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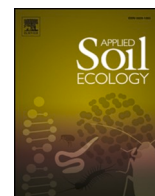
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Effects of conventional and biodegradable microplastics at comparable environmental levels on pesticide degradation in soil[☆]

Pengtao Chen^a, Furong Fu^a, Lixia Zhao^a, Xiaojing Li^a, Yang Sun^{a,*}, Zhenyan Fu^b, Liping Weng^c

^a Agro-Environmental Protection Institute, Ministry of Agriculture and Rural Affairs/Key Laboratory of Original Agro-Environmental Pollution Prevention and Control, MARA/Tianjin Key Laboratory of Agro-Environment and Agro-Product Safety, Tianjin 300191, China

^b The Green Food Development Center of Jizhou District, Tianjin 301900, China

^c Department of Soil Quality, Wageningen University, P.O. Box 47, 6700 AA Wageningen, the Netherlands

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ABSTRACT

The co-existence of microplastics (MPs) and pesticides in agricultural environments, especially under greenhouse conditions, is a common occurrence. However, there is limited information on how MPs affect pesticide degradation under comparable environmental concentrations. In this study, we conducted a laboratory experiment to evaluate the impact of two types of MPs—biodegradable polylactic acid (PLA) and conventional polyethylene (PE)—on the degradation of 2 pesticides, metolachlor (MET) and imidacloprid (IMI), in soil at low (0.1 %) and high (1.0 %) concentrations. Over a 30-day period, we assessed pesticide degradation rates and metabolic products, along with soil properties and the aging status of MPs. Our results show that PLA reduced the degradation rate of IMI with concentration variability — 1 % PLA (w/w) significantly reduced the degradation rate of IMI by a 6.7 % decrease after 30 days compared to the treatment of CK, but had no effect on MET. In contrast, PE did not influence the degradation of either pesticide. PLA significantly inhibited IMI degradation by reducing the soil pH from 7.28 ± 0.01 to 7.12 ± 0.05 , diminishing bacterial diversity, and altering the composition of soil bacterial communities. Furthermore, the accelerated degradation of PLA, compared to PE, resulted in the release of a greater quantity of microplastic particles, exacerbating its impact on soil microbial functions and IMI degradation efficiency. These findings suggest that biodegradable MPs, such as PLA, can hinder the degradation of the two pesticides, posing ecological risks to agricultural environments. Our results provide insights for developing policies to prevent and control farmland pollution.

1. Introduction

Plastic products are widely used in agricultural fields around the world, leading to a significant accumulation of microplastics (MPs) in farmland soils (Geyer et al., 2017; Kawecki and Nowack, 2019). The amount of MPs released into the soil each year is approximately 4 to 23 times greater than that released into the ocean, highlighting that soil has become one of the most affected areas by MP pollution (Horton et al., 2017; Rachman, 2018). MPs in agroecosystems, primarily derived from sources such as plastic mulches and sewage sludge, pose significant risks to soil health, plant growth, and food safety. These MPs can accumulate in soils, alter soil properties and microbial communities, and be absorbed by plants, potentially entering the food chain and posing broader

ecological and health concerns. (Horton et al., 2017; Qaiser et al., 2024). Understanding and mitigating their presence is crucial for sustainable agriculture. At the same time, agricultural production is inseparable from the use of a large number of pesticides. In 2022, global agricultural pesticide use totaled 3.7 million tons (active ingredients), 4 % more than in 2021 and 13 % >10 years ago. The average use of agricultural pesticides was 2.38 kg/ha, an increase of 3 % over 2021 (FAO, 2024). Consequently, many pesticides with long half-lives were found to accumulate in the soil, and the non-negligible risks of currently used pesticides, e. g. environmental ecosystems and human health, have been found in regions with intensive agricultural activities in various countries (Bhandari et al., 2020; Sabzevari and Hofman, 2022). For instance, over 1.0 % of the agricultural soil samples from northern China exhibit

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* Corresponding author.

E-mail address: sunyang01@caas.cn (Y. Sun).

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relatively high ecological risk, in which concentrations of atrazine, metolachlor (MET), imidacloprid (IMI), etc. exceeding 0.1 mg kg^{-1} (Pan et al., 2019). Therefore, the co-existence of various MPs and pesticides in agricultural environments, particularly under greenhouse conditions with high intensity use of pesticides and agricultural film, is a common scenario.

Current research on the effects of MPs on pesticide degradation primarily focuses on aquatic environments (Hu et al., 2021; Wang et al., 2020a). MPs could act as a carrier for pesticides in the water environment and pose a potential risk. At the same time, pH can influence the behavior of pesticides, including IMI, in water (Li et al., 2021). On account of adsorption and gradual desorption, PE evidently increased the degradation half-lives of pesticides in water, especially for the types with medium longevity of degradation and high logKow values. However, PE had no obvious impact on the degradation of pesticides in the water-sediment system because of difference adsorption capacities of alternative compartments (Wang et al., 2020a). In addition, a few studies investigated the effects of MPs on pesticides in soils (Guo et al., 2024; Yang et al., 2018). Yang et al. (2018) found that 7 % and 28 % of MP (unspecified category) additions had no significant effect on the degradation of parent glyphosate, but significantly prolonged the degradation of its metabolite aminomethylphosphonic acid, and significantly enhanced the microbial respiration rates in soils. In another study, the presence of MPs (PE and PET) with the two concentrations of 1 % and 10 % accelerated the degradation of atrazine by stimulating the soil metabolic activity attribute to the enhancement of microbial diversity and functionality in soils (Guo et al., 2024). Furthermore, Wu et al. (2022) compared the effects of new mulch MPs (New-MPs), aged mulch MPs (Aged-MPs) and biodegradable mulch MPs (BioD-MPs) on the degradation of residual pesticides in soil. The results indicated that New-MPs accelerated the degradation of pesticides. However, Aged-MPs and BioD-MPs hindered the dissipation process of pesticides. Overall, the influencing factors of MPs on pesticide degradation mainly include the types and concentrations of pesticides and MPs, soil properties and microbial communities (Chang et al., 2022; Wang et al., 2020a; Xu et al., 2020).

