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Effects of Microplastics on the Transport of Soil Dissolved Organic Matter in the Loess Plateau of China

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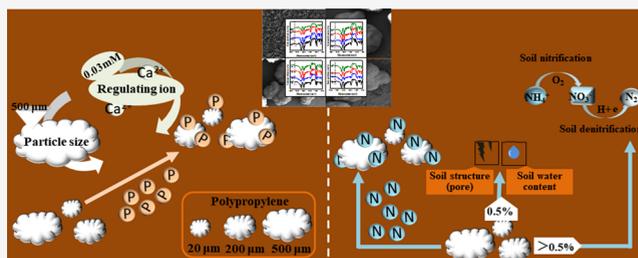
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ABSTRACT: Microplastics (MPs) pollution and dissolved organic matter (DOM) affect soil quality and functions. However, the effect of MPs on DOM and underlying mechanisms have not been clarified, which poses a challenge to maintaining soil health. Under environmentally relevant conditions, we evaluated the major role of polypropylene particles at four micron-level sizes (20, 200, and 500 μm and mixed) in regulating changes in soil DOM content. We found that an increase in soil aeration by medium and high-intensity (>0.5%) MPs may reduce NH_4^+ leaching by accelerating soil nitrification. However, MPs have a positive effect on soil nutrient retention through the adsorption of PO_4^{3-} (13.30–34.46%) and NH_4^+ (9.03–19.65%) and their leached dissolved organic carbon (MP-leached dissolved organic carbon, MP-DOC), thereby maintaining the dynamic balance of soil nutrients. The regulating ion (Ca^{2+}) is also an important competitor in the MP-DOM adsorption system, and changes in its intensity are dynamically involved in the adsorption process. These findings can help predict the response of soil processes, especially nutrient cycling, to persistent anthropogenic stressors, improve risk management policies on MPs, and facilitate the protection of soil health and function, especially in future agricultural contexts.

KEYWORDS: Microplastics, Adsorption, Dissolved organic matter, Nutrient leaching, Soil health



INTRODUCTION

The generation of plastic waste in agricultural soil during the implementation of processes to improve agricultural efficiency and increase the farmers' incomes is a subject of widespread concern.¹ Agricultural practice management (e.g., sewage sludge and plastic film), runoff and sediment in roads or urban areas, atmospheric migration, and large plastics disintegration are the main sources of plastic waste.² Previous reports have revealed that the global agricultural sector uses approximately 12.5 million tons of plastics annually, and the amount is increasing each year.³ Microplastics (MPs, <5 mm) obtained from the decomposition of large-size plastic fragments are more difficult to track than large residual plastic fragments, and the associated MP pollution may have disastrous ecological consequences for agricultural soil biophysical and geochemical processes, especially the transportation of (water) nutrients and crop growth.^{4–6} Because of the porous structure and large specific surface area of MPs, they can participate in soil processes via many pathways, including complexation, coprecipitation, and adsorption. Soil dissolved organic matter (DOM) is an important factor that affects soil properties and functions, and it participates in the accumulation and migration of many chemical substances in the environment, such as pesticides and heavy metals.^{7,8} The potential binding of DOM to chemicals in the environment

and associated interactions with MPs indicate that MPs may participate in ecological processes related to DOM. However, despite the negative consequences of the accumulation of MPs in agricultural soils, only limited studies have evaluated the interaction between DOM and MPs.^{9,10}

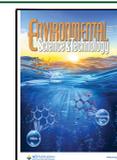
MPs directly or indirectly affect DOM properties in aquatic and terrestrial ecosystems,^{11,12} while DOM molecules tend to participate in the adsorption process of MPs. For example, DOM complexes with metals enhance the adsorption capacity of MPs by reducing the activity of metal ions in the water environment (enhancing hydrophobicity).^{9,13} In addition, DOM may adsorb on MPs to form complexes, which weaken their affinity for antibiotics by affecting their surface area (physical) and surface properties (chemical).¹⁴ The studies presented above elucidate the interaction between MPs and DOM and the role of DOM in the process of MP adsorption (synergy or antagonism). However, several internal (external) factors may affect the interaction between MPs and DOM,

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including the DOM properties (e.g., source and functional groups) and MP diversity (e.g., size and concentration).¹⁵ In addition, the competition of soil components such as ions and other compounds for adsorption sites with MPs in solution has not been clarified.¹⁶ Under normal circumstances, organic additives will inevitably attach to plastics during production and leach into the ecosystem, which may constitute a new source of soil organic carbon (SOC) in the environment and change the carbon cycle.^{17,18} However, the influence of MPs with carbon as the main chain structure on the organic carbon pool, especially on the dissolved organic carbon (DOC) pool, is still not fully understood.¹⁹ These knowledge gaps limit our understanding of the possible impacts and regulatory mechanisms of MPs on DOM and the soil environment, thus limiting our ability to accurately predict the ecological consequences of MPs. Therefore, to obtain a better mechanistic understanding of the ecological effects of MPs, we must consider the role and relative contribution of MPs based on their interaction with DOM.

The Loess Plateau is one of the most fragile ecosystems in the world, with poor (water) nutrient retention capacity due to its loose and porous soil texture and frequent erosion disasters.¹² The agroecosystem's long-term "supply" exceeds its "acquisition", leading to continuous damage to soil structure and reduced soil fertility in this area.²⁰ MPs are small in size and density,²¹ and they can easily be carried by soil particles and migrate rapidly with the flow of water. The Loess Plateau provides a good platform to study the response of soil ecological processes to MP disturbance. Currently, most studies focus on MP accumulation and distribution,²² soil physical structure, and crop growth response,^{23–25} and soil geochemical processes have been neglected. Elucidating nutrient cycling is important to ensuring the stability of the local ecosystem.²⁶ Plastic pollution usually occurs in areas with high urbanization and intensive agricultural practices,² but a large portion, mainly via MPs, may still be transported to remote areas, such as the plateau, through the atmosphere and precipitation.^{27,28} However, there is limited knowledge of the linkage between soil nutrient turnover and MPs in the Loess Plateau and the role of DOM.

