



# Chlorpyrifos degradation and its impacts on phosphorus bioavailability in microplastic-contaminated soil

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## ABSTRACT

Pesticide residues and microplastics (MPs) in agricultural soils are two major concerns for soil health and food safety. The degradation of chlorpyrifos (CPF), an organophosphorus pesticide, releases phosphates. This process may be affected by the presence of MPs in the soil. The combination of CPF and MPs presence in the soil may thus produce interaction effects that alter the soil phosphorus (P) balance. This study explores the degradation pathways of CPF (6 mg kg<sup>-1</sup>, 12 mg kg<sup>-1</sup> of CPF addition) in soils with different levels of polylactic acid MPs (PLA-MPs) (0.0 %, 0.1 %, 0.5 %, 1.0 % w/w), and analyzes soil P fractions and phosphatase enzyme activities to investigate soil P bioavailability under different treatments. Results show that the degradation of CPF fits to a first-order decay model, with half-lives (*DT*<sub>50</sub>) ranging from 11.0 to 14.8 d depending on PLA-MPs treatment. The concentration of its metabolite 3, 5, 6-trichloropyridine 2-phenol (TCP) reached a peak of 0.93–1.67 mg kg<sup>-1</sup> within 7–14 days. Similarly, the degradation of CPF led to a significant transient increase in P bioavailability within 3–7 days ( $p < 0.05$ ), with a peak range of 22.55–26.01 mg kg<sup>-1</sup> for Olsen-P content and a peak range of 4.63–6.76 % for the proportions of available P fractions (H<sub>2</sub>O-P+NaHCO<sub>3</sub>-P+NaOH-P), before returning to prior levels (Olsen-P: 11.28–19.52 mg kg<sup>-1</sup>; available soil P fractions: 4.15–5.61 %). CPF degradation (6 mg kg<sup>-1</sup>) was significantly inhibited in soil with 1.0 % PLA-MPs addition. The effects of MPs and CPF on soil P fractions occur at different time frames, implying that their modes of action and interactions with soil microbes differ.

## 1. Introduction

Due to its high efficacy and broad-spectrum properties, chlorpyrifos [O, O-diethyl O-(3, 5, 6-trichloro-2-pyridinyl) phosphorothioate, CPF] has become one of the most widely used organophosphorus pesticides (OPPs) in agriculture (Dar et al., 2019; Duman and Tiryaki, 2022). Increasing evidence that CPF may affect human and animal health has led to restrictions and bans on its use in the European Union and the United States (Jia et al., 2021). However, due to its persistence and effectiveness, it is still used on a large scale in developing countries (Rahman et al., 2020). After application, excessive CPF can penetrate into soils (Veronika et al., 2018), where 78 %–95 % of CPF may be degraded by soil microorganisms, with a *DT*<sub>50</sub> ranging from 10 to 120 days (Racke et al., 1996; Sardar, Kole, 2005; Farhan et al., 2021a). A common degradation product of CPF is 3, 5, 6-trichloropyridine

2-phenol (TCP) (Barkoski et al., 2018), a persistent metabolite with *DT*<sub>50</sub> values ranging from 65 to 360 days (Li et al., 2010; Maya et al., 2012). TCP is more toxic than the parent compound CPF, and has a synergistic toxicity with CPF (Barkoski et al., 2018).

Phosphorus (P) is an essential nutrient for the growth and development of crops (Lwin et al., 2017). Different P forms in soils vary greatly in bioavailability to plants and microbes (Helfenstein et al., 2018). Thus, the composition of P forms can determine soil P bioavailability to a large extent (Yang, Post, 2011). Furthermore, the various P forms are differently sensitive to external disturbances and agricultural practices. CPF is a phosphoric acid compound that contains phosphate ester bonds, which are easily hydrolyzed (Liu et al., 2001; Kumar et al., 2018) to release phosphate into the soil. After entering the soil, these released phosphate esters may further modify the forms, contents, and bioavailability of soil P. In addition to releasing phosphate esters, CPF and its metabolites may

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also change the soil P bioavailability by affecting soil P solubilizing microorganisms, which control the processes of inorganic P solubilization and organic P mineralization through the secretion of organic acids and phosphatase enzymes (Singh et al., 2011; Nasreen et al., 2012). The application of other organophosphorus pesticides (OPPs) has also been observed to affect soil P fractions and their transformations (Ajiboye et al., 2022; Wang et al., 2022b). Majumder, Das, (2016) found that the OPPs such as profenophos, quinalphos, monocrotophos and triazophos can stimulate the growth and metabolism of phosphate solubilizing microorganisms, promote the release of soil available P, and facilitate crop growth. Das et al. (2012) found that the herbicides pendimethalin and quizalofop significantly stimulated the growth and activity of P solubilizing microorganisms, resulting in higher total P (TP) and available P contents in treated soils than in the control treatment. Zhou et al. (2016) found that the OPP herbicide glyphosate significantly increased soil available P content by promoting the release of soil adsorbed P. Therefore, increased available P may be a benefit of CPF application, in addition to its pesticidal effects. The environmental behavior of CPF may be affected by various factors such as soil pH, temperature, moisture, and application rate (Jaiswal et al., 2017; Atabila et al., 2018). The coexistence of CPF with other pollutants, such as microplastics (MPs), may also affect the environmental behavior of CPF. Ju et al. (2023a) found that biodegradable MPs increased the biogenic transport of CPF by earthworms, and inhibited CPF degradation in soils. Beriot et al. (2020) found that more than 80 % of CPF adsorbed onto biodegradable MPs after 15-days, and suggested that the adsorption of pesticides on MPs may reduce their biodegradation rate. Interactions between MPs and CPF may also change the effects of CPF application on soil P bioavailability. However, as CPF degradation in MPs contaminated soils is not well understood, the responses of soil P fractions and bioavailability to the coexistence of MPs and CPF, and its underlying mechanisms, remain largely unclear.

To address this issue, this study investigates the degradation of CPF and the change in P fractions in MPs-contaminated soils during a 30-day incubation experiment. We hypothesize that MPs may slow down the degradation of CPF thereby negatively affecting soil P bioavailability, and that this effect is enhanced as soil MP concentrations increase.

## 2. Materials and methods

### 2.1. Materials and chemicals

The soil used in this experiment was clay loam collected from farmland topsoil (0–20 cm) in the Loess Plateau in Yangling, Shaanxi Province, China. Crop residues, roots and gravel were removed from the soil. The soil was then air-dried and passed through a 2 mm sieve. Field water capacity was measured using FAO recommendation method (FAO, 1985). Soil pH was measured using a pH meter, with a water to soil ratio of 5: 1 (Mongia et al., 1992). Organic matter was measured using potassium dichromate external heating method described by Nelson, Sommers, (1983). The concentration of total nitrogen (TN) in the soil was determined using Kjeldahl distillation method described by Jones (1991). The polylactic acid microplastics (PLA-MPs) was detected by flotation method described by Chen et al., (2022). The basic properties of the experimental soil are as follows: pH:  $8.31 \pm 0.2$ ; organic matter:  $9.92 \pm 0.25 \text{ g kg}^{-1}$ ; TN:  $0.54 \pm 0.10 \text{ g kg}^{-1}$ ; total P (TP):  $0.73 \pm 0.10 \text{ g kg}^{-1}$ ; Olsen-P:  $22.21 \pm 0.40 \text{ mg kg}^{-1}$ . The background concentration of chlorpyrifos (CPF) and 3, 5, 6-trichloropyridine 2-phenol (TCP) were lower than the limit of quantitation (LOQ) while the background concentration of PLA-MPs was not detected. PLA-MPs (99.6 % purity, Huachuang Plastic Raw Materials Business, Dongwan City, Guangdong Province, China) were used in this experiment, with sizes ranging from 50 to 500  $\mu\text{m}$ . CPF emulsifiable concentrate ( $480 \text{ g L}^{-1}$ , Tongda Chemical Plant, Jining City, Shandong Province, China) was dissolved in ultrapure water to obtain two stock solutions of  $240 \text{ mg L}^{-1}$  and  $480 \text{ mg L}^{-1}$ .