Given the widespread co-occurrence of MPs and pesticides in farmland soil, it is of greater practical significance to investigate the effects of various MPs at environmentally relevant concentrations on the degradation of different pesticides. This approach will help assess the combined pollution of these two organic pollutants, in contrast to studies that focus solely on the effects of high concentrations of a single type of MP on specific pesticides. In this study, we used PE, the most commonly found conventional MP in farmland (Guo et al., 2024), and PLA, a biodegradable MP whose use has increased significantly in recent years (Liu et al., 2023), to evaluate their impact on the degradation and metabolism of two widely used pesticides in agriculture: imidacloprid (IMI) and metolachlor (MET) (Pan et al., 2019). Additionally, we analyzed the key factors influencing MP-mediated pesticide degradation and the morphological changes of MPs during incubation. The results of this study aim to provide a foundation for further research into the mechanisms by which MPs affect pesticide degradation.

2. Materials and methods

2.1. Soils, pesticides and metabolites, and MPs

The soil sample was collected from the topsoil (0–20 cm depth) of a wheat field that have not used agricultural film in Wuqing District, Tianjin ($39^{\circ}37'41''\text{N}$, $117^{\circ}3'51''\text{E}$). Fresh soil was air-dried indoors and passed through a 2-mm sieve to remove organic debris and grits. No traces of MET, IMI, and their metabolites were detected in the soil using the method of *Extraction and determination of pesticides in soil* (presenting in Section 2.3). Meanwhile, the soil was determined by our previous method and found no microplastic residues in it (Fu et al., 2024). The soil type is fluvo-aquic, with a pH of 7.28 ± 0.01 , DOC of 0.23 ± 0.01

$\mu\text{g/g}$, and alkali-hydrolyzable nitrogen content of $83.9 \pm 8.2 \mu\text{g/g}$. The soil texture consisted of 8.15 % clay, 40.81 % silt, and 51.05 % sand.

MET and its six metabolites—MET deschloro (MDES), MET-2-ethoxy (M2E), MET-2-hydroxy (M2H), MET ESA sodium salt (MESA), MET Oxanilic Acid (MOA), and MET mercapturate (MMER)—all with purities $>99.2 \%$, were purchased from Yuanye Biotechnology Co., Ltd. (Shanghai, China). IMI and its seven metabolites—5-hydroxy-IMI (5HI), IMI-guanidine hydrochloride (IGH), IMI-urea (IUR), 6-chloronicotinic acid (6CA), hydroxy-IMI (HI), IMI-olefin (IOL), and 4,5-dihydroxy-IMI (DDI)—all with purities $>99.8 \%$, were purchased from Alta Technology Co., Ltd. (Tianjin, China). The chemical names and structural formulas of the parent compounds and their metabolites were provided in Supporting Information Table S1.

PE (purity $\geq 99.9 \%$, ExxonMobil) and PLA (purity $\geq 99.9 \%$, NatureWorks) particles were purchased from Hengfa Plasticizing Co., Ltd. (Shenzhen, China). To obtain MPs in the size range of 100–200 μm , PE and PLA were separated using 0.2-mm and 0.1-mm screens, respectively. Before and after the experiment, the MPs were washed three times with deionized water and then dried at 60°C . Representative scanning electron microscopy (SEM) images of PE and PLA were presented in Fig. 5 (A) and 5 (D), respectively, highlighting distinct morphological features of the two experimental groups.

2.2. Experimental design

The spiked concentrations of the two pesticides were set at 0.5 mg kg^{-1} for IMI and 2 mg kg^{-1} for MET, respectively, based on their actual concentrations in the surface soil after application at the recommended doses (Sharma et al., 2014; Sun et al., 2019). Two spiked concentrations of MPs, 0.1 % and 1 % (mass percentage), were chosen to reflect their environmentally relevant concentrations in topsoil (Huerta Lwanga et al., 2016; Xu et al., 2020). Five treatments were established as follows: The control treatment (CK), which consisted of natural soil fortified with the above mixed pesticides, was used to evaluate the degradation rates of these pesticides in soil during the cultivation period. LPE and HPE treatments, which were CK treatments fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively, were used to assess the impact of PE on pesticide degradation in soil. LPLA and HPLA treatments, which were CK treatments fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively, were used to evaluate the effect of PLA on pesticide degradation in soil. Each treatment was performed in four replicates. The experiment was conducted in 250-mL glass beakers containing 200 g of soil, with the moisture content adjusted to 23 % (w/w) using high temperature sterilized (121°C for 30 min) pure water (Wahaha, China). These beakers were incubated in an artificial climate chamber under the following conditions: temperature, 20°C ; light-dark cycle of 16:8 h; light intensity, 800 lx; and humidity, 80 %. Sterile water was added to each beaker every 3 days to maintain soil moisture. Soil samples were collected on the 30th day of incubation and stored at -20°C until further use.

2.3. Extraction and determination of pesticides in soil

A modified QuEChERS method was used to extract two parent compounds, MET and IMI, as well as 13 metabolites from soil (Acosta-Dacal et al., 2021). Details of the extraction, purification, and detection procedures for these pesticides and metabolites are provided in the Supporting Information (Text S1 and Table S2). Briefly, the compounds were extracted using acetonitrile and quantified by LC-MS/MS (ExionLC™ + QTRAP 4500, AB SCIEX) after substrate purification. To ensure the stability of instrument performance and the reliability of the test data, one procedural blank and one standard sample were analyzed for every eight samples. No target pesticides were detected in blank samples. Calibration curves were established using five different concentrations of standard samples, ranging from 0.1 to 100 ng mL^{-1} , with correlation coefficients (R^2) >0.996 for all compounds. The recoveries

of all compounds ranged from 68.0 % to 115 % ($n = 4$, $RSD < 11$ %) at spiked concentrations of 5, 10, and 100 ng g⁻¹. The limits of quantification (LOQ), defined as a signal-to-noise ratio of 10, were all below 2.0 ng mL⁻¹. Further details are provided in Table S3.

2.4. Characterization of soil physicochemical properties

Soil pH was measured using a combined glass electrode (Mettler Toledo FE28-Standard, Switzerland). The soil was freeze-dried and ground, then sifted through a 0.15-mm screen and measured by mixing it with deionized water at a ratio of 1:2.5 (soil to water) (Sun et al., 2019).

Water-soluble organic carbon (DOC) in the soil was determined using a TOC Analyzer (Shimadzu SSM-5000 A, Japan). Briefly, 4.0 g of freeze-dried soil, ground through a 0.15-mm sieve, was mixed with 20 mL of ultrapure water in a centrifuge tube. The mixture was shaken at 180 rpm for 9 h. Afterward, the supernatant was removed and filtered through a 0.45-μm membrane before analysis (Ji et al., 2019).