To elucidate the key role of MPs in regulating the soil nutrient pool, particularly the DOC pool, we selected typical loam soil from the Loess Plateau and performed soil column and adsorption experiments. We predict that (1) MPs will reduce the leaching of PO_4^{3-} and NH_4^+ in soil by adsorption, increase the leaching of DOC in soil by derivative substances, and regulate the soil nutrient dynamics; (2) changes in Ca^{2+} intensity (≥ 0.03 mM) will be dynamically involved in the adsorption process of MPs; (3) considering the diversity of MPs, PO_4^{3-} will be more sensitive to the particle size of MPs than the concentration and large-sized (500 μm) MPs will greatly regulate the dynamic changes of soil nutrients; (4) further consideration of the soil environment related to MPs may reveal that increases in the soil oxygen circulation degree partially explain the change of NH_4^+ . These findings are expected to enhance our understanding of the role of MPs in regulating soil nutrient pools while also improving our ability to ensure soil health and food production.

MATERIALS AND METHODS

Collection of Soil Samples. In April 2022, soil samples were collected in Yangling County, Shaanxi Province, on the southern Loess Plateau (107.8~108.3° E, 34.1~34.5° N) (see

Text S1 for the specific process of sample collection). The area belongs to the temperate semihumid and semiarid climate zone and has an altitude of approximately 534 m, annual average temperature of 12.9 °C, and average annual precipitation of 630 mm²⁹ (Figure S1). The clean plough layer of soil (0–20 cm) without plastic film (vulnerable to natural and man-made disturbances) was selected (see Table 1 for soil properties and

Table 1. Principle Properties of Selected Soil

properties	value
<0.002 mm (Clay) (%)	25.42
0.002–0.02 mm (Silt) (%)	36.7
0.02–2 mm (Sand) (%)	37.88
Soil organic carbon ($\text{g}\cdot\text{kg}^{-1}$)	6.80
Total nitrogen ($\text{g}\cdot\text{kg}^{-1}$)	0.18
Total phosphorus ($\text{g}\cdot\text{kg}^{-1}$)	0.45
Nitrate nitrogen ($\text{mg}\cdot\text{kg}^{-1}$)	4.58
Ammonium nitrogen ($\text{mg}\cdot\text{kg}^{-1}$)	3.15
Available phosphorus ($\text{mg}\cdot\text{kg}^{-1}$)	4.41
Soil water content (%)	9.28
pH	8.64

Text S2 for details of determinations). The soil samples were air-dried at room temperature, passed through a 2 mm sieve, and then divided into three parts for the subsequent soil leaching experiments, adsorption experiments, and soil physicochemical properties analyses.

MPs and Characterization. Polypropylene particles (Beijing Zhonglian Company, China) are frequently used, and thus, a high level of their residues are found in agricultural soil.³⁰ According to the actual field conditions, four common particle sizes were selected as the research objects: 500 μm (P500), 200 μm (P200), 20 μm (P20), and mixed treatment (PX, 500:200:20 μm = 1:1:1) (the principle properties of tested MPs are detailed in Table S1).

The microscopic characteristics of the MPs were observed by using a scanning electron microscope (SEM, Nova Nano SEM-450, FEI). Then, the MPs were characterized via Fourier-transform infrared (FTIR) spectroscopy (Vetex 70, Bruker, Germany), and the changes in MP functional groups after treatment were observed (see Text S3 and Figure S2 for details).

Preparation of Soil Columns. The soil column consists of two parts: soil–MP mixture (abbreviated as mixture) and plexiglass tubes (inner diameter, 7 cm; length, 25 cm). In May 2022, we applied four particle sizes of MPs to 0.5% (C0.5), 1% (C1), and 2% (C2) of the tested soil (w/w) to prepare the mixture.^{22,31,32} At the same time, a control sample (0%, CK) without MPs (containing only the tested soil) was prepared. Each treatment (including the CK) was performed in quadruplicate (see Table S2 for more information on the MP treatments). Then, the mixture of various treatments after manual mixing was placed on a multifunctional shaker (HY-2A, Guohua, China) and then shaken for 10 min³³ (see Figure S3 for details on the mixture).

The bottom of the plexiglass tube was affixed with an end-cap, and the drain pipe was connected to it using a small hole in the center of the end-cap (plexiglass tubes in Figure S4A). Before use, the plexiglass tube was rinsed with distilled water three times and then rinsed with distilled water in an ultrasonic cleaning machine (Kunshan Shumei Company, China) for 10 min. Before adding the mixture, filter paper was placed at the