### 2.2. Experimental design

Before the experiment, 4 kg of soil was mixed with 0.0, 4.0, 8.0, 40.0 g of PLA-MPs, respectively, to obtain four mass-concentration levels of PLA-MPs (w/w): 0.0 % (control), 0.1 %, 0.5 %, 1.0 %. The soil was then incubated for 7 days in an artificial climate chamber, with a cycle of 16 hours of light and 8 hours of darkness. During the incubation, the temperature of the climate chamber was maintained at  $25 \pm 0.5 \text{ }^\circ\text{C}$ , and soil moisture was maintained at 12 % (w/w), equivalent to 60 % of field water capacity. After pre-incubation, CPF was applied and in total there were 12 treatments, with 18 replicates per each treatment for six sampling times. For each treatment, 60.0 g of incubated soil was weighed into an aluminum box (diameter: 6 cm, height: 6 cm). Then, 1.5 mL of  $240 \text{ mg L}^{-1}$  and 1.5 mL of  $480 \text{ mg L}^{-1}$  CPF stock solution was sprayed evenly on the soil surface, respectively, with the application rate of  $6 \text{ mg kg}^{-1}$  and  $12 \text{ mg kg}^{-1}$  (w: w). This concentration of CPF in soil corresponded to a maximum application rate of  $3.3 \text{ L ha}^{-1}$  ( $480 \text{ g L}^{-1}$ ) (recommended for chemical fallow against insecticide), assuming a soil depth of 2 cm and soil bulk density of  $1300 \text{ kg m}^{-3}$ . Meanwhile, the application rates mentioned above were used as the starting point of CPF degradation. After pesticide application, the soil was quickly mixed and then put into the same climate chamber (temperature:  $25 \pm 0.5 \text{ }^\circ\text{C}$ , soil moisture: 12 %) for 30 days. Soil samples were collected at 0, 1, 3, 7, 14 and 30 days, and each sampling time we took there samples per treatment as replicates. Afterwards, each sample was divided into three portions: one portion was stored at  $-18 \text{ }^\circ\text{C}$  for CPF and TCP analysis; one portion was stored at  $4 \text{ }^\circ\text{C}$  for alkaline phosphatase activity analysis; and one portion was air-dried for P fraction analysis.

### 2.3. Sample analysis

#### 2.3.1. Chlorpyrifos and TCP analysis

Ten grams of a soil sample was weighed into a 150 mL plastic bottle containing 20 mL of water and 100 mL of ethyl acetate. The mixture was shaken for 1 h at 180 rpm with an oscillator. The extract was filtered through a filter paper containing sodium sulfate, into a round bottomed receiving flask. The filtrate was evaporated using a rotating vacuum evaporator at  $40 \text{ }^\circ\text{C}$  until it was almost dry, and the residue was then re-dissolved in 1 mL ethyl acetate. The concentrated extract was eluted in a florisil SPE cartridge pre-washed with 6 mL acetonitrile and 6 mL ethyl acetate. The eluted fraction was re-concentrated using an evaporator, and the residue was eluted in 1 mL of acetonitrile, then filtered through a  $0.22 \mu\text{m}$  filter membrane for high performance liquid chromatography analysis (Nexera LC-30A, Shimadzu Production House, Japan) with a C18 column (diameter:  $1.6 \mu\text{m}$ , length: 75 mm, width: 2.0 mm; column temperature:  $40 \text{ }^\circ\text{C}$ ). Acetonitrile/water mobile phase (90:10, v:v) (flow rate:  $1 \text{ mL min}^{-1}$ ) was used for chromatographic separation. The injected volume was 10  $\mu\text{L}$ , and the signal was recorded at 300 nm.

Two stock solutions for CPF and TCP at  $100 \mu\text{g mL}^{-1}$  were prepared in acetonitrile by adding 0.01 g of CPF and TCP and diluting it with acetonitrile to a volume of 100 mL, respectively. A working standard solution at a concentration of  $20 \mu\text{g mL}^{-1}$  was made by transferring 10 mL of CPF and TCP stock solutions to a 50 mL flask and diluting with acetonitrile. 0, 0.5, 1.0, 2.5, 5.0, 10.0, 25.0, 50.0 mL of CPF and TCP standard solution was diluted with acetonitrile to 50 mL, yielding CPF and TCP concentrations of 0, 0.2, 0.4, 1.0, 2.0, 4.0, 10.0, 20.0  $\mu\text{g mL}^{-1}$ , respectively. A standard calibration curve was prepared according to the relationship between peak area and concentration. The scattering was linearly fitted and displayed strong linearity, and the coefficient of determination was  $R^2 > 0.999$  in the standard range of 0–20  $\mu\text{g mL}^{-1}$ .

The CPF recovery rate was calculated by adding 1 mL of CPF stock solutions ( $5.0 \mu\text{g mL}^{-1}$ ,  $10.0 \mu\text{g mL}^{-1}$ ,  $50.0 \mu\text{g mL}^{-1}$ , and  $100.0 \mu\text{g mL}^{-1}$ ) at 0.5, 1.0, 5.0, and  $10.0 \mu\text{g g}^{-1}$  concentrations to five repeated 10.0 g blank soil samples. Another 5 blank soil samples were used to calculate the TCP recovery rate. These samples were spiked with 1 mL of TCP stock solution ( $1.0 \mu\text{g mL}^{-1}$ ,  $10.0 \mu\text{g mL}^{-1}$ ) at 0.1 and  $1.0 \mu\text{g g}^{-1}$ . The

CPF and TCP residues were then extracted using the above methods. The recovery rate was calculated using the recovery percentage of the spiked analyte. The mean recoveries of CPF at 0.5, 1.0, 5.0 and 10.0  $\mu\text{g g}^{-1}$  levels were  $72.4 \pm 5.6\%$ ,  $74.8 \pm 3.5\%$ ,  $80.4 \pm 4.9\%$ , and  $83.2 \pm 2.9\%$ , respectively. The mean recoveries of TCP at 0.5 and 1.0  $\mu\text{g g}^{-1}$  levels were  $67.8 \pm 4.2\%$  and  $74.2 \pm 4.7\%$  respectively. The concentrations of CPF and TCP in samples were corrected by the average recovery accordingly. Furthermore, the limit of quantifications (LOQ) of CPF and TCP were obtained by calibration curve, with an average recovery between 80% and 120% and a relative standard deviation  $\leq 20\%$ . Thus, the LOQ for CPF and TCP in soil samples were  $0.01 \mu\text{g g}^{-1}$  and  $0.02 \mu\text{g g}^{-1}$ , respectively.

Based on the kinetics of CPF attenuation in the soil, a first-order kinetic degradation model:

$$C_t = C_0 e^{-kt} \quad (1)$$

was used to fit the measured data in the experiment, where  $C_t$  is the concentration of CPF ( $\text{mg kg}^{-1}$ ) at time  $t$  (d) after being applied to the soil,  $C_0$  is the initial concentration ( $\text{mg kg}^{-1}$ ), and  $k$  ( $\text{d}^{-1}$ ) is the degradation rate constant. The half-life ( $DT50$ ) of CPF was calculated according to the equation:

$$DT50 = \ln 2 / k \quad (2)$$

### 2.3.2. Soil phosphorus determination

Soil Olsen-P was extracted using the colorimetric analysis method after 30 min extraction with  $0.5 \text{ mol L}^{-1} \text{ NaHCO}_3$  at pH 8.5 and  $25^\circ\text{C}$  (Olsen et al., 1954; Hu et al., 2012). In order to control the quality of the analysis, the extraction was conducted in the room with air-conditioner. Soil TP was digested with sulfuric acid and perchloric acid, and quantified using the Molybdenum-antimony resistance colorimetric method (Kara et al., 1997). Soil P fractions were determined using the sequential fractionation methods of Tiessen, Moir, (1993) and Kaiser et al., (2003).

### 2.3.3. Soil alkaline phosphatase activity

After sampling, 3.0 g of fresh soil was added to a 300 mL flask, along with 125 mL modified universal buffer of pH 11, and briefly mixed with a maglev stirrer. 150  $\mu\text{L}$  of the suspension and 50  $\mu\text{L}$  *p*-nitrophenyl phosphate were added to an enzymic labeled plate and incubated at  $25^\circ\text{C}$  for 0.5 h. Then, fluorescence values were measured at the excitation wavelength of 365 nm and the emission wavelength of 450 nm using a fluorescence plate reader (Marx et al., 2005).

## 2.4. Statistical analysis

The mean values and standard deviations were calculated to compare treatments. Logarithmic functions were used to obtain normality and equal variance. Data normality was tested with the Shapiro-Wilk test ( $p > 0.05$ ), and the equal variance of data was tested with Levene's test ( $p > 0.05$ ). One-way ANOVA with Duncan's post-hoc comparisons was used to test the differences among treatments and compare significant differences in CPF residues, TCP residues, Olsen-P, P fractions and alkaline phosphatase (ALP), among different levels of PLA-MPs addition at the same incubation times ( $p < 0.05$ ). Two-way ANOVA with Duncan's post-hoc test was used to analyze the effects of CPF, MPs, and their interactions on P fractions. Origin Pro 9.1 was used to fit the first-order degradation model and plot the data.

## 3. Results

### 3.1. CPF degradation

#### 3.1.1. CPF and TCP residues

CPF degraded rapidly in the first 7 days, and over 50% of applied CPF was degraded by day 7 (D7). At D7, CPF residues were at 2.45–2.90  $\text{mg kg}^{-1}$  and 5.44–6.39  $\text{mg kg}^{-1}$ , in treatments with

6  $\text{mg kg}^{-1}$  (Fig. 1a) and 12  $\text{mg kg}^{-1}$  of CPF application (Fig. 1c), respectively. Afterwards, CPF residues declined steady and changed slightly, especially in treatments with 6  $\text{mg kg}^{-1}$  of CPF application. At D30, over 75% of CPF was degraded, and its residues were at 0.81–1.08  $\text{mg kg}^{-1}$  and 1.96–2.41  $\text{mg kg}^{-1}$  in treatments with 6  $\text{mg kg}^{-1}$  and 12  $\text{mg kg}^{-1}$  of CPF application, respectively. Furthermore, CPF residues did not differ significantly across different levels of PLA-MPs contamination, under the same application rate of CPF.