The continuous reduction diffusion method was used to determine alkali-hydrolyzed nitrogen (AN) in the soil (Jing et al., 2014). Briefly, a 1.0 mol L⁻¹ NaOH solution was used to hydrolyze the soil in a diffusion dish, converting potentially available nitrogen into NH₃, which was subsequently absorbed by a 20 g L⁻¹ H₃BO₃ solution after diffusion. The NH₃ absorbed in the solution was then titrated with a 0.00998 mol L⁻¹ standard boracic acid to calculate the AN content in the soil.

2.5. Characterization of MP deformation

The morphology and surface structure of the MPs were analyzed using a SEM. At the start and end of the experiment, the MPs were gold-coated using a Quorum SC7620 sputter coater, followed by imaging with a TESCAN MIRA LMS SEM at various magnifications. The method of recovering MPs from soil is referred to one of our previous works (Fu et al., 2024). Briefly, MPs in soil were extracted by three steps, including floatation, digestion and re-floatation.

Fourier transform infrared (FTIR) spectroscopy was used to characterize the functional group structure of the MPs. In brief, a MP sample (1–2 mg) was finely ground with 200 mg of KBr, placed in a mold, and then pressed into a transparent pellet using a hydraulic press. The resulting sample was subsequently analyzed using an infrared spectrometer. The measurement was taken in the wavenumber range of 4000–400 cm⁻¹, with 32 scans and a resolution of 4 cm⁻¹.

2.6. DNA extraction and sequencing

The soil bacterial community was analyzed using high-throughput sequencing, following a series of steps: DNA extraction, PCR amplification, Illumina MiSeq sequencing, and sequencing data analysis. The procedures were as follows: (1) DNA was extracted using the E.Z.N.A.® Soil DNA Kit, and the quality of the extraction was assessed by 1 % agarose gel electrophoresis; (2) the V3-V4 region of the 16S rRNA gene was amplified via PCR using primers 338F (5'-ACTCCTACGGGAGGCAGCAG-3') and 806R (5'-GGACTACHVGGGTWTC TAAT-3'); (3) PCR products were separated by 2 % agarose gel electrophoresis, purified with the AxyPrep DNA Gel Extraction Kit, eluted in Tris-HCl buffer, and quantified using QuantiFluor™; (4) The purified amplicons were processed according to Illumina MiSeq platform protocols. They were then constructed into a library and sequenced on the MiSeq PE300 platform (Duan et al., 2021); (5) Raw sequencing data were processed using Trimmomatic software for quality control and FLASH software for read merging. Sequences were clustered into Operational Taxonomic Units (OTUs) at 97 % similarity using UPARSE software, with singletons and chimeric sequences removed during clustering. Species classification and annotation were performed by comparing the sequences to the Silva 138 database using the RDP classifier.

2.7. Data analyses

Excel 2021 was used to record, analyze, and calculate the original data, with the mean values expressed as the average ± standard deviation. The residual levels of chemicals were determined based on the soil dry weight. Using two sets of initial and final pesticide residues, the degradation rate of pesticide (DR) was calculated per the equation: $DR = (IC - FC) \times 100 \% / IC$, where IC represents the initial concentration and FC represents the final concentration after 30 days of incubation. Statistical analysis was performed using one-way analysis of variance (ANOVA) in Excel 2021, with Tukey's post-hoc test for pairwise comparisons (if data were not normally distributed or variances were not homogeneous, the Kruskal-Wallis test was used). A significance level of $P < 0.05$ was considered statistically significant. Microbial data were analyzed using the Meiji BioCloud platform, and figures were generated using SciDAVs 1.2 (Ye et al., 2023).

3. Results and discussion

3.1. Effect of MPs on degradation of pesticides

Within the range of environmentally relevant concentrations of MPs in topsoil (Huerta Lwanga et al., 2016), two concentrations of PE and PLA (0.1 % and 1 %) were selected to assess their effects on pesticide degradation in soil. As shown in Fig. 1(A), degradation rates of MET were not significantly different across all treatments, indicating no noticeable effect of either conventional or biodegradable MPs on MET degradation. Four metabolites of MET, i.e. MDES, M2H, MESA, and MOA—were detected in soil samples after 30 days of incubation (Fig. 1B). The concentrations of these metabolites were ranked as $MOA \geq MESA > M2H > MDES$, as also shown in Table S4. The predominant metabolites, MOA and MESA, accounted for >90 % of the total metabolites detected. These metabolic patterns were consistent with findings from other studies (Rose et al., 2018; Sun et al., 2019). The production levels of each metabolite in all treatments, including the control (CK), showed no significant differences, suggesting that PE and PLA did not substantially alter the metabolic pathway of MET.

Similar to MET, both 0.1 % and 1 % concentrations of PE and 0.1 % PLA had negligible impacts on the degradation of IMI (Fig. 1C). Interestingly, however, 1 % PLA significantly reduced the degradation rate of IMI, with a 6.7 % decrease in degradation after 30 days of incubation compared to the treatment of CK. As shown in Fig. 1D, three metabolites—IMI olefin (IOL), 5-hydroxy IMI (5HI), and 6-chloronicotinic acid (6CA)—were detected. Among these metabolites, IOL was the primary product, with concentrations ranging from 1.56 ± 0.08 to 1.99 ± 0.24 μg kg⁻¹ across all treatments (Table S4). Significant differences in IOL concentrations were only observed between the LPLA treatment and the CK, which contrasted with the metabolic pattern observed in the parent compound. The other two metabolites, 6CA and 5HI, had concentrations ranging from 0.17 ± 0.08 to 0.45 ± 0.08 μg kg⁻¹ and 0.49 ± 0.14 to 0.67 ± 0.19 μg kg⁻¹, respectively, which were 2–10 times lower than IOL. Except for the LPE treatment, the concentration of 6CA in all other treatments was lower than that in the CK. However, the production of 5HI showed no significant differences across all treatments, including the CK. Notably, four other target metabolites—IMI guanidine (IGH), IMI urea (IUR), hydroxyl-IMI (HI), and 4,5-Dihydroxy-imidacloprid (DDI)—were not detected in the soil, possibly due to their lower production levels below detection limits or rapid conversion rates (Cheng et al., 2022; Sharma et al., 2014). Previous studies have indicated that IGH and IUR are easily mineralized in the environment, while hydrolysis products like 5HI, DDI, and HI can produce IOL through elimination reactions. 6CA could also be formed from these intermediates, but it was easily mineralized to carbon dioxide and water (Phugare et al., 2013; Yin et al., 2023).

