from polluted water. *Journal of Cleaner Production*, 231: 214–223
- Balabane M, van Oort F (2002). Metal enrichment of particulate organic matter in arable soils with low metal contamination. *Soil Biology and Biochemistry*, 34(10): 1513–1516
- Besnard E, Chenu C, Balesdent J, Puget P, Arrouays D (1996). Fate of particulate organic matter in soil aggregates during cultivation. *European Journal of Soil Science*, 47(4): 495–503
- Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham M B, Scheckel K (2014). Remediation of heavy metal (loid)s contaminated soils—to mobilize or to immobilize? *Journal of Hazardous Materials*, 266: 141–166
- Boots B, Russell C W, Green D S (2019). Effects of microplastics in soil ecosystems: Above and below ground. *Environmental Science & Technology*, 53(19): 11496–11506
- Bradl H B (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, 277(1): 1–18
- Brennecke D, Duarte B, Paiva F, Caçador I, Canning-Clode J (2016). Microplastics as vector for heavy metal contamination from the marine environment. *Estuarine, Coastal and Shelf Science*, 178: 189–195
- Cabrera C, Ortega E, Lorenzo M L, López M C (1998). Cadmium contamination of vegetable crops, farmlands, and irrigation waters. *Reviews of Environmental Contamination and Toxicology*, 154: 55–81
- Chen X, Xu M, Yuan L M, Huang G Z, Chen X J, Shi W (2021). Degradation degree analysis of environmental microplastics by micro FT-IR imaging technology. *Chemosphere*, 274(1): 1297
- de Souza Machado A A, Lau C W, Till J, Kloas W, Lehmann A, Becker R, Rillig M C (2018). Impacts of microplastics on the soil biophysical environment. *Environmental Science & Technology*, 52(17): 9656–9665
- de Souza Machado A A, Lau C W, Kloas W, Bergmann J, Bachelier J B, Faltin E, Becker R, Görlich A S, Rillig M C (2019). Microplastics can change soil properties and affect plant performance. *Environmental Science & Technology*, 53(10): 6044–6052
- Deng J, Guo P, Zhang X, Su H, Zhang Y, Wu Y, Li Y (2020). Microplastics and accumulated heavy metals in restored mangrove wetland surface sediments at Jinjiang Estuary (Fujian, China). *Marine Pollution Bulletin*, 159: 111482
- Dobaradaran S, Schmidt T C, Nabipour I, Khajeahmadi N, Tajbakhsh S, Saeedi R, Javad Mohammadi M, Keshkar M, Khorsand M, Faraji Ghasemi F (2018). Characterization of plastic debris and association of metals with microplastics in coastline sediment along the Persian Gulf. *Waste Management (New York, N.Y.)*, 78: 649–658
- Fu D D, Zhang Q J, Fan Z Q, Qi H Y, Wang Z Z, Peng L C (2019). Adsorption characteristics of copper ions on polystyrene microplastics. *Environmental Science*, 39(11): 4769–4775 (in Chinese)
- Gewert B, Plassmann M M, MacLeod M (2015). Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science. Processes & Impacts*, 17(9): 1513–1521
- Geyer R, Jambeck J R, Law K L (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3(7): e1700782
- Guo X, Wang J (2021). Projecting the sorption capacity of heavy metal ions onto microplastics in global aquatic environments using artificial neural networks. *Journal of Hazardous Materials*, 402(1): 123709
- Guo X, Zhang S, Shan X Q, Luo L E, Pei Z, Zhu Y G, Liu T, Xie Y N, Gault A (2006). Characterization of Pb, Cu, and Cd adsorption on particulate organic matter in soil. *Environmental Toxicology and Chemistry*, 25(9): 2366–2373