TCP concentrations and dynamics, a metabolite of CPF degradation, were different across treatments (Fig. 1b, d). In treatments with 6  $\text{mg kg}^{-1}$  of CPF application (Fig. 1b), the TCP residues peaked at D14 with content ranging from 1.02 to 1.24  $\text{mg kg}^{-1}$  in treatments with 0–0.5% PLA-MPs addition, while TCP residues peaked at D7 with  $0.93 \pm 0.15 \text{ mg kg}^{-1}$  in the treatment with 1.0% PLA-MPs addition. In treatments with 12  $\text{mg kg}^{-1}$  of CPF application (Fig. 1d), TCP residues peaked at D7 with  $1.35 \pm 0.11 \text{ mg kg}^{-1}$  in the treatment with 0.1% PLA-MPs addition, while TCP residues peaked at 1.49–1.68  $\text{mg kg}^{-1}$  on D14 in the rest of the treatments.

#### 3.1.2. Degradation kinetics of CPF

CPF residue concentrations fit to the first-order kinetic degradation model well ( $R^2 > 0.85$ ), with  $DT50$  varying from  $11.0 \pm 1.44$ – $14.8 \pm 0.26$  d, in the treatments with 6 and 12  $\text{mg kg}^{-1}$  CPF application, respectively (Table 1). Specifically, in treatments with 6  $\text{mg kg}^{-1}$  CPF application, the  $DT50$  was significantly higher in the treatment with 1.0% PLA-MPs than that in control, but no significant difference of  $DT50$  was found among different levels of PLA-MPs addition. In treatments with 12  $\text{mg kg}^{-1}$  CPF application, however, no significant difference of  $DT50$  was found among the treatments.

## 3.2. Soil phosphorus properties

### 3.2.1. Soil available phosphorus (Olsen-P)

On the day of CPF application (D0), soil Olsen-P contents were significantly lower in the treatments with 0.1% and 0.5% PLA-MPs addition (11.25–14.10  $\text{mg kg}^{-1}$ ) than that in control (17.53–17.84  $\text{mg kg}^{-1}$ ), regardless of the CPF application rate. Although Olsen-P contents were significantly higher in the treatments with 1.0% PLA-MPs addition than in other treatments with PLA-MPs addition, no significant difference was observed between 0% and 1.0% PLA-MPs treatments. For the following three groups of treatments (0, 6 and 12  $\text{mg kg}^{-1}$  of CPF application), soil Olsen-P content peaked at D3 and then slowly declined till the observation period ended. Variations of Olsen-P in different CPF application groups were observed across treatments at the same sampling day, and in the same treatment across different sampling days. Interestingly, compared to treatment groups without CPF application, Olsen-P increased slightly at D30 in the treatment groups with CPF application. Fig. 2

### 3.2.2. Soil P fractions

Occluded-P was the main P fraction, as it accounted for more than 90% in all treatments (Table 2,  $p < 0.05$ ). The proportions of different P fractions decreased in the following order: Occluded-P >  $\text{NaHCO}_3\text{-P}$  ( $\text{NaHCO}_3\text{-Pi}$  and  $\text{NaHCO}_3\text{-Po}$ ) >  $\text{NaOH-P}$  ( $\text{NaOH-Pi}$  and  $\text{NaOH-Po}$ ) >  $\text{H}_2\text{O-P}$ . The proportions of Occluded-P decreased significantly to its lowest value at D3 or D7 in 0–0.5% treatments ( $p < 0.05$ ), and then increased to a level similar to the initial condition by the end of incubation period.

In treatments without CPF addition (Table 2a), soil labile P fractions ( $\text{H}_2\text{O} + \text{NaHCO}_3\text{-Pi} + \text{NaHCO}_3\text{-Po} + \text{NaOH-Pi} + \text{NaOH-Po}$ ) increased to the highest values at D3 (0.1% PLA-MPs and 0.5% PLA-MPs treatments) and at D7 (0.0% and 1.0% PLA-MPs treatments). At D3,  $\text{H}_2\text{O-P}$  in 0.1% PLA-MPs treatment ( $1.45 \pm 0.08\%$ ) was significantly higher than that in the 0.0% PLA-MPs ( $1.04 \pm 0.23\%$ ) and 1.0% PLA-MPs ( $0.66 \pm 0.05\%$ ) treatments.  $\text{NaOH-Pi}$  in the 0.5% PLA-MPs treatment ( $0.52 \pm 0.05\%$ ) was significantly higher than that in other treatments ( $p < 0.05$ ). At D7,

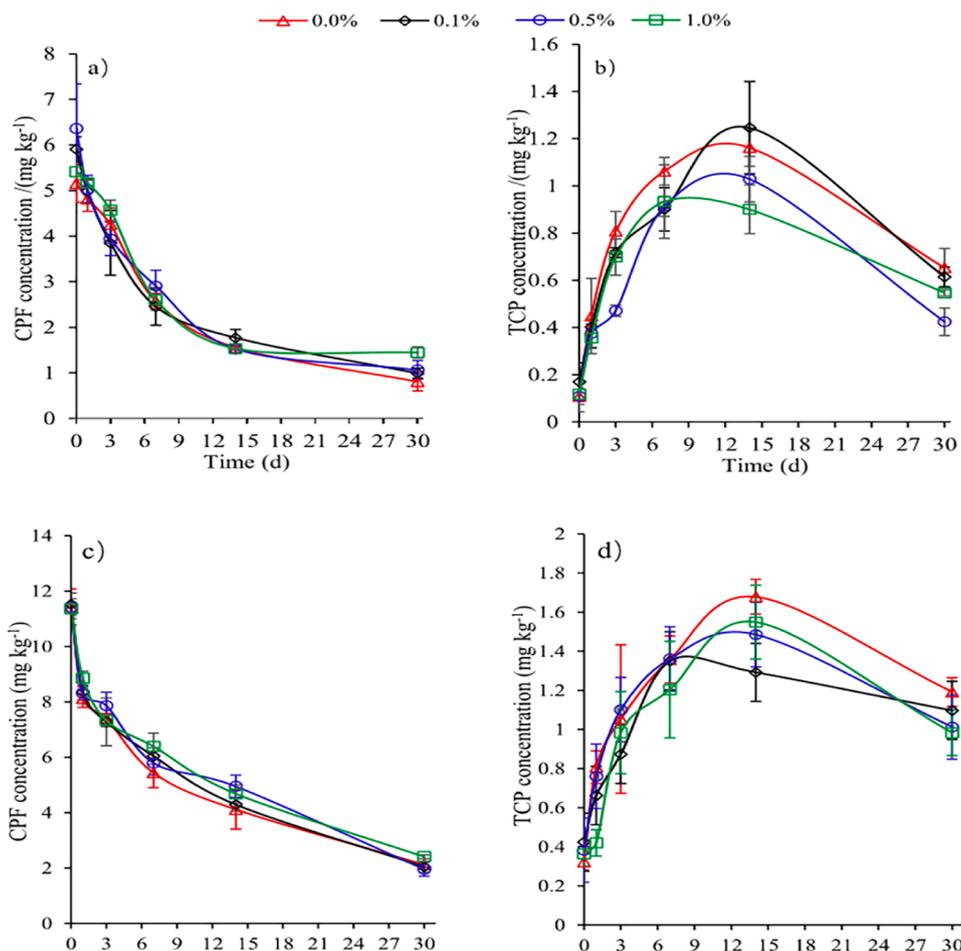


Fig. 1. CPF and TCP residues in different treatments during the observation days (a-b: CPF and TCP residues in the treatments with 6 mg kg<sup>-1</sup> of CPF application; c-d: CPF and TCP residues in the treatments with 12 mg kg<sup>-1</sup> of CPF application; the error bar represents the standard deviation (n = 3).