In summary, we found that two concentrations of PE and PLA (i.e., 0.1 % and 1.0 %) had no significant impact on the degradation of MET

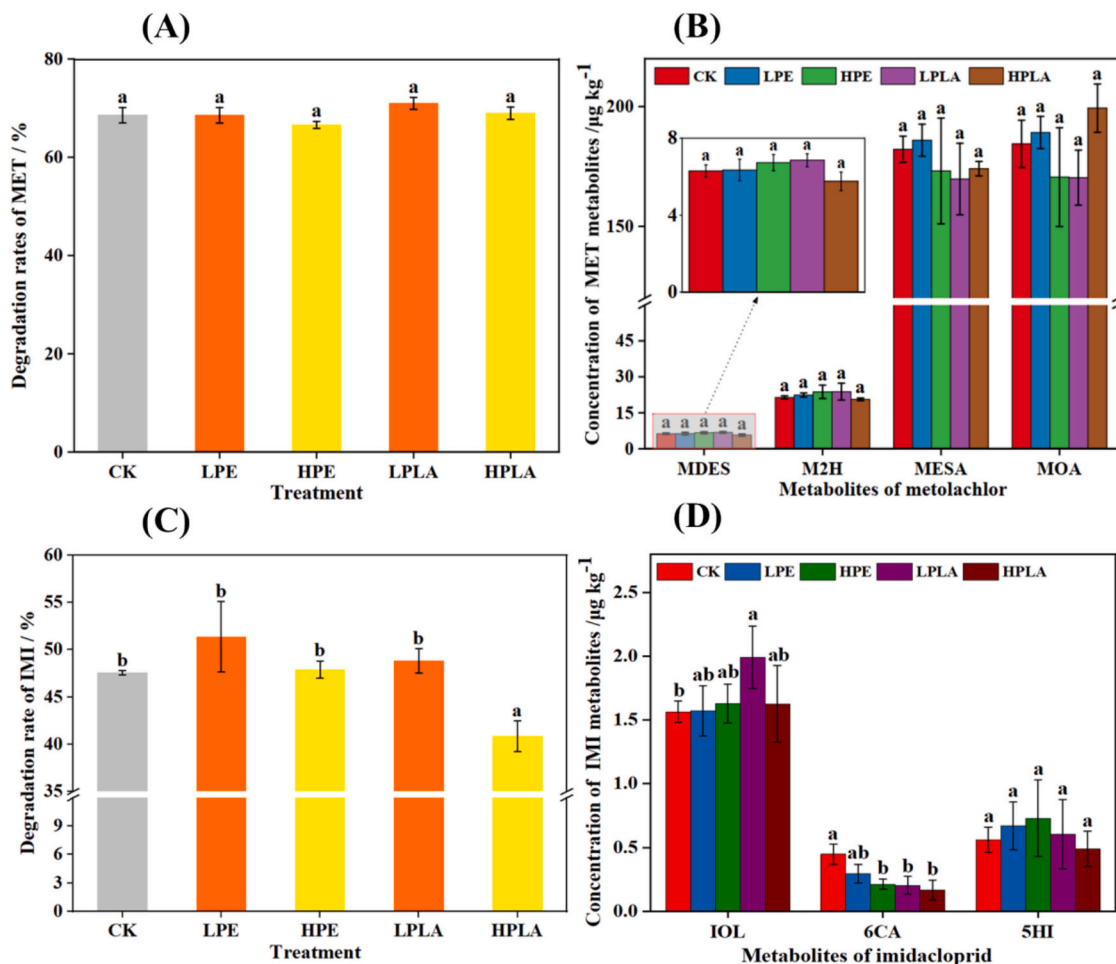


Fig. 1. Effects of microplastics on the degradation and transformation of pesticides in soil after 30 days of incubation. (A) metolachlor parent; (B) metolachlor metabolites; (C) imidacloprid parent; (D) imidacloprid metabolites. Note: CK, natural soil fortified with the mixed (0.5 mg kg^{-1} IMI and 2 mg kg^{-1} MET) pesticides; LPE and HPE, CK fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively. Lower case letters (a, b) refer to significant differences (ANOVA, Duncan's test, $P < 0.05$) between treatments, identical letters indicate no significant differences, and vice versa.

and IMI, except for a distinct influence of 1.0 % PLA on IMI degradation. The mechanisms by which MPs affect the degradation of organic pollutants are complex and are primarily influenced by factors such as the type and aging of MPs, the polarity of the organic pollutants, and soil environmental conditions (Liu et al., 2011; Qiu et al., 2024; Zhang et al., 2018). These factors can lead to varying results. For example, a previous study found that polystyrene (PS) fragments and polyvinyl chloride (PVC) beads, at environmentally relevant concentrations, had negligible effects on thiacloprid degradation (Xu et al., 2020). Similarly, the addition of 28 % polypropylene (PP) to loess soils in China had a negligible effect on glyphosate degradation (Yang et al., 2018). In contrast, the incorporation of 0.5 % polystyrene (PS) and 1.0 % polyethylene (PE) significantly inhibited the degradation of tetracycline and ciprofloxacin, respectively (Sun et al., 2018; Wang et al., 2020b). Due to its longer half-life (174 days in the field for IMI versus 21 days for MET) and higher water solubility (610 mg L^{-1} at 20°C for IMI vs. 530 mg L^{-1} for MET) (Lewis et al., 2016), IMI was more susceptible to the effects of PLA, as demonstrated in a previous study (Wang et al., 2020a). This may be because the two-phase distribution system between soil pore water and soil particles could affect the degradation of pesticides (Collins et al., 1999). Additionally, in a maize field, PE more effectively inhibited the dissipation of tebuconazole compared to azoxystrobin, although they had no impact on metalaxyl (Qiu et al., 2024). The production and degradation of MET metabolites were not influenced by the two types of MPs. However, 0.1 % PLA significantly increased the production of IMI

metabolites IOL while decreasing the production of 6CA. Additionally, high concentrations of both MPs significantly reduced the production of 6CA. However, the effects of MPs on the formation and dissipation of pesticide metabolites have not been reported in previous studies.