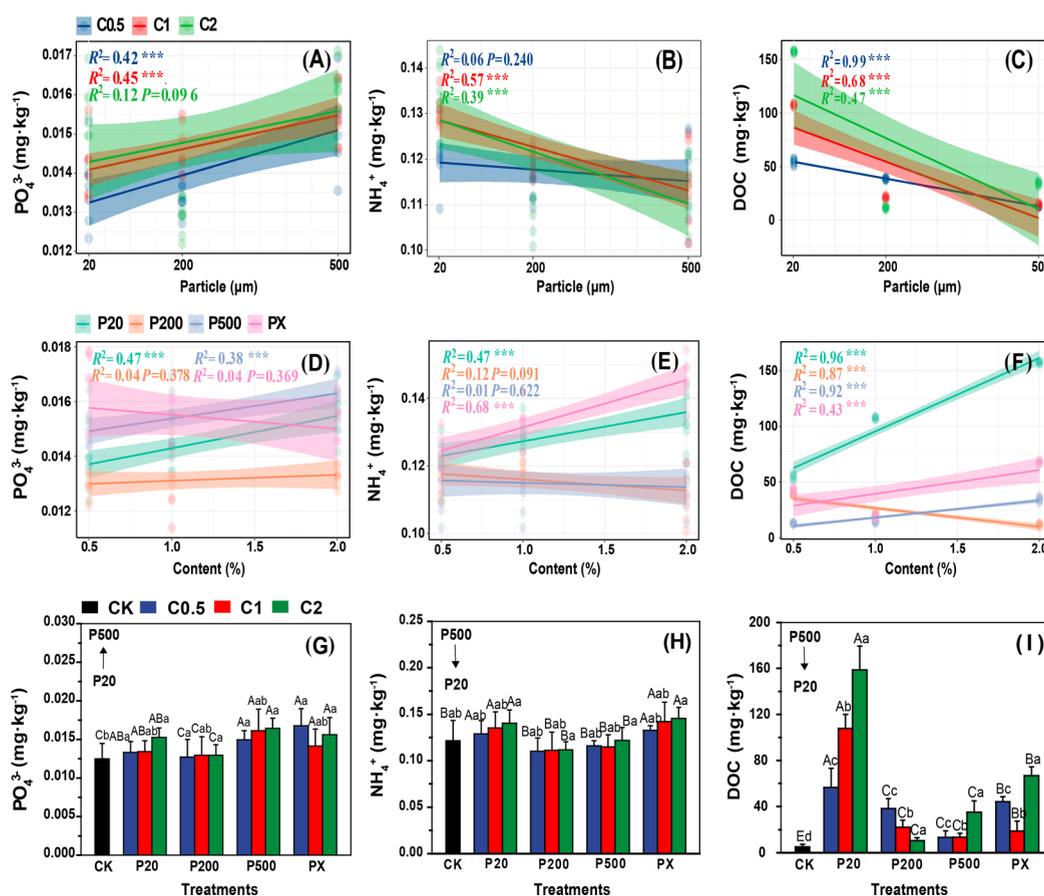


Figure 1. Environmental behavior of MPs, including the influence of MPs on the adsorption content of PO_4^{3-} , NH_4^+ and content of DOC. (A–C) The linear relationships between MP treatments with different particle sizes, PO_4^{3-} and NH_4^+ adsorption, and DOC content. P values were indicated by asterisks: *** $P < 0.001$. The shaded part represents a 95% confidence interval. (D–F) The linear relationships between MP treatments with different concentrations and PO_4^{3-} and NH_4^+ adsorption and DOC content. P values were indicated by asterisks: *** $P < 0.001$. The shaded part represents a 95% confidence interval. (G–I) The effects of MPs on the adsorption of PO_4^{3-} , NH_4^+ and content of DOC, respectively. The uppercase letters denote the difference after being treated with MPs with the same concentration and different particle sizes, and the lowercase letters denote the difference after being added with MPs with the same particle size and different concentrations ($P < 0.05$). P20 treatment represents 20 μm MP treatment; P200 treatment represents 200 μm MP treatment; P500 treatment represents 500 μm MP treatment; PX treatment represents 20:200:500 $\mu\text{m} = 1:1:1$. CK (black): 0%; C0.5 (blue): 0.5%; C1 (red): 1%; C2 (green): 2%. The abbreviation of DOM in soil is suitable for the above methods.

bottom of the plexiglass tube to prevent the loss of soil particles and then covered with approximately 100 g of coarse sand to fill the concave part (0.5 mm) of the end-cap. Four kilograms of the mixture was manually added to the plexiglass tube using a wooden compaction tool, and the bulk density is controlled at 1.3 g cm^{-3} (determined according to the soil bulk density in the study area). Then, the filter paper was placed on the surface of the soil column and allowed to settle for 1 week under natural laboratory conditions ($25 \pm 1 \text{ }^\circ\text{C}$) to ensure that interference did not occur during the period.

Leaching Experiments. Batch Mariotte bottles and soil columns were used to establish and maintain a constant flow rate during the leaching experiments. During the experiment, the water head of the soil column was kept constant at 3 cm. The leachate from each soil column was collected continuously using a 50 mL beaker for approximately 24 h after the start of the leaching event, and the beaker below the column was replaced every 30 min (Figure S4B for the leaching experiment device). Once the sample collection was completed, the beaker was immediately placed at $4 \text{ }^\circ\text{C}$. Filter paper was always placed on the beaker during the test to minimize water loss caused by

evaporation. Sample analyses were immediately performed once the samples were collected.

Batch Adsorption Experiments. Batch adsorption experiments were performed to study the interaction between MPs and DOM. Each treatment, including the CK, was performed in quadruplicate. Blank experiments were conducted under the same conditions to eliminate the interference of 50 mL centrifuge tubes and improve accuracy. To simulate the natural soil environment, all samples contained 0.01 mM CaCl_2 as the ion background.

The adsorption kinetics, adsorption isotherms, and regulating ion effects of MPs were studied (see Text S4 for a detailed description of adsorption experiments). After the adsorption experiment, the supernatant was obtained by using a $0.45 \mu\text{m}$ filter for subsequent analysis.

Determination of DOC. First, 2 g of the mixture and 20 mL of distilled water were placed in 50 mL centrifuge tubes, which were then placed in a multifunction shaker and run at 150 rpm for 24 h. The solution was then centrifuged at 4000 rpm for 10 min, filtered by using a $0.45 \mu\text{m}$ filter, and stored at $4 \text{ }^\circ\text{C}$ for subsequent analysis. All samples, including the CK, were performed in quadruplicate and treated equivalently. In