**Table 1**  
Kinetic equations of CPF degradation in different treatments.

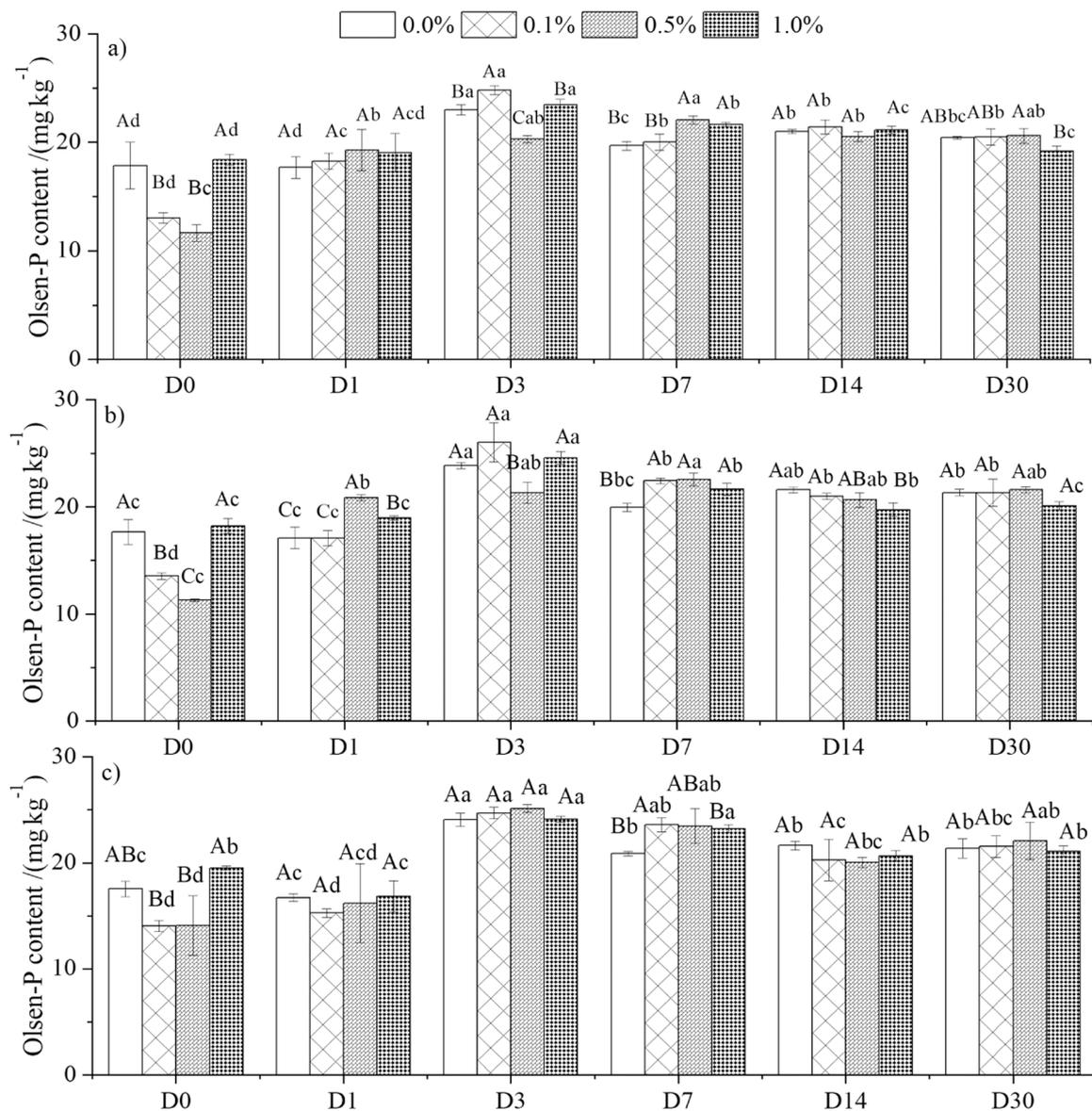
CPF concentration (mg kg <sup>-1</sup> )	PLA-MPs level	Kinetic equation	DT50	R <sup>2</sup>
6	0.0 %	C <sub>t</sub> = 4.72e <sup>-0.063t</sup>	11.0 ± 1.44	0.97
	0.1 %	C <sub>t</sub> = 4.73e <sup>-0.057t</sup>	12.2 ± 1.61	0.90
	0.5 %	C <sub>t</sub> = 4.92e <sup>-0.058t</sup>	12.0 ± 1.09	0.90
	1.0 %	C <sub>t</sub> = 4.62e <sup>-0.047t</sup>	14.7 ± 0.70	0.87
12	0.0 %	C <sub>t</sub> = 9.09e <sup>-0.050t</sup>	13.9 ± 0.70	0.88
	0.1 %	C <sub>t</sub> = 9.38e <sup>-0.052t</sup>	13.3 ± 0.86	0.90
	0.5 %	C <sub>t</sub> = 9.56e <sup>-0.053t</sup>	13.1 ± 0.90	0.91
	1.0 %	C <sub>t</sub> = 9.41e <sup>-0.047t</sup>	14.8 ± 0.26	0.91

Note: DT50 is presented as mean ± SD (n = 3); different lowercase letters indicate significant differences among treatments with different PLA-MPs addition levels with same amount of CPF addition (p < 0.05).

NaHCO<sub>3</sub>-Pi in the 1.0 % PLA-MPs treatment (2.91 ± 0.05 %) was significantly higher, while NaHCO<sub>3</sub>-Po in the 1.0 % PLA-MPs treatment (0.26 ± 0.09 %) was significantly lower than that in the 0.0 % PLA-MPs treatment (NaHCO<sub>3</sub>-Pi: 2.18 ± 0.12 %; NaHCO<sub>3</sub>-Po: 1.23 ± 0.37 %). NaOH-Pi (0.51 ± 0.07 %) was significantly lower and NaOH-Po (0.75 ±

0.06 %) were significantly higher in control than those in other treatments (p < 0.05).

In treatments with CPF application (Table 2b and Table 2c), soil Occluded-P was transformed into soil labile P (H<sub>2</sub>O+NaHCO<sub>3</sub>-Pi+NaHCO<sub>3</sub>-Po+NaOH-Pi+NaOH-Po) at D3-D7. Specifically, in treatments with 6 mg kg<sup>-1</sup> CPF application, soil labile P fractions (H<sub>2</sub>O+NaHCO<sub>3</sub>-Pi+NaHCO<sub>3</sub>-Po+NaOH-Pi+NaOH-Po) increased to the highest values at D3 in treatment of 0.0 % and 0.1 % PLA-MPs and at D7 in treatment of 0.5 % and 1.0 % PLA-MPs. At D3, H<sub>2</sub>O-P in 0.5 % PLA-MPs treatment (1.42 ± 0.11 %) and NaHCO<sub>3</sub>-Pi in the 0.1 % PLA-MPs treatment (2.99 ± 0.17 %) were significantly higher than that in other treatments (p < 0.05). At D7, H<sub>2</sub>O-P in the 0.0 % PLA-MPs treatment (1.18 ± 0.13 %) was significantly lower than that in the 0.1 % PLA-MPs treatment (1.47 ± 0.08 %) while NaHCO<sub>3</sub>-Po in the 0.0 % PLA-MPs treatment (0.82 ± 0.10 %) was significantly higher than that in the 1.0 % PLA-MPs treatment (0.46 ± 0.06 %). NaOH-Pi increased significantly in 0.5–1.0 % PLA-MPs treatment comparing with in control. Similarly, in treatments with 12 mg kg<sup>-1</sup> CPF application, soil labile P fractions (H<sub>2</sub>O+NaHCO<sub>3</sub>-Pi+NaHCO<sub>3</sub>-Po+NaOH-Pi+NaOH-Po) peaked at D3 in 0.1 % PLA-MPs treatment and D7 in treatment of 0.0 %, 0.5 % and 1.0 % PLA-MPs treatment. At D7, NaHCO<sub>3</sub>-Pi in 0.5 % PLA-MPs treatment (2.94 ± 0.10 %) was significantly higher than that in control (2.34 ± 0.24 %), while NaHCO<sub>3</sub>-Po in control (1.36 ± 0.07 %) was significantly higher than that in the 0.1 % PLA-MPs (0.50 ± 0.17 %) and 0.5 % PLA-MPs (0.34 ± 0.10 %) treatments (p < 0.05). NaOH-Pi in 0.5 % PLA-MPs treatment (1.15 ± 0.04 %) was significantly higher than that in control (0.42 ± 0.06 %) and 0.1 % PLA-MPs (0.64 ± 0.07 %) treatments (p < 0.05). However, NaOH-Po significantly declined in treatments with



**Fig. 2.** Soil Olsen-P content in different treatments during the observation days (a: 0 mg kg<sup>-1</sup> of CPF application; b: 6 mg kg<sup>-1</sup> of CPF application; c: 12 mg kg<sup>-1</sup> of CPF application; different lowercase letters indicate significant differences among different sampling days in the same level of PLA-MPs addition and CPF application ( $p < 0.05$ ); different capital letters indicate significant differences among different PLA-MPs addition levels at the same sampling day and CPF application ( $p < 0.05$ ); the error bar represents the SD ( $n = 3$ ).

PLA-MPs addition, comparing with that in 0 % ( $p < 0.05$ ).