- Hartmann N B, Hüffer T, Thompson R C, Hassellöv M, Verschoor A, Daugaard A E, Rist S, Karlsson T, Brennholt N, Cole M, Herrling M P, Hess M C, Ivleva N P, Lusher A L, Wagner M (2019). Are we speaking the same language? recommendations for a definition and categorization framework for plastic debris. *Environmental Science & Technology*, 53(3): 1039–1047
- Hodson M E, Duffus-Hodson C A, Clark A, Prendergast-Miller M T, Thorpe K L (2017). Plastic bag derived-microplastics as a vector for metal exposure in terrestrial invertebrates. *Environmental Science & Technology*, 51(8): 4714–4721
- Holmes L A, Turner A, Thompson R C (2012). Adsorption of trace metals to plastic resin pellets in the marine environment. *Environmental Pollution*, 160(1): 42–48
- Holmes L A, Turner A, Thompson R C (2014). Interactions between trace metals and plastic production pellets under estuarine conditions. *Marine Chemistry*, 167: 25–32
- Huang W, Song B, Liang J, Niu Q, Zeng G, Shen M, Deng J, Luo Y,

- Wen X, Zhang Y (2021). Microplastics and associated contaminants in the aquatic environment: A review on their ecotoxicological effects, trophic transfer, and potential impacts to human health. *Journal of Hazardous Materials*, 405: 124187
- Huerta Lwanga E, Mendoza Vega J, Ku Quej V, Chi J L A, Sanchez Del Cid L, Chi C, Escalona Segura G, Gertsen H, Salánki T, van der Ploeg M, Koelmans A A, Geissen V (2017). Field evidence for transfer of plastic debris along a terrestrial food chain. *Scientific Reports*, 7(1): 14071
- Jambeck J R, Geyer R, Wilcox C, Siegler T R, Perryman M, Andrady A, Narayan R, Law K L (2015). Plastic waste inputs from land into the ocean. *Science*, 347(6223): 768–771
- Kabir A H M E, Sekine M, Imai T, Yamamoto K, Kanno A, Higuchi T (2021). Assessing small-scale freshwater microplastics pollution, land-use, source-to-sink conduits, and pollution risks: Perspectives from Japanese rivers polluted with microplastics. *Science of the Total Environment*, 768(10): 144655
- Khalid N, Aqeel M, Noman A (2020). Microplastics could be a threat to plants in terrestrial systems directly or indirectly. *Environmental Pollution*, 267: 115653
- Komy Z R, Shaker A M, Heggy S E M, El-Sayed M E (2014). Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid. *Chemosphere*, 99: 117–124
- Labanowski J, Sebastia J, Foy E, Jongmans T, Lamy I, van Oort F (2007). Fate of metal-associated POM in a soil under arable land use contaminated by metallurgical fallout in northern France. *Environmental Pollution*, 149(1): 59–69
- Lair G J, Gerzabek M H, Haberhauer G (2007). Retention of copper, cadmium and zinc in soil and its textural fractions influenced by long-term field management. *European Journal of Soil Science*, 58(5): 1145–1154
- Li G X, Cao S K, Zheng S J, Wang W J, Cao Y X, Wang J W (2015). Crystallization, melting behavior, and crystal structure of reactive, intumescent, flame-retardant polypropylene. *Journal of Applied Polymer Science*, 132(5): 41374
- Li M, Liu Y, Xu G, Wang Y, Yu Y (2021). Impacts of polyethylene microplastics on bioavailability and toxicity of metals in soil. *Science of the Total Environment*, 760: 144037
- Li X, Mei Q, Chen L, Zhang H, Dong B, Dai X, He C, Zhou J (2019). Enhancement in adsorption potential of microplastics in sewage sludge for metal pollutants after the wastewater treatment process. *Water Research*, 157: 228–237
- Liu M, Lu S, Song Y, Lei L, Hu J, Lv W, Zhou W, Cao C, Shi H, Yang X, He D (2018). Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai, China. *Environmental Pollution*, 242(Pt A): 855–862