3.2. Soil chemical properties

Soil chemical properties, such as pH, dissolved organic carbon (DOC), and available nitrogen (AN), are key factors influencing pesticide degradation in soil (Zhang et al., 2021). MPs have been shown to influence soil physicochemical properties significantly, with notable effects on soil pH, DOC, and nutrient dynamics. The degradation of MPs in soil can release acidic additives, leading to soil acidification and a reduction in pH levels (Boots et al., 2019; Rillig et al., 2019). Concurrently, MPs alter microbial activity and organic matter decomposition processes, often resulting in elevated DOC concentrations due to enhanced microbial metabolism and the release of organic compounds from MP surfaces (Liu et al., 2017). Furthermore, MPs affect nutrient availability by modifying soil structure and microbial community composition. Specifically, MPs can adsorb essential nutrients such as nitrogen and phosphorus, or disrupt microbial-mediated nutrient cycling, thereby reducing their bioavailability (Zhao et al., 2022). These alterations underscore the intricate interactions between MPs and soil ecosystems, emphasizing the need for further research to elucidate their long-term ecological consequences. Importantly, changes in soil pH,

DOC, and nutrient availability may significantly influence microbial activity, potentially shifting the predominant pathways of pesticide degradation, particularly biodegradation, with implications for soil health and ecosystem functioning. In the present study, as shown in Table 1, two concentrations of PE and 0.1 % PLA had no significant effect on soil pH. However, 1 % PLA significantly lowered the pH value. This trend could be attributed to the release of lactic acid from PLA, which occurs through the formation of cracks in the polymer surface during mineralization, leading to a decrease in soil pH (Ainali et al., 2022). Nevertheless, the addition of both PE and PLA did not significantly affect soil DOC or AN, with values ranging from 0.23 ± 0.01 to 0.26 ± 0.03 g kg⁻¹ for DOC and 76.4 ± 3.6 to 89.5 ± 1.9 g kg⁻¹ for AN, regardless of the concentrations used (Table 1). Similarly, several previous studies have found that MP contamination does not alter soil organic carbon, likely due to the inert nature of MPs and their functional differences compared to organic matter (Ren et al., 2020; Rillig, 2018). Although previous studies have reported that MP contamination always risks soil C and N depletion (Iqbal et al., 2024), our study found that PE and PLA had no significant effects on soil DOC or AN. This may be attributed to the relatively short incubation period, which resulted in a low degree of MP aging.

3.3. Soil bacterial community

Microbial degradation is the primary mode of pesticide breakdown in soil, as microorganisms can utilize pesticides as sources of carbon or nitrogen for their growth and reproduction (Kandil et al., 2015). In the present study, to assess the impact of MP addition on pesticide degradation through changes in microbial communities, we determined the within-sample diversity (α -diversity) and community structure of bacteria. As shown in Table 2, there were no significant differences in the richness index (ACE) across the groups. However, the Simpson index of the HPLA group was higher than that of the other groups, indicating lower bacterial community diversity in the HPLA group. A similar trend was observed in the Shannon index, although no significant differences were found between the groups. Previous studies have suggested that biodegradable plastics, due to their more easily degradable nature compared to conventional plastics, may generate more MPs in the same amount of time (Song et al., 2024; Yang et al., 2022), leading to greater MP pollution in soil. This, in turn, can decrease soil bacterial community diversity (Beltran-Sanahuja et al., 2021; Liao and Chen, 2021).

The predominant bacterial phyla, as shown in Fig. 2(A), were Actinobacteriota, Proteobacteria, Acidobacteriota, Firmicutes, and Chloroflexi, which together accounted for >80 % of the total abundance in all treatment soils. However, the relative abundance of these phyla did not differ significantly among the treatments ($P > 0.05$, Kruskal-Wallis test). Additionally, the changes in bacterial community abundance across the treatment soils were evaluated. The top 30 genera are presented in the heatmap (Fig. 2(B)), with dominant genera including *Bacillus*, *Pseudarthrobacter*, *Rhodococcus*, *Sphingomonas*, *Skermanella*, and others,

Table 1
Effects of two kinds of MPs on soil chemical properties.

Treatment	pH	DOC / (μg/g)	AN / (μg/g)
CK	7.28 ± 0.01 a	0.23 ± 0.01 a	83.9 ± 8.2 a
LPE	7.30 ± 0.04 a	0.25 ± 0.01 a	79.9 ± 1.8 a
HPE	7.33 ± 0.06 a	0.24 ± 0.02 a	85.0 ± 5.6 a
LPLA	7.34 ± 0.06 a	0.24 ± 0.05 a	76.4 ± 3.6 a
HPLA	7.12 ± 0.05 b	0.27 ± 0.02 a	89.5 ± 1.9 a

Note: CK, natural soil fortified with the mixed (0.5 mg kg⁻¹ IMI and 2 mg kg⁻¹ MET) pesticides; LPE and HPE, CK fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively. DOC, dissolved organic carbon; AN, alkali-hydrolyzable nitrogen. Lower case letters (a, b) refer to significant differences (ANOVA, Duncan's test, $P < 0.05$) between treatments, identical letters indicate no significant differences, and vice versa.

Table 2
Richness and diversity indices of the soil bacterial communities.

Treatment	ACE	Simpson	Shannon
CK	4581 ± 326 a	0.0040 ± 0.0006 b	6.700 ± 0.325 a
LPE	4369 ± 611 a	0.0042 ± 0.0010 b	6.652 ± 0.614 a
HPE	4365 ± 630 a	0.0041 ± 0.0010 b	6.665 ± 0.558 a
LPLA	4368 ± 847 a	0.0046 ± 0.0008 ab	6.614 ± 0.593 a
HPLA	4477 ± 623 a	0.0051 ± 0.0012 a	6.609 ± 0.722 a

Note: CK, natural soil fortified with the mixed (0.5 mg kg⁻¹ IMI and 2 mg kg⁻¹ MET) pesticides; LPE and HPE, CK fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively. Lower case letters (a, b) refer to significant differences (ANOVA, Duncan's test, $P < 0.05$) between treatments, identical letters indicate no significant differences, and vice versa.

indicating their tolerance to mixed contamination with IMI and MET. Several of these bacteria, such as *Bacillus* (Carles et al., 2018; Shang et al., 2023), *Rhodococcus* (Arnold et al., 1996), and *Sphingomonas* (Dong et al., 2015; Erguven and Demirci, 2021), have been identified as capable of degrading organic pollutants, including IMI and MET, as well as antibiotics and polycyclic aromatic hydrocarbons in soil.