### 3.3. Soil phosphatase activity

Significant differences of ALP were observed between treatments with and without PLA-MPs additions, especially in treatments with CPF application (Fig. 3). There were no significant differences in ALP activity among treatments with 0 and 12 mg kg<sup>-1</sup> CPF addition at D0. In treatments with 6 mg kg<sup>-1</sup> CPF, ALP activity was significantly higher at D0 in CK ( $111.08 \pm 2.21$  nmol g<sup>-1</sup> h<sup>-1</sup>) than in treatments with PLA-MPs addition ( $71.29$ – $75.72$  nmol g<sup>-1</sup> h<sup>-1</sup>). ALP activity in the 0.1 % PLA-MPs treatments peaked at D1 in treatments without CPF application ( $137.27 \pm 27.36$  nmol g<sup>-1</sup> h<sup>-1</sup>), while it peaked at D14 in treatments with 6 ( $179.50 \pm 16.00$  nmol g<sup>-1</sup> h<sup>-1</sup>) and 12 mg kg<sup>-1</sup> CPF application ( $162.00 \pm 28.70$  nmol g<sup>-1</sup> h<sup>-1</sup>). For the 0.5 % PLA-MPs treatments, ALP activity peaked at D14 and D30, in treatments with 0/6 mg kg<sup>-1</sup> CPF application and 12 mg kg<sup>-1</sup> CPF, respectively. ALP activity in the 1.0 % PLA-MPs

treatments varied during the observation period, and peaked at D30 ( $130.53$ – $194.52$  nmol g<sup>-1</sup> h<sup>-1</sup>).

### 3.4. CPF, PLA-MPs and their interactions on the soil P fractions

H<sub>2</sub>O-P was significantly affected by PLA-MPs and PLA-MPs×CPF until D14, but was only effected by CPF application at D30 (Table 3). PLA-MPs and PLA-MPs×CPF had significant effects on NaHCO<sub>3</sub>-Pi throughout the whole experiment, while CPF and PLA-MPs×CPF were the most significant driving factors that influenced NaHCO<sub>3</sub>-Po at D30. PLA-MPs had significant effects on NaOH-Pi during the whole experiment, while CPF only showed significant effects at D1 and D30. NaOH-Po was significantly influenced by PLA-MPs at the first 2 weeks, and was impacted with CPF from D3 to D7. PLA-MPs had significant effects on Occluded-P until D14, while CPF only had significant effects on Occluded-P at D30.

**Table 2a**  
Percentage of soil P fractions in treatments without pesticide application.

MPs	Days	H <sub>2</sub> O-P	NaHCO <sub>3</sub> -Pi	NaHCO <sub>3</sub> -Po	NaOH-Pi	NaOH-Po	Occluded-P
0.0 %	D0	0.88 ± 0.21 %ABb	2.37 ± 0.10 %Ab	0.31 ± 0.09 %Ab	0.47 ± 0.11 %Ba	0.77 ± 0.12 %Ab	95.19 ± 0.33 %Aa
	D1	0.72 ± 0.12 %Ab	2.54 ± 0.11 %Aa	0.49 ± 0.04 %Ab	0.51 ± 0.11 %Ba	0.68 ± 0.08 %Ab	95.06 ± 0.15 %Aa
	D3	1.04 ± 0.23 %BCab	2.72 ± 0.28 %Aa	0.47 ± 0.17 %ABb	0.23 ± 0.01 %Cb	1.42 ± 0.28 %ABa	94.12 ± 0.33 %Bb
	D7	1.42 ± 0.22 %ABa	2.18 ± 0.12 %Bb	1.23 ± 0.37 %Aa	0.51 ± 0.07 %Ca	0.75 ± 0.06 %Ab	93.92 ± 0.42 %Ab
	D14	1.12 ± 0.15 %Aab	2.57 ± 0.01 %Aa	0.35 ± 0.07 %Ab	0.48 ± 0.11 %ABa	0.77 ± 0.09 %Ab	94.70 ± 0.14 %Aab
0.1 %	D30	1.01 ± 0.16 %Bab	1.42 ± 0.10 %Bc	1.39 ± 0.18 %ABa	0.66 ± 0.10 %Ba	0.58 ± 0.15 %Ab	94.94 ± 0.55 %Aa
	D0	0.65 ± 0.07 %Bc	2.32 ± 0.06 %Ab	0.19 ± 0.04 %Ac	0.85 ± 0.11 %Aa	0.39 ± 0.02 %Bd	95.61 ± 0.06 %Aa
	D1	0.84 ± 0.14 %Abc	2.71 ± 0.14 %Aa	0.47 ± 0.07 %Abc	0.92 ± 0.15 %Aa	0.65 ± 0.19 %ABbc	94.50 ± 0.48 %Aa
	D3	1.45 ± 0.08 %Aa	2.65 ± 0.23 %Aab	0.88 ± 0.21 %Ab	0.29 ± 0.01 %BCc	1.29 ± 0.11 %ABa	93.44 ± 0.26 %Ba
	D7	1.17 ± 0.14 %Bab	2.41 ± 0.18 %Bb	1.00 ± 0.56 %ABab	0.78 ± 0.14 %Bab	0.47 ± 0.09 %Bcd	94.17 ± 0.33 %Aa
0.5 %	D14	1.32 ± 0.21 %Aa	2.63 ± 0.07 %Aab	0.25 ± 0.12 %Ac	0.33 ± 0.06 %BCc	0.72 ± 0.04 %ABb	94.76 ± 0.34 %Aa
	D30	0.72 ± 0.16 %Bc	1.74 ± 0.09 %Ac	1.48 ± 0.02 %Aa	0.66 ± 0.04 %Bb	0.68 ± 0.05 %Abc	94.73 ± 0.31 %Aa
	D0	0.64 ± 0.23 %Bc	2.34 ± 0.05 %Ac	0.50 ± 0.24 %Abc	0.84 ± 0.12 %Ab	0.38 ± 0.11 %Bd	95.29 ± 0.27 %Aa
	D1	0.66 ± 0.04 %Ac	2.75 ± 0.06 %Aa	0.26 ± 0.04 %Ac	1.25 ± 0.19 %Aa	0.23 ± 0.16 %Bd	94.92 ± 0.14 %Aab
	D3	1.23 ± 0.11 %ABb	2.43 ± 0.09 %Ac	0.53 ± 0.31 %ABbc	0.52 ± 0.05 %Ac	1.64 ± 0.06 %Aa	93.70 ± 0.51 %Bc
1.0 %	D7	1.56 ± 0.16 %Aa	2.46 ± 0.26 %ABbc	0.97 ± 0.49 %ABab	0.85 ± 0.05 %Bb	0.45 ± 0.08 %Bcd	93.71 ± 0.51 %Ac
	D14	1.37 ± 0.09 %Aab	2.67 ± 0.06 %Aab	0.65 ± 0.28 %Aabc	0.29 ± 0.07 %Cc	0.81 ± 0.03 %Ab	94.21 ± 0.39 %Abc
	D30	1.45 ± 0.19 %Aab	1.71 ± 0.02 %Ad	1.31 ± 0.19 %ABa	0.94 ± 0.04 %Ab	0.59 ± 0.02 %Ac	93.99 ± 0.11 %Ac
	D0	1.12 ± 0.11 %Ab	2.44 ± 0.08 %Ac	0.31 ± 0.04 %Ab	0.81 ± 0.08 %Ab	0.56 ± 0.14 %ABb	94.75 ± 0.12 %Abc
	D1	0.84 ± 0.05 %Ac	2.71 ± 0.06 %Ab	0.51 ± 0.27 %Ab	1.09 ± 0.13 %Aa	0.35 ± 0.11 %Bb	94.58 ± 0.35 %Abc
1.0 %	D3	0.66 ± 0.05 %Cc	2.54 ± 0.04 %Abc	0.18 ± 0.04 %Bb	0.30 ± 0.03 %Bd	1.10 ± 0.17 %Ba	95.37 ± 0.16 %Aa
	D7	1.51 ± 0.14 %ABa	2.91 ± 0.05 %Aa	0.26 ± 0.09 %Bb	1.22 ± 0.13 %Aa	0.31 ± 0.17 %Bb	93.80 ± 0.16 %Ad
	D14	1.24 ± 0.04 %Ab	2.71 ± 0.10 %Ab	0.43 ± 0.11 %Ab	0.62 ± 0.06 %Ac	0.61 ± 0.06 %Bb	94.39 ± 0.00 %Ac
	D30	0.85 ± 0.13 %Bc	1.77 ± 0.13 %Ad	1.03 ± 0.26 %Ba	0.81 ± 0.09 %ABbc	0.53 ± 0.07 %Ab	95.01 ± 0.20 %Aab