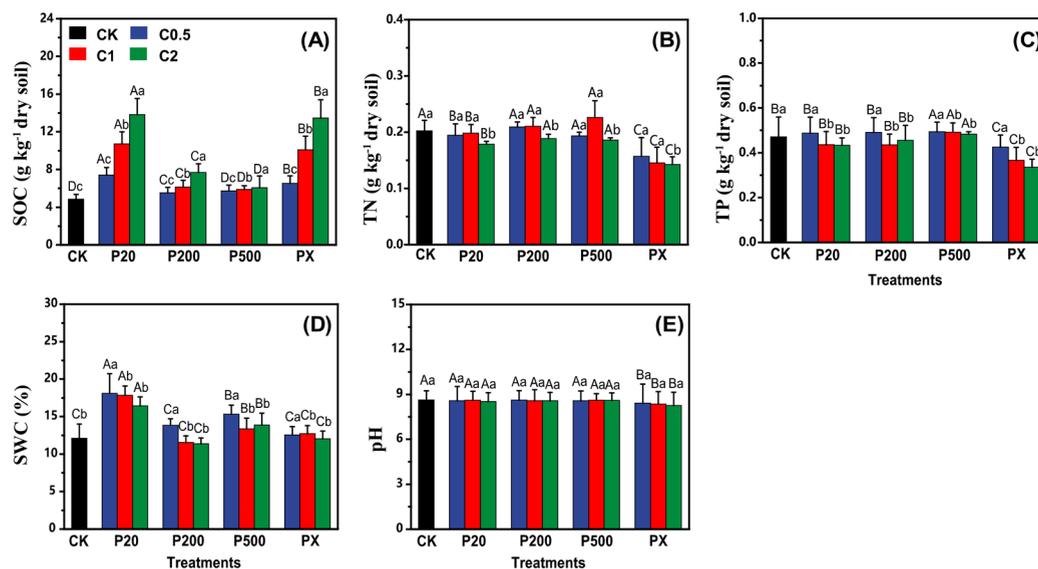


Figure 2. Effects of MPs on soil environmental factors (soil nutrients and soil properties). (A–C) Soil nutrients, representing the changes of SOC, TN, and TP, respectively. (D, E) Soil properties, representing changes in SWC and pH, respectively. The uppercase letters denote the difference after being treated with MPs with the same concentration and different particle sizes, and the lowercase letters denote the difference after being added with MPs with the same particle size and different concentrations ($P < 0.05$). P20 treatment represents 20 μm MP treatment; P200 treatment represents 200 μm MP treatment; P500 treatment represents 500 μm MP treatment; PX treatment represents 20:200:500 $\mu\text{m} = 1:1:1$. CK (black): 0%; C0.5 (blue): 0.5%; C1 (red): 1%; C2 (green): 2%. The abbreviation of soil environmental factors is applied to the above methods.

addition, the content of MP-leached dissolved organic carbon (MP-DOC) was determined (see Text S5 for a detailed description).

Sample Analysis. Leachate from leaching experiments and supernatant from adsorption experiments were used for the analysis of water parameters. Standard procedures were used to determine total dissolved nitrogen (TDN),³⁴ total dissolved phosphorus (TDP),³⁵ NH_4^+ , phosphate (PO_4^{3-}),³⁶ DOC, and MP-DOC (see Text S6 and Figure S5 for details).

Standard procedures were used to analyze the soil parameters. Soil nutrients were determined using air-dried soil, including SOC,³⁷ soil total nitrogen (TN),³⁸ and soil total phosphorus (TP),³⁹ and soil properties were determined as pH and soil water content (SWC) (see Text S7 and Figure S5 for details).

Data Analysis. Statistical analyses were performed using SPSS software (version 21.0; IBM Corp., Armonk, NY, USA) and the R environment (version 4.1.3; <https://www.r-project.org>). If the data passed the variance homogeneity test and significant differences were observed ($P < 0.05$), multiple comparisons were carried out using the least significant difference (LSD) test. Then, the effect of the diversity of MPs (particle size and concentration) on the change of DOM content was determined by two-way ANOVA. Then, variance partition analysis (VPA) was used to estimate the interpretation rate of environmental factors (MP diversity, soil nutrients, and soil properties) affecting the DOM content. Soil nutrients include SOC, TN, and TP, and soil properties include pH and SWC. Then, Pearson rank correlation, multiple linear regression, and ANOVA were used to clarify the relationship between each environmental factor and the DOM content and quantify the contribution of each factor. Subsequently, principal component analysis (PCA) was performed to test the interaction mode between various environmental factors and DOM. In addition, random forest models (RFMs) were used to predict the relative importance of various environ-

mental factors affecting DOM content. Finally, partial least-squares path models (PLS-PMs) were used to determine the direct and indirect contributions of environmental variables to explore the influence pathways of DOM content change and its (potential) driving factors. SPSS software was used for two-way ANOVA and LSD tests. Pearson rank correlation, PCA, VPA, and RFMs were performed in the R environment using the “vegan” and “randomforest” packages, while PLS-PMs and multiple linear regression were performed using the “plsmpm” and “relaimpo” packages, respectively.

RESULTS

Environmental Behavior of MPs. Particle size and concentration were important factors on the environmental behavior of MPs, significantly affecting PO_4^{3-} and NH_4^+ adsorption and DOC content (Figure 1, $P < 0.05$). With increasing particle size, PO_4^{3-} adsorption content increased linearly (except C2 treatment), while NH_4^+ (except C0.5 treatment) and DOC contents decreased significantly (Figure 1A–C, $P < 0.05$). Compared with CK, PO_4^{3-} in the C1 treatment increased from 0.012 to 0.017 mg kg^{-1} (Figure 1G, $P < 0.05$). Similarly, NH_4^+ and DOC increased significantly in the C2 treatment, ranging from 0.122 to 0.142 mg kg^{-1} and from 4.93 to 107.86 mg kg^{-1} , respectively (Figure 1H,I, $P < 0.05$). With increasing MP concentration, PO_4^{3-} (P20 and P500 treatments), NH_4^+ (P20 and PX treatments), and DOC (except P200 treatment) adsorption contents increased linearly (Figure 1D–F, $P < 0.05$). Compared with CK, PO_4^{3-} and NH_4^+ in the PX treatment increased significantly, ranging from 0.012 to 0.017 mg kg^{-1} and 0.122 to 0.145 mg kg^{-1} , respectively (Figure 1G,H, $P < 0.05$). Similarly, DOC of the P20 treatment increased from 4.93 to 66.73 mg kg^{-1} (Figure 1I, $P < 0.05$).