PCA analysis was performed to explore the differences in bacterial communities among the treatment soils. As shown in Fig. 3, except for the HPLA treatment, the bacterial communities in the other treatments overlapped and clustered together. In other words, the bacterial community in the HPLA treatment was distinctly separated from the others along the PC2 axis ($P < 0.01$, Adonis), indicating that 1 % PLA had a significant effect on the soil bacterial community, whereas the two concentrations of PE and 0.1 % PLA showed no significant effects. Kruskal-Wallis analysis was conducted to assess the statistical differences in the abundance of bacterial genera, revealing significant differences in 15 bacterial genera across treatments ($P < 0.05$) (Fig. 4). The abundance of *Pseudarthrobacter*, *Skermanella*, and *Bradyrhizobium* in the HPLA treatment was significantly higher than in the other treatments, with increases of 1.30–1.54 times, 1.39–1.59 times, and 1.18–1.59 times, respectively. This suggests that the growth of these three bacteria was stimulated by 1 % PLA, which may serve as a carbon source. *Pseudarthrobacter* has been shown to efficiently degrade five types of phthalate acid esters (plasticizers), with degradation rates exceeding 65.3 % within 48 h (Chen et al., 2021). *Skermanella* was observed to significantly increase in abundance during PET degradation (Han et al., 2024). Additionally, Qi et al. (2020) found that 1 % biodegradable MPs significantly increased the abundance of *Bradyrhizobium* in soil.

3.4. MPs properties

The surface morphology of MPs-PE and PLA at the beginning and end of the experimental incubation is illustrated in Fig. 5. As shown in the SEM images (Fig. 5A, B), the surface of PE exhibited no noticeable changes between day 0 and day 30 of incubation, remaining relatively smooth. Spectroscopic and thermally analyses indicated that conventional MPs did not degrade after exposure to soil under varying environmental conditions (Beltran-Sanahuja et al., 2021). In contrast, the SEM images in Fig. 5 (D, E) revealed significant crevices and voids on the surface of PLA after 30 days of incubation, compared to the relatively flat surface observed at day 0. Similarly, one study reported the formation of cavities and cracks on the surface of PLA during hydrolysis within a short period, with the diameter of the cavities increasing as the temperature rose (Yu et al., 2023). Notably, PLA exhibited significant degradation, leading to the production of more MPs, including nano-plastics (NPs) (Fan et al., 2022). This degradation resulted in increased pollution of soil microorganisms and a subsequent reduction in microbial metabolic function (Sun et al., 2022).

FTIR analysis revealed the changes in functional groups of MPs-PE and PLA after 30 days of incubation (Fig. 5 C, F). The characteristic infrared absorption peaks of PE were observed at 2916 cm⁻¹, 2850

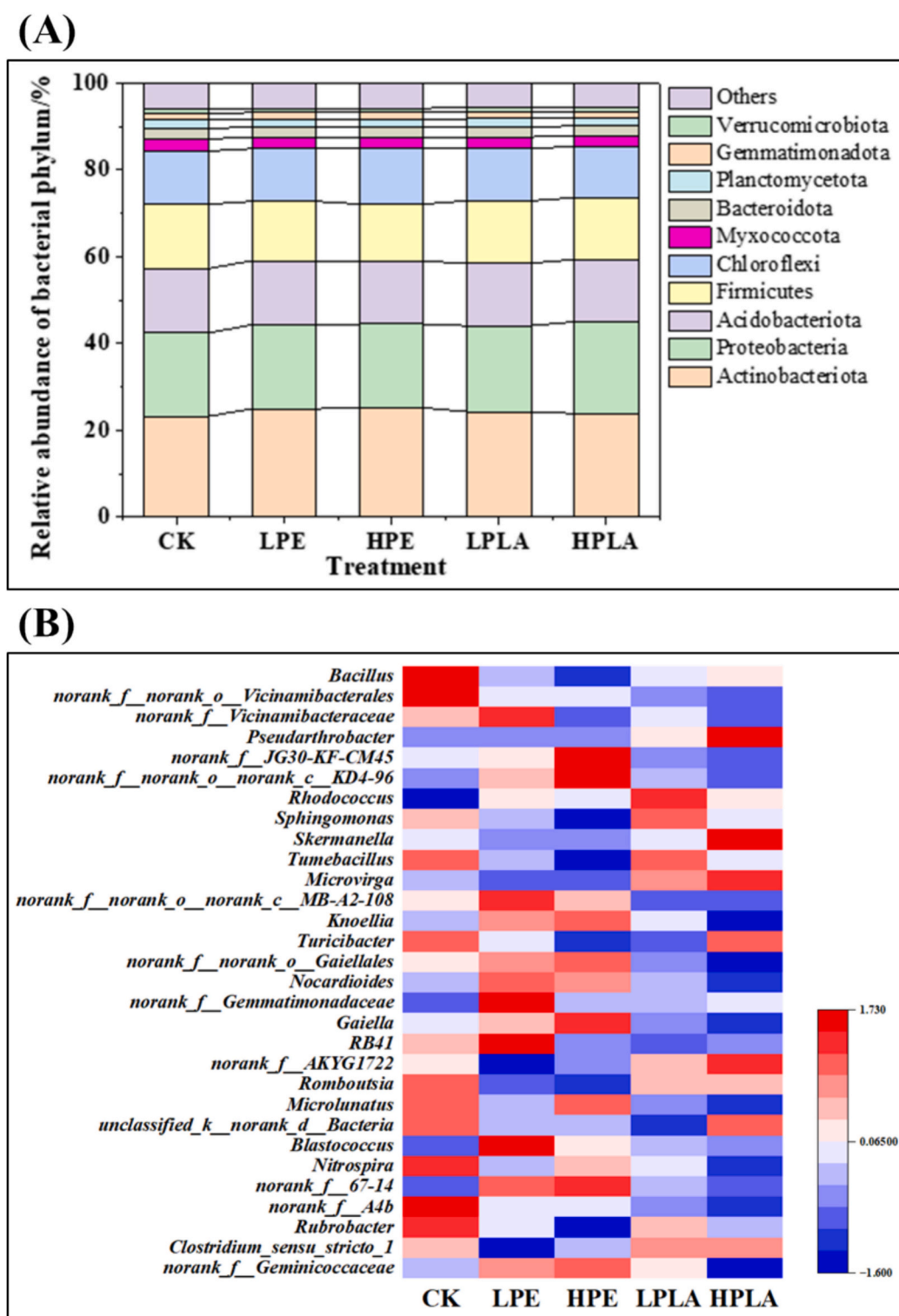


Fig. 2. Effects of microplastics on soil bacterial diversity and community composition. (A) Bacterial phyla; (B) Top 30 bacterial genera. *Note:* CK, natural soil fortified with the mixed (0.5 mg kg^{-1} IMI and 2 mg kg^{-1} MET) pesticides; LPE and HPE, CK fortified with low (0.1%) and high (1%) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1%) and high (1%) concentrations of PLA, respectively. The bacterial abundance level represents the color scale, with red representing high expression and blue representing low expression.