**Table 2b**  
Percentage of soil P fractions in treatments with pesticide application (6 mg kg<sup>-1</sup> of CPF).

MPs	Days	H <sub>2</sub> O	NaHCO <sub>3</sub> -Pi	NaHCO <sub>3</sub> -Po	NaOH-Pi	NaOH-Po	Occluded-P
0.0 %	D0	0.81 ± 0.11 %ABab	2.35 ± 0.05 %Bc	0.30 ± 0.15 %Ac	0.79 ± 0.03 %Ab	0.50 ± 0.06 %Ad	95.24 ± 0.35 %Aa
	D1	0.57 ± 0.12 %Bb	2.74 ± 0.05 %Aa	0.26 ± 0.04 %Bc	0.68 ± 0.14 %Bcb	0.47 ± 0.07 %Acd	95.28 ± 0.08 %Aa
	D3	1.11 ± 0.18 %Bab	2.53 ± 0.06 %BCb	0.74 ± 0.42 %Ab	0.35 ± 0.07 %Ad	1.22 ± 0.07 %ABa	94.05 ± 0.66 %ABa
	D7	1.18 ± 0.13 %Ba	2.47 ± 0.12 %Ab	0.82 ± 0.10 %Ab	0.49 ± 0.08 %Bcd	0.91 ± 0.07 %Ab	94.14 ± 0.30 %Aa
	D14	1.10 ± 0.06 %Bab	2.60 ± 0.04 %Ab	0.23 ± 0.07 %Ac	0.47 ± 0.11 %ABcd	0.66 ± 0.11 %ABc	94.94 ± 0.17 %Aa
0.1 %	D30	1.01 ± 0.62 %Aab	1.63 ± 0.09 %Bd	1.54 ± 0.04 %Ba	0.86 ± 0.12 %Aa	0.57 ± 0.08 %Acd	94.40 ± 0.75 %Aa
	D0	0.67 ± 0.18 %Bd	2.74 ± 0.18 %Aa	0.22 ± 0.04 %Ad	0.84 ± 0.01 %Aa	0.40 ± 0.05 %Ab	95.13 ± 0.31 %Aa
	D1	0.80 ± 0.07 %ABc	2.77 ± 0.09 %ABab	0.27 ± 0.19 %Bcd	1.02 ± 0.01 %BCa	0.66 ± 0.38 %Ab	94.52 ± 0.20 %Bab
	D3	1.13 ± 0.09 %Bb	2.99 ± 0.17 %Aa	0.66 ± 0.14 %Abc	0.47 ± 0.12 %Ac	1.51 ± 0.14 %Aa	93.24 ± 0.28 %Bc
	D7	1.47 ± 0.08 %Aa	2.41 ± 0.23 %Ab	0.74 ± 0.21 %ABb	0.67 ± 0.13 %Bb	0.85 ± 0.19 %Ab	93.86 ± 0.45 %Abc
0.5 %	D14	1.40 ± 0.17 %Aa	2.85 ± 0.36 %Aa	0.32 ± 0.17 %Acd	0.43 ± 0.03 %Bc	0.66 ± 0.05 %ABb	94.34 ± 0.40 %Aab
	D30	0.99 ± 0.09 %Abc	1.66 ± 0.12 %ABc	1.54 ± 0.10 %Ba	0.96 ± 0.10 %Aa	0.62 ± 0.22 %Ab	94.23 ± 0.32 %Abc
	D0	0.92 ± 0.29 %ABc	2.14 ± 0.05 %Bc	0.43 ± 0.21 %Ab	0.05 ± 0.05 %Ac	0.45 ± 0.06 %Ab	95.28 ± 0.41 %Aa
	D1	0.88 ± 0.14 %Ac	2.82 ± 0.07 %Aa	0.60 ± 0.07 %Ab	2.07 ± 0.33 %Aa	0.44 ± 0.12 %Bc	94.09 ± 0.17 %Cab
	D3	1.42 ± 0.11 %Aab	2.53 ± 0.18 %Cb	0.43 ± 0.10 %Ab	0.39 ± 0.01 %Ad	1.05 ± 0.12 %Ba	94.19 ± 0.38 %ABb
1.0 %	D7	1.27 ± 0.02 %ABab	2.60 ± 0.06 %Aab	0.63 ± 0.19 %ABb	1.12 ± 0.17 %Ab	0.55 ± 0.30 %Ab	93.83 ± 0.05 %Aab
	D14	1.43 ± 0.13 %Aa	2.63 ± 0.19 %Ab	0.41 ± 0.10 %Ab	0.32 ± 0.07 %Bd	0.80 ± 0.10 %Aab	94.41 ± 0.10 %Aab
	D30	1.12 ± 0.06 %Ab	1.63 ± 0.14 %ABd	1.25 ± 0.18 %Ba	0.90 ± 0.10 %Abc	0.61 ± 0.13 %Ab	94.48 ± 0.16 %Aab
	D0	0.93 ± 0.19 %Ab	2.64 ± 0.14 %Aa	0.34 ± 0.14 %Ab	0.81 ± 0.11 %Ab	0.89 ± 0.58 %Ab	94.39 ± 0.29 %Aab
	D1	0.71 ± 0.02 %ABb	2.73 ± 0.10 %Ba	0.35 ± 0.09 %Bb	1.33 ± 0.15 %Ba	0.10 ± 0.08 %Bc	94.85 ± 0.09 %Ba
1.0 %	D3	0.84 ± 0.07 %Bb	2.67 ± 0.07 %ABa	0.19 ± 0.14 %Ab	0.40 ± 0.05 %Ac	1.18 ± 0.19 %ABa	94.80 ± 0.47 %Aa
	D7	1.44 ± 0.17 %ABa	2.60 ± 0.05 %Aa	0.46 ± 0.06 %Bb	1.20 ± 0.10 %Aa	0.50 ± 0.14 %Ab	93.80 ± 0.12 %Ab
	D14	1.48 ± 0.14 %Aa	2.70 ± 0.07 %Aa	0.48 ± 0.15 %Ab	0.67 ± 0.13 %Ab	0.55 ± 0.03 %Bb	94.12 ± 0.22 %Ab
	D30	0.77 ± 0.11 %Ab	1.78 ± 0.05 %Ab	2.07 ± 0.34 %Aa	0.83 ± 0.08 %Ab	0.50 ± 0.09 %Ab	94.04 ± 0.38 %Ab

## 4. Discussion

### 4.1. Degradation kinetics of CPF in MPs-contaminated soil

CPF is widely used in farming systems, and great attention being paid to its environmental risks and food safety risks (Ju et al., 2024). It has been reported that CPF degradation in soils mainly depends on soil microbial degradation, which is strongly affected by soil type and co-existing pollutants (Farhan et al., 2021b; Ju et al., 2023a, 2023b). Sun et al. (2012) reported that the *DT*<sub>50</sub> of CPF significantly differs among soil types, ranging from 14.7 to 19.4 d, while Mali et al., (2022) showed that the *DT*<sub>50</sub> of CPF in anaerobic soils was 15 and 58 d in loam and clay soil, respectively. Furthermore, Singh et al., (2003) reported that the *DT*<sub>50</sub> of CPF was 256 d in soils with pH 4.7 and 58 d in soils with pH 5.7. Wang et al. (2013) reported that it varied from 16 to 33

d depending on soil moisture. In this present study, we found that the degradation of CPF in PLA-contaminated soil fit to the first-order exponential decay curve, with *DT*<sub>50</sub> of 11.0–14.8 d (Table 1). This implies that we have found degradation rates much faster than reported by the other studies discussed above. These differences likely result from differing experimental conditions and design (Weber et al., 2010; Nawaz et al., 2011; Elshikh et al., 2022). In addition, Ju et al., (2023) a) indicated that the presence of microplastics inhibited CPF degradation leading to longer degradation days, especially in the presence of biodegradable microplastics (85 % poly (butylene adipate co-terephthalate) + 10 % PLA). Our results show that with PLA-MPs addition, *DT*<sub>50</sub> of CPF was significantly higher than that in control, which is in line with the findings as Ju et al., (2023a). TCP has been found to be a major metabolite of CPF biodegradation (Li et al., 2010). In this study, with the degradation of parent compound CPF, the residues of