- Luo Y, Wu Y, Shu J, Wu Z (2019). Effect of particulate organic matter fractions on the distribution of heavy metals with aided phytostabilization at a zinc smelting waste slag site. *Environmental Pollution*, 253: 330–341
- Mao R F, Lang M F, Yu X Q, Wu R R, Yang X M, Guo X T (2020). Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. *Journal of Hazardous Materials*, 393: 122515
- Mbachu O, Jenkins G, Kaparaju P, Pratt C (2021). The rise of artificial soil carbon inputs: Reviewing microplastic pollution effects in the soil environment. *Science of the Total Environment*, 780: 146569
- Park J H, Lamb D, Paneerselvam P, Choppala G, Bolan N, Chung J W (2011). Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *Journal of Hazardous Materials*, 185(2–3): 549–574
- Qi Y, Ossowicki A, Yang X, Huerta Lwanga E, Dini-Andreote F, Geissen V, Garbeva P (2020). Effects of plastic mulch film residues on wheat rhizosphere and soil properties. *Journal of Hazardous Materials*, 387: 121711
- Qu C, Chen W, Hu X, Cai P, Chen C, Yu X Y, Huang Q (2019). Heavy metal behaviour at mineral-organo interfaces: Mechanisms, modelling and influence factors. *Environment International*, 131(6): 104995
- Quan G, Fan Q, Sun J, Cui L, Wang H, Gao B, Yan J (2020). Characteristics of organo-mineral complexes in contaminated soils with long-term biochar application. *Journal of Hazardous Materials*, 384: 121265
- Rillig M C (2018). Microplastic disguising as soil carbon storage. *Environmental Science & Technology*, 52(11): 6079–6080
- Rios L M, Moore C, Jones P R (2007). Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Marine Pollution Bulletin*, 54(8): 1230–1237
- Samiey B, Cheng C H, Wu J (2014). Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A review. *Materials (Basel)*, 7(2): 673–726
- Sari A, Tuzen M (2014). Cd(II) adsorption from aqueous solution by raw and modified kaolinite. *Applied Clay Science*, 88–89: 63–72
- Scudo A, Liebmann B, Corden C, Tyrer D, Kreissig J, Warwick O (2017). Intentionally added microplastics in products- Final report of the study on behalf of the European Commission. Available online at the website of www.researchgate.net/publication/327982467_Intentionally_added_microplastics_in_products (accessed April 26, 2021)
- Sebastia J, van Oort F, Lamy I (2008). Buffer capacity and Cu affinity of soil particulate organic matter (POM) size fractions. *European Journal of Soil Science*, 59(2): 304–314
- Shang E P, Xu E Q, Zhang H Q, Huang C H (2018). Spatial-temporal trends and pollution source analysis for heavy metal contamination of cultivated soils in five major grain producing regions of China. *Environmental Science*, 39(10): 4670–4683 (in Chinese)
- Shi J, Wu Q, Zheng C, Yang J (2018). The interaction between particulate organic matter and copper, zinc in paddy soil. *Environmental Pollution*, 243(Pt B): 1394–1402
- Sun Q H, Li J, Wang C, Chen A Q, You Y L, Yang S P, Liu H H, Jiang G B, Wu Y N, Li Y S (2022). Research progress on distribution, sources, identification, toxicity, and biodegradation of microplastics in the ocean, freshwater, and soil environment. *Frontiers of Environmental Science & Engineering*, 16(1): 1
- Tian Y, Yang J J, Hussain S (2021). Molecular mechanism of Cu(II) adsorption by organo-mineral complexes of red soil. *Acta Pedologica Sinica*, 58(3): 722–731 (in Chinese)
- Wan Y, Wu C, Xue Q, Hui X (2019). Effects of plastic contamination on water evaporation and desiccation cracking in soil. *Science of the Total Environment*, 654: 576–582
- Wang F, Yang W, Cheng P, Zhang S, Zhang S, Jiao W, Sun Y (2019). Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere*, 235: 1073–1080