Adsorption Kinetics. Changes in the adsorption efficiency over time are used to reflect the temporal behavior of PO_4^{3-} and NH_4^+ adsorption on MPs. Initially, the adsorption

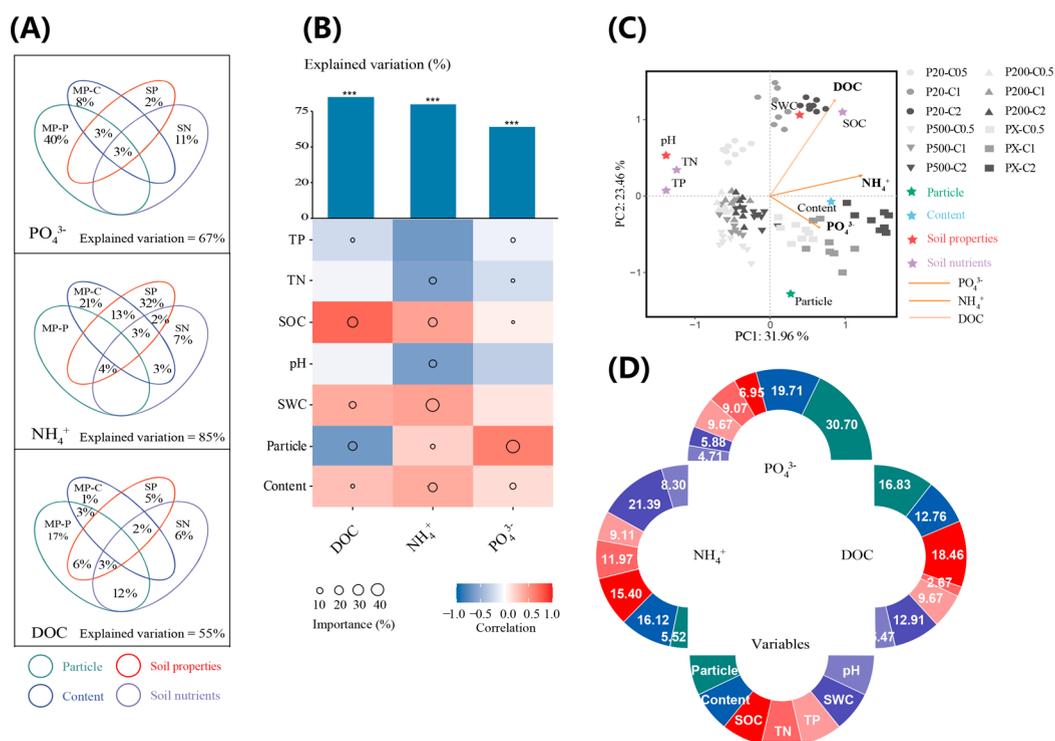


Figure 3. Driving factors affecting leachate content of soil column under the interference of MPs. (A) Variance partition analysis (VPA) was used to determine the relative contributions of MP diversity (particle size and concentration) and soil environmental factors (soil nutrients and soil properties) to PO_4^{3-} , NH_4^+ , and DOC. Soil nutrients (SNs) and soil properties (SPs) were expressed by the first component of principal component analysis (PCA) (63.96% and 51.06%). SNs include SOC, TN, and TP, and SPs include the pH and SWC. (B) Based on the correlation and optimal multivariate regression model, the contribution of MP particle size, MP concentration, soil nutrients, and soil properties to the change of soil leachate content was determined. In this study, the correlation between the above environmental variables and PO_4^{3-} , NH_4^+ , and DOC was investigated, and the important indexes indicating the change of soil leachate content were determined. Pearson correlation is represented by different colors, where blue represents negative correlation and red represents positive correlation. Circles of different sizes represent the importance of variables (the proportion of explanatory variables calculated by multiple regression models and variance decomposition). (C) Principal component analysis (PCA) showed the factors affecting PO_4^{3-} , NH_4^+ , and DOC. According to the size and content of MP particles, the sampling points were colored. (D) Pointing out the relative importance of each variable and estimating the contribution of environmental variables (MSE increased by %) based on random forest models (RFMs). MP particle size, concentration, soil nutrients, and soil properties were used as explanatory variables, while PO_4^{3-} , NH_4^+ , and DOC were used as response variables. Abbreviations for soil DOM, soil nutrients, and soil properties are applied to the above methods. The particle sizes (MP-P) include P20 (20 μm), P200 (200 μm), P500 (500 μm), and PX (20:200:500 μm = 1:1:1). The contents (MP-C) included CK (0%), C0.5 (0.5%), C1 (1%), and C2 (2%).

capacities of PO_4^{3-} and NH_4^+ increased rapidly but then gradually reached equilibrium at approximately 350 and 300 min, respectively (Figure S6). Compared with the pseudo-first-order model, the simulated values of the pseudo-second-order model showed lower deviations from the experimental values of PO_4^{3-} (0.0136–0.0195) and NH_4^+ (0.1286–0.1804), which is more suitable for describing the adsorption behavior of MPs for PO_4^{3-} and NH_4^+ ($0.9204 < R^2 < 0.9808$, Table S3). As the MP concentration increased, the PO_4^{3-} and NH_4^+ contents decreased in the P20 treatment and increased in the P500 treatment (Figure S6B,D and Table S3). In addition, as the MP particle size increased, the PO_4^{3-} and NH_4^+ contents decreased in the C0.5 treatment while the PO_4^{3-} contents increased and NH_4^+ contents decreased in the C1 and C2 treatments (Figure S6B,D and Table S3).

Adsorption Isotherm. Compared with the Langmuir model, the Freundlich model ($0.9109 < R^2 < 0.9922$) more accurately represented the adsorption process of PO_4^{3-} (0.0058–0.1815) and NH_4^+ (0.2044–1.2950) under different MP treatments (Figure S7 and Table S4). With the increase in MP concentration, the K_F values of PO_4^{3-} and NH_4^+ in the P20 treatment decreased while those in the P500 treatment

increased (Table S4). In addition, the K_F values of PO_4^{3-} and NH_4^+ in the C0.5 treatment decreased along with an increase in MP size (Table S4). The above results are consistent with the kinetic results.