**Table 2c**  
Percentage of soil P fractions in treatments with pesticide application (12 mg kg<sup>-1</sup> of CPF).

MPs	Days	H <sub>2</sub> O	NaHCO <sub>3</sub> -Pi	NaHCO <sub>3</sub> -Po	NaOH-Pi	NaOH-Po	Occluded-P
0.0 %	D0	0.49 ± 0.14 %Ac	2.26 ± 0.19 %Bb	0.24 ± 0.06 %Bc	0.77 ± 0.08 %Ab	0.51 ± 0.01 %Abc	95.85 ± 0.29 %Aa
	D1	0.85 ± 0.07 %ABb	2.61 ± 0.05 %Aab	0.36 ± 0.04 %Abc	0.93 ± 0.08 %Aa	0.54 ± 0.04 %Abc	94.71 ± 0.24 %Aab
	D3	1.23 ± 0.19 %Aa	2.61 ± 0.09 %ABab	0.74 ± 0.40 %Ab	0.36 ± 0.05 %Ac	1.18 ± 0.14 %Aa	93.87 ± 0.72 %Ab
	D7	1.25 ± 0.21 %Aa	2.34 ± 0.24 %Bb	1.36 ± 0.07 %Aa	0.42 ± 0.06 %Cc	0.97 ± 0.20Aa	93.66 ± 0.14 %Ab
	D14	1.15 ± 0.14 %Bab	2.67 ± 0.09 %Aa	0.23 ± 0.04 %Ac	0.34 ± 0.07 %Bc	0.73 ± 0.05 %Bb	94.88 ± 0.15 %Aab
	D30	0.51 ± 0.13 %Bc	1.51 ± 0.12 %Ab	1.58 ± 0.06 %Aa	0.72 ± 0.05 %Ab	0.47 ± 0.03 %Ac	95.21 ± 0.21 %Aa
0.1 %	D0	0.99 ± 0.38 %Abc	2.78 ± 0.09 %Aa	0.41 ± 0.19 %ABb	0.90 ± 0.03 %Aab	0.42 ± 0.06 %Ad	94.50 ± 0.46 %Aa
	D1	0.60 ± 0.05 %BCd	2.66 ± 0.09 %Aa	0.42 ± 0.14 %Ab	1.02 ± 0.08 %Aa	0.49 ± 0.15 %Acd	94.81 ± 0.10 %Aa
	D3	1.30 ± 0.03 %Aab	2.57 ± 0.09 %Ba	0.73 ± 0.09 %Ab	0.39 ± 0.04 %Ad	1.31 ± 0.07 %Aa	93.69 ± 0.08 %Aa
	D7	1.59 ± 0.22 %Aa	2.61 ± 0.09 %ABa	0.50 ± 0.17 %BCb	0.64 ± 0.07 %Bc	0.57 ± 0.10 %Bcd	94.08 ± 0.37 %Aa
	D14	1.58 ± 0.19 %Aa	2.71 ± 0.36 %Aa	0.37 ± 0.16 %Ab	0.35 ± 0.05 %Bd	0.87 ± 0.06 %Ab	94.12 ± 0.43 %Aa
	D30	0.90 ± 0.11 %Abc	1.88 ± 0.20 %Ab	1.53 ± 0.29 %Aa	0.92 ± 0.09 %Ab	0.64 ± 0.08 %Ac	94.13 ± 0.46 %Aa
0.5 %	D0	1.07 ± 0.19 %Ac	2.51 ± 0.21 %ABa	0.44 ± 0.05 %Ab	0.77 ± 0.06 %Ac	0.61 ± 0.17 %Ab	94.61 ± 0.44 %Aa
	D1	1.11 ± 0.16 %Abc	2.61 ± 0.33 %Aa	0.18 ± 0.13 %Ab	1.00 ± 0.08 %Aab	0.43 ± 0.14 %Ab	94.67 ± 0.19 %Aa
	D3	0.67 ± 0.09 %Bd	2.82 ± 0.24 %ABa	0.44 ± 0.08 %Ab	0.40 ± 0.09 %Ad	1.14 ± 0.12 %Aa	94.53 ± 0.45 %Aa
	D7	1.47 ± 0.04 %Aa	2.94 ± 0.10 %Aa	0.34 ± 0.10 %Cb	1.15 ± 0.04 %Aa	0.41 ± 0.13 %Bb	93.69 ± 0.16 %Ab
	D14	1.35 ± 0.14 %ABab	2.64 ± 0.15 %Aa	0.38 ± 0.04 %Ab	0.42 ± 0.05 %Bd	0.65 ± 0.07 %Bb	94.56 ± 0.23 %Aa
	D30	0.78 ± 0.07 %Ad	1.81 ± 0.09 %Ab	1.25 ± 0.10 %ABa	0.96 ± 0.04 %Ab	0.48 ± 0.06 %ABb	94.73 ± 0.09 %Aa
1.0 %	D0	0.83 ± 0.17 %Ab	2.49 ± 0.11 %Bc	0.31 ± 0.11 %ABb	0.97 ± 0.19 %Aa	0.65 ± 0.25 %Ab	94.75 ± 0.13 %Aab
	D1	0.58 ± 0.16 %Cb	2.86 ± 0.08 %Aa	0.26 ± 0.10 %Ab	1.08 ± 0.16 %Aa	0.54 ± 0.33 %Ab	94.78 ± 0.25 %Aab
	D3	0.84 ± 0.21 %Bb	2.80 ± 0.13 %Aab	0.23 ± 0.11 %Ab	0.43 ± 0.05 %Ac	1.07 ± 0.06 %Aa	94.63 ± 0.22 %Aab
	D7	1.34 ± 0.12 %Aa	2.67 ± 0.09 %ABabc	0.96 ± 0.39 %ABa	1.20 ± 0.06 %Aa	0.58 ± 0.04 %Bb	93.25 ± 0.50 %Ac
	D14	1.42 ± 0.05 %ABa	2.63 ± 0.12 %Abc	0.48 ± 0.12 %Ab	0.59 ± 0.08 %Abc	0.63 ± 0.04 %Bb	94.25 ± 0.12 %Ab
	D30	0.80 ± 0.13 %Ab	1.90 ± 0.02 %Ad	0.98 ± 0.05 %Bb	0.90 ± 0.21 %Aab	0.37 ± 0.13 %Bb	95.05 ± 0.22 %Aa

Note: the data is presented as mean ± SD (n=3); different lowercase letters indicate significant differences among different sampling days in the same level of PLA-MPs addition and CPF application ( $p < 0.05$ ); different capital letters indicate significant differences among different PLA-MPs addition levels at the same sampling day and CPF application ( $p < 0.05$ ). The first column in the tables represents different MPs gradient treatments; the second column in the tables represents the incubation time; columns 3 through 8 in the tables represent the different soil P fractions.

TCP increased quickly and peaked at D7/D14 (Fig. 1). After reaching the peak, TCP residues slowly decreased with the observation time, and converging towards similar levels among treatments by D30, in agreement with the findings of Sardar and Kole, (2005). However, Vidal and Báez, (2023) found that TCP residues increased with the degradation of CPF but leveled off after 17 d. This is perhaps because the previous study conducted their experiment with a duration of 17 days, so the generation rate of TCP was faster than or equal to the degradation rate of TCP. But it is worth attention that our study only conducted within 30 days with 6 observation data. In this case, it is hardly to know the peak between D7 and D14, leading to difficulties to estimate degradation of TCP in this study. Furthermore, our results showed that CPF levels did not significantly affect TCP generation, but the peak levels differed with PLA-MPs addition. At the end of the experiment (D30), TCP residues were still positively detected in soil samples, but with 30 % lower concentrations than at its peak level (D7/D14). TCP is a moderately mobile and persistent compound in soils, and is ecotoxic with a high antimicrobial activity (Jaiswal et al., 2017). Therefore, it is necessary to pay attention to the environmental risks of TCP (Barkoski et al., 2018).

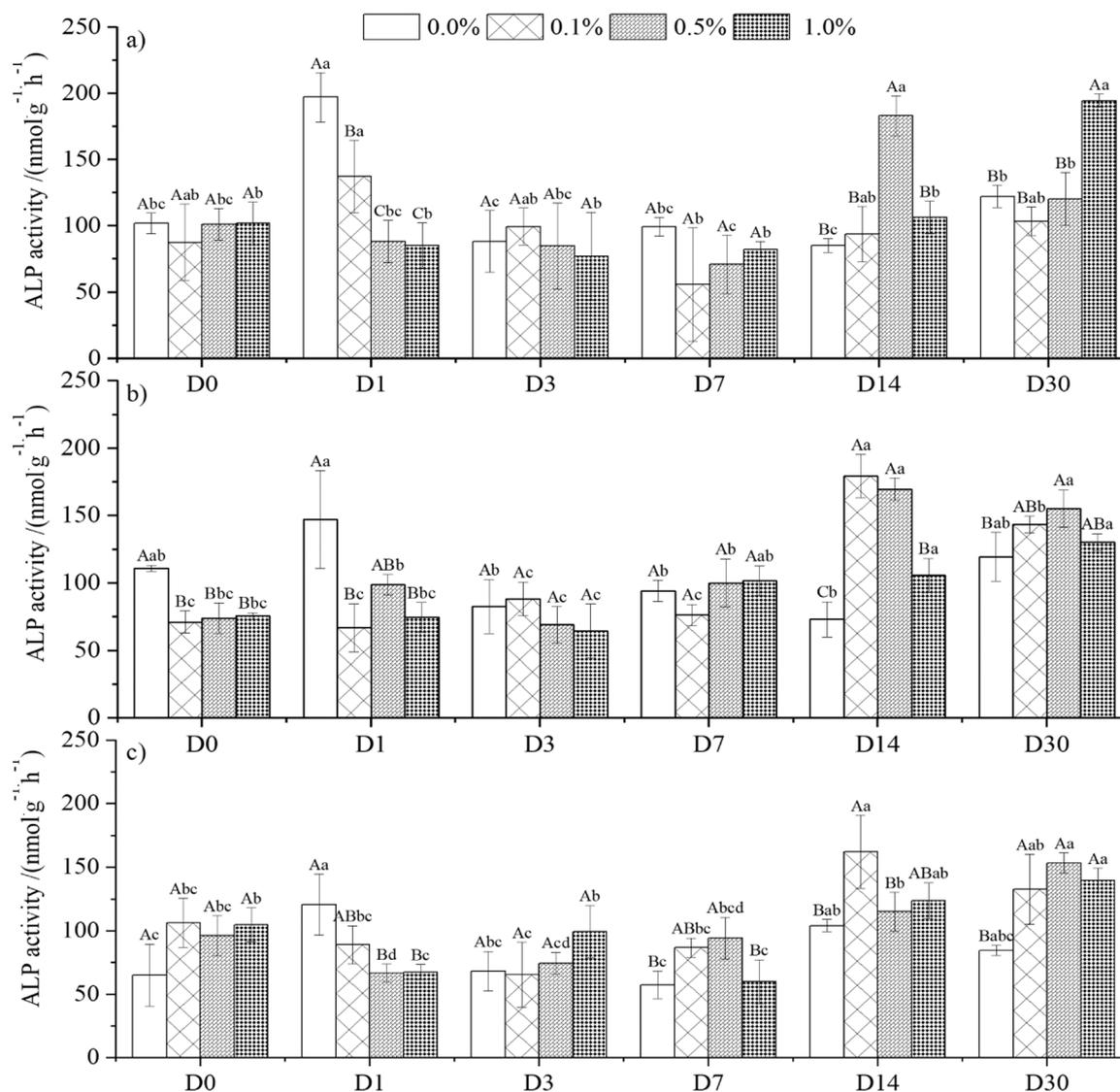
Interestingly, in this study, only 1.0 % PLA-MPs treatment significantly inhibited the degradation rate of CPF (6 mg kg<sup>-1</sup>). This result agrees with a previous study conducted by Ju et al. (2023a). The inhibition by PLA-MPs of CPF degradation may be due to the adsorption of CPF onto the surface of MPs, which reduces the bioavailability of CPF to soil microorganisms (Beriot et al., 2020; Zhang et al., 2023). Ju et al. (2024) found that biodegradable MPs significantly inhibited the degradation of CPF, compared to the low-density polyethylene MPs. Note that our study uses biodegradable MPs, which usually has a higher specific surface area, higher porosity, and different chemical properties, possibly leading to even higher adsorption capacities compared to conventional plastics (Gong et al., 2019; Jiang et al., 2020). Therefore, the type, size and concentration of MPs may be important factors that affect the degradation of pesticides (Peña et al., 2023). In addition, as reviewed by Zhang et al. (2021), the presence of MPs in the soil changes the physicochemical properties of the soil, and disturbs the functional and structural diversity of soil microbial communities. If soil microorganisms are affected by MP contamination, and soil enzyme activities