- Wang J, Peng J, Tan Z, Gao Y, Zhan Z, Chen Q, Cai L (2017). Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals. *Chemosphere*, 171: 248–258
- Wen Y, Liu W, Deng W, He X, Yu G (2019). Impact of agricultural fertilization practices on organo-mineral associations in four long-term field experiments: Implications for soil C sequestration. *Science of the Total Environment*, 651(Pt 1): 591–600
- Wu Y H, Zhou D M, Gao J, Si Y B (2015). Adsorption of three phthalic Acid esters on different clay minerals. *Journal of Agro-Environment Science*, 34(06): 1107–1114 (in Chinese)
- Yan X, Yang X, Tang Z, Fu J, Chen F, Zhao Y, Ruan L, Yang Y (2020). Downward transport of naturally-aged light microplastics in natural loamy sand and the implication to the dissemination of antibiotic resistance genes. *Environmental Pollution*, 262: 114270
- Yang J, Wang J Y, Qiao P W, Zheng Y M, Yang J X, Chen T B, Lei M, Wan X M, Zhou X Y (2020). Identifying factors that influence soil heavy metals by using categorical regression analysis: A case study in Beijing, China. *Frontiers of Environmental Science & Engineering*, 14(3): 37
- Yang L, Zhang Y, Kang S, Wang Z, Wu C (2021). Microplastics in soil: A review on methods, occurrence, sources, and potential risk. *Science of the Total Environment*, 780(1): 146546
- Yang X, Bento C P M, Chen H, Zhang H, Xue S, Lwanga E H, Zomer P, Ritsema C J, Geissen V (2018). Influence of microplastic addition on glyphosate decay and soil microbial activities in Chinese loess soil. *Environmental Pollution*, 242(Pt A): 338–347
- Yu H, Hou J, Dang Q, Cui D, Xi B, Tan W (2020). Decrease in bioavailability of soil heavy metals caused by the presence of microplastics varies across aggregate levels. *Journal of Hazardous Materials*, 395(2): 122690
- Zhang G S, Liu Y F (2018). The distribution of microplastics in soil aggregate fractions in southwestern China. *Science of the Total Environment*, 642(15): 12–20
- Zhang M K (2006). Distribution of organic carbon, nutrients and heavy metals in different size fractions in sandy soil. *Acta Pedologica Sinica*, 43(4): 584–591 (in Chinese)
- Zhang M K, Ke Z X (2004). Copper and zinc enrichment in different size fractions of organic matter from polluted soils. *Pedosphere*, 14(1): 27–36
- Zhang S, Han B, Sun Y, Wang F (2020). Microplastics influence the adsorption and desorption characteristics of Cd in an agricultural soil. *Journal of Hazardous Materials*, 388: 121775
- Zhang Z Q, Zhang Y P, Zhu Z H (2000). Study on the characteristics of kinetic of cadmium retention on soils. *Journal of Environmental Sciences*, 20(3): 370–375 (in Chinese)
- Zhou J, Wen Y, Marshall M R, Zhao J, Gui H, Yang Y D, Zeng Z H, Jones D L, Zang H D (2021). Microplastics as an emerging threat to plant and soil health in agroecosystems. *Science of the Total Environment*, 787: 147444
- Zhou T, Wu L, Luo Y, Christie P (2018). Effects of organic matter fraction and compositional changes on distribution of cadmium and zinc in long-term polluted paddy soils. *Environmental Pollution*, 232: 514–522
- Zhou Y, Liu X, Wang J (2019). Characterization of microplastics and the association of heavy metals with microplastics in suburban soil of central China. *Science of the Total Environment*, 694(7): 133798
- Zhuang G T (2015). Current situation of national soil pollution and strategies on prevention and control. *Bulletin of the Chinese Academy of Sciences*, 30(04): 477–483 (in Chinese)