cm^{-1} , 1472 cm^{-1} , and 718 cm^{-1} . The peaks at 2916 cm^{-1} and 2850 cm^{-1} were attributed to C—H stretching vibrations, while the peaks at 1472 cm^{-1} and 718 cm^{-1} corresponded to C—H in-plane deformation and out-of-plane deformation vibrations, respectively (Li et al., 2021). These characteristic peaks showed no significant changes, with the exception of a slight absorption peak at 1051 cm^{-1} , which was

attributed to C—O stretching vibrations appearing after 30 days of incubation (Fig. 5 C). This suggests a weak oxidation process occurring on the surface of PE during incubation (Rodriguez-Seijo et al., 2017). In contrast, for PLA (Fig. 5 F), the absorption peaks at 2999 cm^{-1} , 1458 cm^{-1} , and 760 cm^{-1} were associated with C—H vibrations, while the peak at 1759 cm^{-1} corresponded to the stretching vibration of C=O.

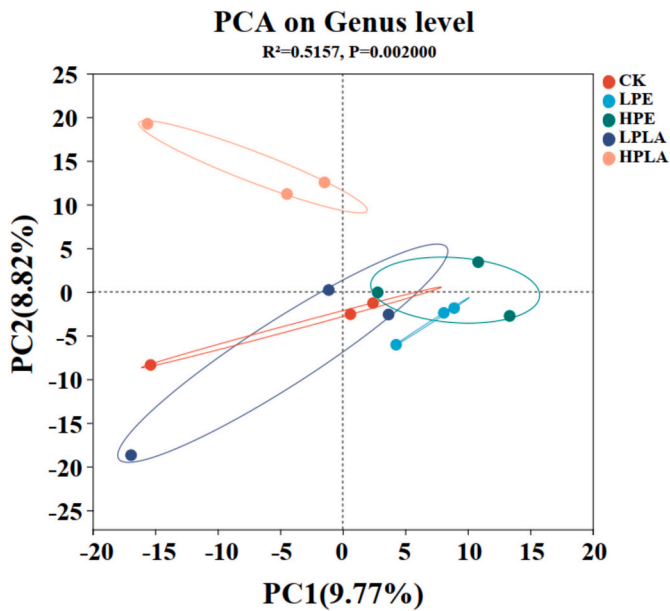


Fig. 3. PCA analysis of bacterial community (at the genus level) in different treatments. *Note:* CK, natural soil fortified with the mixed (0.5 mg kg⁻¹ IMI and 2 mg kg⁻¹ MET) pesticides; LPE and HPE, CK fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively.

Notably, a significant change was observed in the absorption peak at 1621 cm⁻¹, attributed to the stretching vibration of C=O, indicating substantial degradation of MPs-PLA (Zhou et al., 2021).

Similar to previous studies (Fan et al., 2022; Liao and Chen, 2021), the combined results of SEM images and FTIR analysis suggest that biodegradable MPs are more prone to degradation than conventional MPs, probably resulting in the production of more MPs within the same short period. Consequently, PLA has a greater potential to disrupt the soil environment compared to PE, thereby exerting a more significant impact on the degradation of pesticides in soil.

4. Conclusion

This study demonstrated that biodegradable MP (PLA) and conventional MP (PE) have distinct effects on the degradation of different pesticides in soil. Specifically, PLA was found to reduce the degradation rate of IMI in a concentration-dependent manner, but had no effect on the degradation of MET. In contrast, PE showed no impact on the degradation of either pesticide. The reduced degradation rate of IMI was attributed to a decrease in soil pH and the reduction of microbial community. PLA, being more susceptible to degradation than PE, released acidic substances and more MP particles during the incubation period, which in turn lowered the soil pH and negatively affected soil microorganisms. It is important to note, however, that the study's scope was limited to the specific types of MPs and pesticides examined. Future research should explore a broader range of MPs and pesticides to systematically evaluate the impact of MPs on the dissipation of