Regulating Ions. With the increase of $CaCl_2$ concentration, the adsorption capacity of PO_4^{3-} decreased significantly while that of NH_4^+ had no significant change (Figure S8A, $P < 0.05$). Specifically, when the concentration of Ca^{2+} increased to 0.05 mM, the adsorption capacity of PO_4^{3-} decreased significantly by 37.62–73.71% (Figure S8A, $P < 0.05$). In addition, MPs in the P500 treatment showed strong adsorption capacity for PO_4^{3-} in different soil environments, which increased significantly by 49.37–69.45% (Figure S8B, $P < 0.05$).

Soil Nutrients and Soil Properties. With the increase of MP concentration, the SOC content increased, the TN, TP, and SWC content decreased significantly, and the pH showed no significant change (Figure 2, $P < 0.05$). Compared with CK, the SOC and SWC of the P20 treatment increased, ranging from 4.862 to 13.824 g kg^{-1} and from 12.08% to 18.112%, respectively (Figure 2A,D, $P < 0.05$). However, the TN and TP in the PX treatment decreased from 0.202 to 0.143 g kg^{-1} and

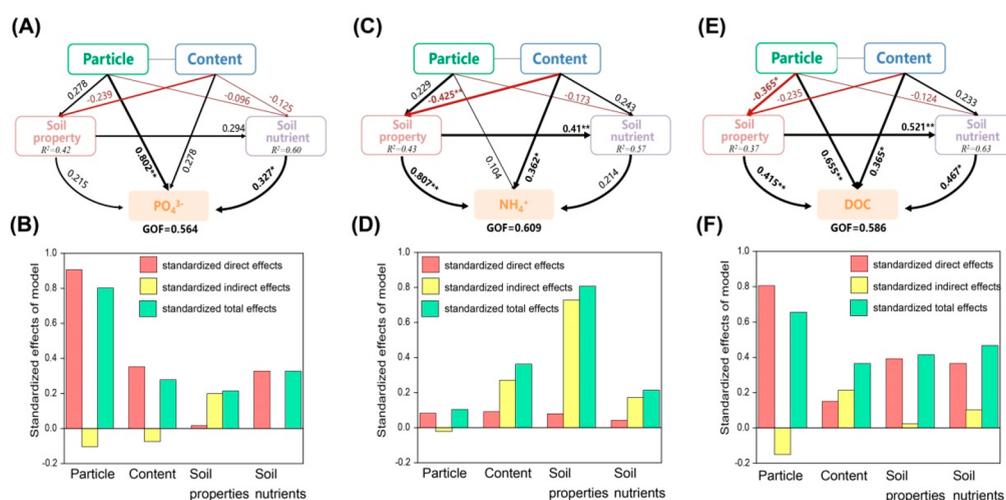


Figure 4. Partial least-squares path models (PLS-PMs) show the effects of MPs on (A) PO_4^{3-} , (C) NH_4^+ , and (E) DOC, as well as the standardized effects of environmental variables (B, D, and F). Standardized effects include standardized direct effects, standardized indirect effects, and standardized total effects. Black and red arrows represent positive and negative flows of causality, respectively, and the width of arrows is proportional to the strength of the relationship. The numbers on the arrows represent standardized path coefficients (>0.3 in bold). When $P < 0.05$, the significance is expressed by *, and when $P < 0.01$, the significance is expressed by **. R^2 represents the variance of the dependent variable explained by the model. Goodness of Fit (GOF) measures the overall predictive performance of the model and uses GOF statistics to evaluate models with different structures. The first component of principal component analysis (PCA) is used to represent soil nutrients and soil properties (63.96% and 51.06%). Soil nutrients include SOC, TN, and TP, and soil properties include pH and SWC. Abbreviations for soil DOM, soil nutrients, and soil properties are applied to the above methods. The particle sizes include P20 (20 μm), P200 (200 μm), P500 (500 μm), and PX (20:200:500 $\mu\text{m} = 1:1:1$). The contents of the chromatograms include CK (0%), C0.5 (0.5%), C1 (1%), and C2 (2%).

from 0.471 to 0.336 g kg^{-1} , respectively (Figure 2B,C, $P < 0.05$). In addition, with the increase of MP particle size, the SOC and SWC decreased while TN and TP increased significantly (Figure 2A–D, $P < 0.05$). Compared with CK, the SWC of the P20 treatment increased from 12.08% to 18.112% (Figure 2D, $P < 0.05$). In addition, the TN of the P500 treatment decreased from 0.202 to 0.186 g kg^{-1} , while the TP increased from 0.471 to 0.493 g kg^{-1} (Figure 2B,C, $P < 0.05$).

Driving Factors of Changes in the Soil Column Leaching Solution Content. The effects of environmental factors (MP particle size, concentration, soil nutrients, and soil properties) on PO_4^{3-} and NH_4^+ adsorption and DOC contents were simulated to explore the main role of interference by MPs in regulating the change in DOM content. The diversity of MPs and properties of soil significantly interacted with PO_4^{3-} , NH_4^+ , and DOC. Among them, the MP particle size explained most of the changes of PO_4^{3-} , while soil properties explained most of the changes of NH_4^+ , followed by MP concentration (Figure 3A). SWC was positively correlated with NH_4^+ for each soil properties parameter assessed (Figure 3B). When the diversity of MP was further considered, an analysis of the relationship between SWC and NH_4^+ showed that NH_4^+ increased to different degrees under different levels of MPs. However, the mutual response pattern between them was significant only for the 0.5% MP treatment and was not associated with changes in MP particle size (Figure S9). PCA was selected to test the role of this model in the change of DOM content, and the results showed that more interpretational variance was observed when MP particle size and soil properties were considered (Figure 3C). Finally, the RFMs predicted the importance of the patterns mentioned above in the change of DOM content (Figure 3D). The results showed that, although MPs reduced the leaching of PO_4^{3-} and NH_4^+ in soil by direct adsorption, soil properties, especially the SWC,

partially mediated the adsorption process of NH_4^+ by MPs. The PLS-PM results further validated the behavioral pattern of MPs (Figure 4). MP particle size had the highest total effect on PO_4^{3-} (0.802) (Figure 4A,B), and the MP concentration was an influencing factor for NH_4^+ and drove the change in NH_4^+ content by altering the soil properties (0.807) (Figure 4C,D). MP particle size and soil properties, in particular, SWC, were the main drivers of changes in DOM content (Figures 4 and S9).