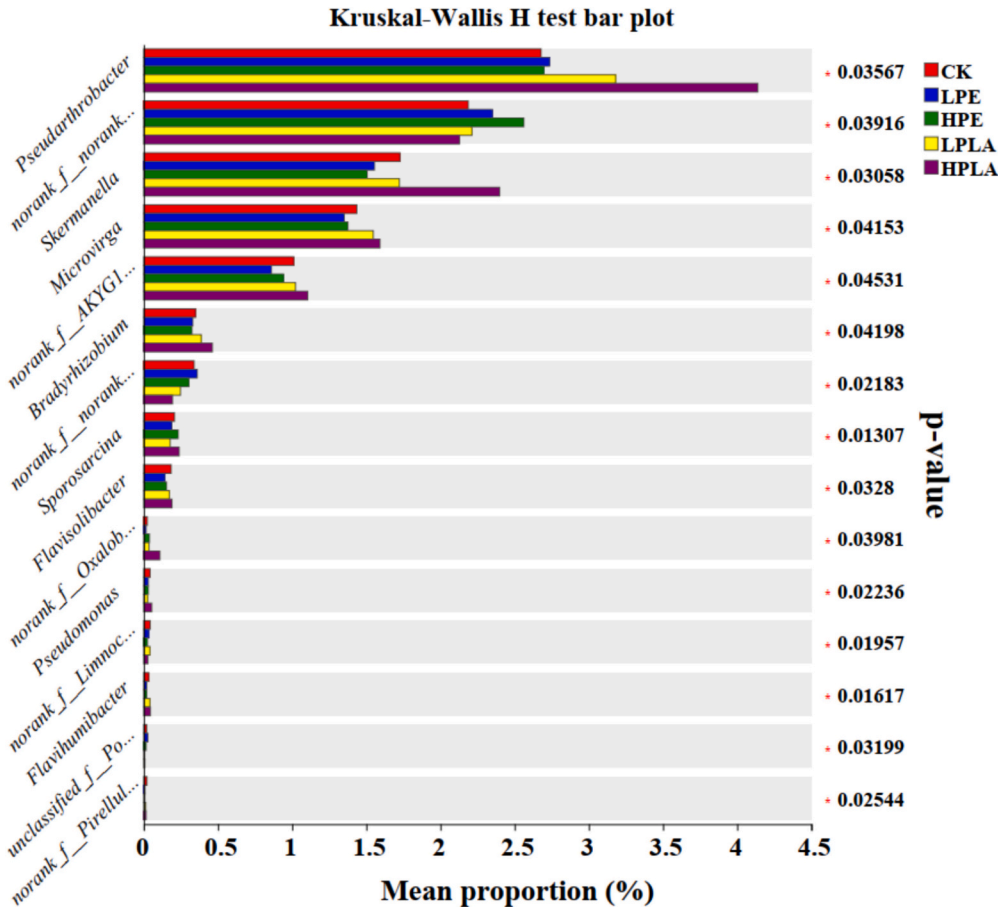


Fig. 4. Significant differences in the relative abundance of some bacteria at the genus level across all analyzed soils unveiled by 16S rDNA high-throughput sequencing. *Note:* CK, natural soil fortified with the mixed (0.5 mg kg⁻¹ IMI and 2 mg kg⁻¹ MET) pesticides; LPE and HPE, CK fortified with low (0.1 %) and high (1 %) concentrations of PE, respectively; LPLA and HPLA, CK fortified with low (0.1 %) and high (1 %) concentrations of PLA, respectively. For the *t*-test analysis: * denotes *P* < 0.05.

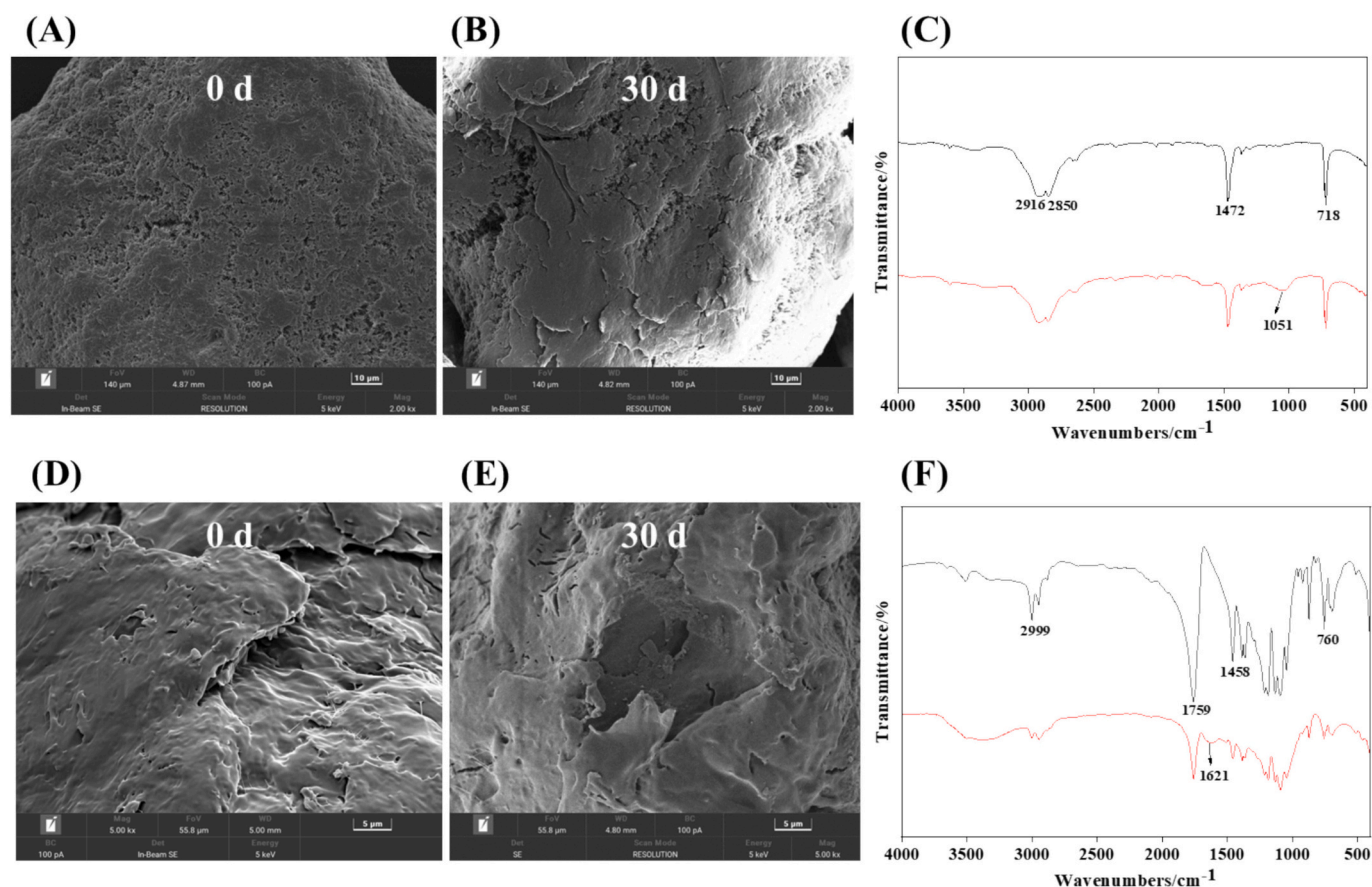


Fig. 5. Representative morphological changes of microplastics photographed by a scanning electron microscope (SEM) in soils and the identification by Fourier transform infrared spectroscopy (FTIR) after the 30 d-incubation. (A-B): SEM images of PE, and their FTIR spectrums (C), (D-E): SEM images of PLA, and their FTIR spectrums (F).

agrochemicals in agricultural environments. This study offers significant insights into the ecological risks posed by MPs and pesticide residues, presenting robust scientific evidence to inform sustainable pesticide management strategies and regulate the alternative use of biodegradable plastics in facility agriculture environment.

CRedit authorship contribution statement

Pengtao Chen: Data curation, Software, Writing – original draft. **Furong Fu:** Conceptualization, Formal analysis, Writing – original draft. **Lixia Zhao:** Software, Writing – review & editing. **Xiaojing Li:** Conceptualization, Methodology. **Yang Sun:** Funding acquisition, Project administration, Resources, Writing – review & editing. **Zhenyan Fu:** Writing – review & editing. **Liping Weng:** Validation, Writing – review & editing.

Declaration of competing interest

The authors declare no conflict of interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsoil.2025.106189>.

Data availability

Data will be made available on request.

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