DISCUSSION

Direct Influence of MPs. External interfering substances can alter soil mineral nutrient cycling by directly releasing the nutrients contained in soil, thereby affecting nutrient mineralization or adsorption.⁴⁰ Our study found that MPs tend to reduce the concentrations of PO_4^{3-} and NH_4^+ in leachate. Changes of PO_4^{3-} in the leachate are dependent on the direct adsorption of MPs to a great extent, and changes in the leachate concentration may be closely related to the change of MP concentration and size (Figures 1A,D and S10A). (Micro) macroscopic cracks formed by mechanical wear of the polymer matrix caused by the screening and mixing process may lead to higher adsorption rates⁴¹ by promoting the mass transfer and diffusion within MPs (Figures S2A and S6). Previous studies have provided similar evidence showing that wrinkles and wear on the surface of mechanically worn MPs⁴² will increase the specific surface area and “potential adsorption sites” of MPs.⁴³ In addition, the chemical properties of MPs, such as the formation or quantity change of oxygen-containing groups, can also affect their adsorption capacity.^{10,44} Previous studies have shown that the weathering/aging of plastic polymers is usually characterized by an increase of oxygen-containing groups, such as carbonyl groups ($\text{C}=\text{O}$),⁴⁵ whereas the hydroperoxide group ($-\text{COOH}$) can decompose to produce other products, including $\text{C}=\text{O}$.¹⁰ Our study gives

similar evidence that FTIR images after leaching experiments show more obvious absorption peaks at 1656–1662 cm^{-1} (carbonyl groups $\text{C}=\text{O}$) (Figure S2B).

Further observations showed that larger MPs had a stronger effect on the soil nutrient content (Figure 1A,D,G). This finding is inconsistent with previous studies, which showed that smaller MPs had a large specific surface area and strong adsorption capacity, so their environmental effects were more prominent.^{46–48} However, such MPs are easily encapsulated by soil particles, and the aggregation degree between particles is higher (strong attraction).⁴⁹ With the increase in MP size, the possibility of MPs being encapsulated by soil gradually decreases and MPs are more responsive to the shear effect during mechanical mixing, which may increase the number of adsorption sites⁴² (Figure 5). In addition, changes in the

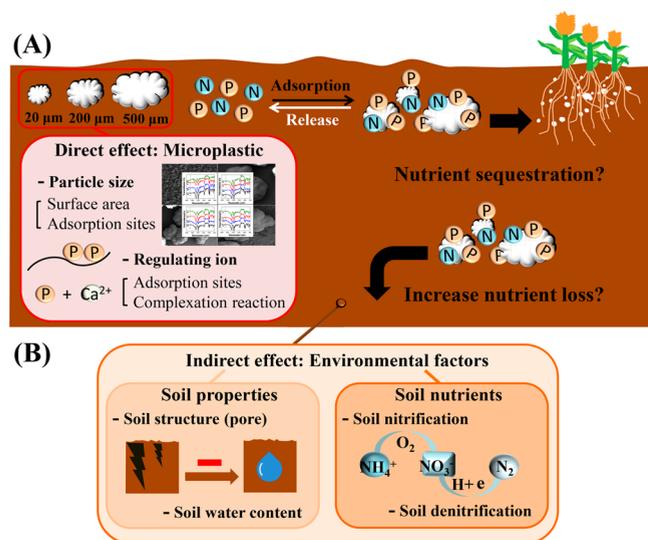


Figure 5. Concept diagram shows the main factors influencing the interaction of MPs with PO_4^{3-} and NH_4^+ in the soil environment. MPs are represented by white irregular spheres, and PO_4^{3-} and NH_4^+ are represented by orange and blue spheres, respectively. (A) The direct influencing factors of MPs (e.g., possible particle size sensitivity of MPs and competition of regulating ions) are outlined. (B) Focus on indirect impacts of soil environmental factors in response to MPs including soil properties (e.g., soil structure and water content) and soil nutrients (e.g., nitrification and denitrification processes).

regulating ion concentration may also influence the MP adsorption process. Specifically, the existence of high-strength Ca^{2+} (≥ 0.03 mM) greatly hinders the adsorption of PO_4^{3-} by MPs (Figure S8). Low concentrations of regulating ions are highly dispersed in the adsorption system, which may lead to weak interactions between them and adsorbents or adsorbates.⁵⁰ However, with the increase of the amount of Ca^{2+} in the adsorption system, the contact opportunity with PO_4^{3-} increases, and thus, the possibility of complex formation between Ca^{2+} and PO_4^{3-} gradually increases⁵¹ (Figure 5), which mostly occurs in alkaline environments. In addition to forming a complex with PO_4^{3-} , Ca^{2+} may also compete with PO_4^{3-} for the adsorption sites of MPs. Ca^{2+} has a high affinity for MPs and thus may compete with coexisting ions for adsorption sites.¹⁶

As a heterogeneous organic compound with carbon content exceeding 90%,⁵² MPs will inevitably loosely combine with a large number of compounds on the particle surface during the

production process, and the leaching of these components in soil solution may cause biogeochemical changes.¹ Considering that plastics can supplement organic matter in the form of carbon from polymer improvers⁵³ and MP-DOC is still soluble in aqueous solution,^{54,55} an increase in the MP-DOC content may also lead to an increase in the apparent DOC content (Figure S11). This finding is consistent with previous studies in which MPs were shown to produce local hot spots of DOC⁵⁵ and increases in the MP concentration lead to an increase in the DOC content in water environments. Unlike the strong interaction between large-sized MPs and PO_4^{3-} , we found that DOC is more sensitive to small-sized MPs (Figure 1F,I). Small-sized MPs have a large specific surface area, which may potentially increase the content of MP-DOC.⁵⁵ In addition, the change of soil DOC content usually depends on an imbalance between accumulation and consumption.^{54,56}

MP-DOC systems have high bioavailability, and microorganisms can remineralize leached DOC in less than 5 days when the bioavailability exceeds 50%.⁵⁵ Furthermore, a higher DOC content with smaller particle sizes of MPs also may provide more living substrates for microorganisms, which enhances microbial activity,^{57,58} however, this consumption rate may be far less than the increased content of MP-DOC.

Indirect Influence of the Soil Environment in Response to MP Interference. The interaction between complex (non)biological factors in the MP–soil system seems to present negative net effects, which may be largely due to the inability to compensate for the negative effects of MPs.^{59,60} In contrast, soil environments related to MPs, such as SWC (and its related influencing factors), may mitigate the negative effects of MPs and explain the positive changes in soil nutrient retention to a certain extent (Figure 3). We found that these changes may be involved in the cycling of nutrient elements in the soil ecosystem, especially N elements.

The results showed that NH_4^+ was highly sensitive to lower MP concentrations (0.5%). Generally, nutrient leaching is related to soil aggregation, which is regulated by soil moisture.⁴² Soil with poor moisture status has a poor overall structure, which inevitably forms many soil cracks that may accelerate soil nutrients leaching during rewetting (Figure 5). The SWC is proportional to the NH_4^+ concentration in leachate (Figure S9A), which may be related to the positive influence of low concentrations of MPs on the soil structure. The aggregates formed by MPs have higher surface tension and thus a stronger ability to adsorb organic matter and aggregate microorganisms, which promotes the formation of more organic colloidal substances and increases the stability of aggregates.⁶¹ In addition, increased soil porosity by MPs will further expand the mineral surface area of soil,³ which may also promote the adsorption process and reduce nutrient leaching.

Further consideration of the interference intensity of MPs revealed that the concentration of NH_4^+ leachate decreases along with the MP interference intensity, especially under higher intensities ($>0.5\%$) (Figure S10C). In addition to the possible effects of adsorption, MPs may also increase the nitrification rate by increasing the amount of soil porosity, which is often proportional to the amount of MPs.³³ Previous studies have also reported that MPs reduce NH_4^+ leaching by increasing the nitrification rate with NH_4^+ as substrate.⁵³ Although a higher organic matter content and oxygen concentration may also promote increased mineralization,⁶² the rate of nitrification appears to be sufficient to remove excess NH_4^+ (Figure 5). However, the opposite conclusion has

also been reported, with studies showing that MPs have limited influence on soil available nutrient content.⁴⁰ Many studies have found that the diversity of MPs provides additional evidence for exploring stressors that affect soil functions and services; therefore, the relative contribution of combinations of MPs with different particle sizes and concentrations may explain the different effects of nutrient element content changes to a certain extent.^{31,61} In addition, different kinds of additives will inevitably be doped in the manufacturing process of plastic products,¹ and these toxic substances may also affect the composition of the MP biosphere in a biased way, thus selectively affecting the direction and process of ecological processes.

The study provided experimental evidence that revealed the main role of MP adsorption and indirect MP effects on soil processes and functions in mediating the change in soil DOM content. We found that 0.5% MPs accelerated soil nitrification and decreased NH_4^+ leaching by increasing oxygen cycling. However, the adsorption of PO_4^{3-} and NH_4^+ by MPs and the increase of soil DOC content by MP-DOC have positive effects on soil nutrient retention and ultimately regulate soil nutrient dynamics. Moreover, changes in the intensity of regulating ions (Ca^{2+} , ≥ 0.03 mM) in MP-DOM adsorption systems must also be considered.

The study described the important relationship between MPs (and influencing factors) and changes in soil DOM content and emphasized the short-term interaction mode between MPs and the soil environment. In the long run, MPs, as a persistent stressor in soil, may change with time, accumulate, and transfer in soil. The aging of MPs and the possible long-term impacts of MPs on soil processes are also important to consider. Considering the constant MP atmospheric transport and deposition and that remote areas, such as highlands, have been or will likely be loaded with excessive plastic pollution for a long period of time, the potential ecological impacts of MPs and their eventual fate should not be overlooked, especially in fragile ecosystems. Our results provide valuable information for improving risk management strategies on MPs in terrestrial ecosystems and protecting soil health and function, especially in future agricultural contexts.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c04023>.

Text S1, Soil sample collection; Text S2, Determination of tested soil; Text S3, Microplastic (MP) characterization; Text S4, Batch adsorption experiments; Text S5, Determination of MP-leached DOC (MP-DOC); Text S6, Determination of water parameters; Text S7, Determination of soil parameters. Figure S1, Location of the study area; Figure S2, Characterization of MPs; Figure S3, Mixture of MPs and tested soil; Figure S4, Schematic diagram of experimental preparation; Figure S5, Schematic diagram of water and soil parameter determination; Figure S6, Adsorption kinetics; Figure S7, Adsorption isotherms; Figure S8, Regulating ion (Ca^{2+}) and adsorption process; Figure S9, Relationship between NH_4^+ and SWC under different MP treatments; Figure S10, Concentration change of soil column leaching solution under different MP treatments; Figure

S11, The leaching content change of MP-DOC. Table S1, The basic properties of MPs; Table S2, The processing setting of the experiment; Table S3, Parameters of adsorption kinetic model; Table S4, Parameters of adsorption isotherm model (PDF)

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Notes

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