altered, CPF degradation could be strongly affected (Chishti et al., 2013). Therefore, further studies are needed to explore the underlying mechanisms that relate MPs to CPF fate in soils.

#### 4.2. Effects of CPF and MPs on soil P availability

OPPs are chemical compounds containing phosphate molecules (Aissa et al., 2021), with C-P bonds that can be cleaved to phosphate (HPO<sub>4</sub><sup>2-</sup>) by various phosphatase enzymes (Sviridov et al., 2015). It has been reported that the use of OPPs affect the accumulation and cycling of P in the soil (Hébert et al., 2019). Soil Olsen-P is one of the most effective chemical markers for the biodegradation of OPPs (Yu et al., 2011). Our study shows that the degradation of CPF stimulates the Olsen-P content in the soil, in agreement with previous research (Wang et al., 2022b). Furthermore, studies have shown that the use of CPF and its metabolites stimulate the growth and activity of P solubilizing microorganisms, and increase P mineralization, thereby improving the availability of soil P (Arora, Gaur, (1979); Sardar, Kole, (2005). Based on our findings, it seems that CPF and TCP are degraded into inorganic phosphates, which could increase soil available P (Singh et al., 2006).

In this present study, MPs addition and CPF application showed opposite impacts on specific P fractions. The effects of MPs on soil easily labile P fractions (H<sub>2</sub>O) and labile P fractions (NaHCO<sub>3</sub>-Pi and NaHCO<sub>3</sub>-Po) were significant until D14. Afterwards, these fractions were significantly affected by CPF application. The different influence of PLA-MPs and CPF application on the various soil P fractions may be due to the different mode of actions of PLA-MPs and CPF. As we have observed (Table 3), P fractions were mainly affected by PLA-MPs at the early stages of incubation. The addition of PLA-MPs may change the balance of soluble and adsorbed P fractions, as it provides different forms and quantities of P sorption sites (Dong et al., 2021; Ya et al., 2021). Meanwhile, MPs may change soil physicochemical properties, thereby indirectly regulating soil enzyme activities and the various chemical forms of P (Wang et al., 2022a). In the later stages, with the degradation of CPF, bound organic P might be released into the soil as moderately labile P. Provided that all of the bounded-P from CPF and TCP have been released, the mineralization process of soil organic P to soluble inorganic



**Fig. 3.** Soil alkaline phosphatase (ALP) activity in different treatments during the observation days (a: 0 mg kg<sup>-1</sup> of CPF application; b: 6 mg kg<sup>-1</sup> of CPF application; c: 12 mg kg<sup>-1</sup> of CPF application; different lowercase letters indicate significant differences among different sampling days in the same level of PLA-MPs addition and CPF application ( $p < 0.05$ ); different capital letters indicate significant differences among different PLA-MPs addition levels at the same sampling day and CPF application ( $p < 0.05$ ); the error bar represents the SD ( $n=3$ ).

P dominates soil P transformation, thereby increasing P bioavailability. Besides, CPF degradation results in the production of carbon fragments, fatty amines and inorganic phosphates (Singh et al., 2006), thereby promoting the transformation of insoluble P fractions to active P fractions ( $H_2O-P+NaHCO_3-P+NaOH-P$ ). These active P forms can be easily absorbed and used by crops, thus improving soil fertility and promoting plant growth (Elhaisoufi et al., 2022).

Soil phosphatase plays a key role in promoting the mineralization of soil organic P (Liu et al., 2023). Previous studies have showed that glyphosate application inhibited ALP compared with control treatments, but MPs addition (7%/28%) significantly increased ALP, especially in treatments with high level of MPs (Yang et al., 2018). In contrast, in this study ALP activity did not change significantly at the early stages of CPF application, but increased significantly at D14 and D30 with PLA-MP addition, which could transform the released moderately labile P into labile and very labile P. Yun et al. (2010) reported that CPF application did not affect soil ALP activity at the early stages, but eventually increased ALP activity after 60 d incubation. However, Jastrzębska (2011) found that the application of CPF had an inhibitory effect on soil ALP activity which, in turn, might slow down CPF degradation.

However, after the microbial community develops a tolerance to CPF and an increased ability for co-metabolism of soil microbes, microbial populations and soil enzyme activities increase (Franco-Andreu et al., 2016; Kumar et al., 2022), facilitating P mineralization and P bioavailability in soil. Although the increase in soil P availability was relatively short-time in our study, the increase in P bioavailability will greatly promote plant uptake P, especially when plants are in a rapid growth period and require large amounts of P. Meanwhile, this transient increase of AP implies that CPF contributes to soil P releasing and may increase P utilization (Yadav et al., 2012). Besides, the presence of vegetation affect the behavior of CPF and MPs, especially those contaminants co-existing in soil-plant environment. Our resent study showed that plants were uptake CPF in MPs contaminated soil (Ju et al., 2024), thereby the behavior of CPF degradation might differ than its in soil without plant. In light of the importance of P in soil and OPPs application, further studies are needed to explore the effects of CPF on the P balance, especially in soils with plants and other coexisting environmental stressors.

**Table 3**

Results of two-way ANOVA on the effects of CPF, PLA-MPs and their interactions on the soil P fractions.

P fractions	Factors	F value					
		D0	D1	D3	D7	D14	D30
H <sub>2</sub> O-P	CPF	0.02	0.36	1.43	0.72	1.49	3.41*
	PLA-MPs	1.54	3.45*	14.98***	1.40	6.48**	2.51
	CPF×PLA-MPs	2.37	5.91***	6.67***	2.48	0.78	1.91
NaHCO <sub>3</sub> -Pi	CPF	2.70	1.18	1.20	2.17	0.17	2.52
	PLA-MPs	8.28***	1.23	0.97	8.64***	0.44	8.39***
	CPF×PLA-MPs	4.09**	0.93	2.70*	2.82*	0.33	1.19
NaHCO <sub>3</sub> -Po	CPF	0.09	2.10	0.05	1.05	0.44	6.55**
	PLA-MPs	2.53	0.13	7.20***	4.77**	3.59*	2.57
	CPF×PLA-MPs	0.69	3.21*	0.52	2.67*	0.98	5.88***
NaOH-Pi	CPF	1.55	10.43***	3.29	0.22	0.99	3.74*
	PLA-MPs	7.12***	24.21***	4.93**	65.65***	15.63***	3.81*
	CPF×PLA-MPs	2.24	7.24***	3.71**	2.21	1.38	1.60
NaOH-Po	CPF	0.08	0.41	3.67*	4.14*	2.80	2.02
	PLA-MPs	2.55	3.21*	3.42*	10.23***	9.23***	2.78
	CPF×PLA-MPs	1.06	1.51	3.37*	0.97	3.93**	0.24
Occluded-P	CPF	1.73	0.27	0.15	1.29	2.80	3.99**
	PLA-MPs	6.45**	4.64*	12.55***	1.85	9.23***	2.52
	CPF×PLA-MPs	3.76**	3.76**	1.43	0.71	3.93**	2.37

Note: the F value with an asterisk represents statistical significance (\*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$ ).

## 5. Conclusion

This study investigated the degradation kinetics of CPF in soil contaminated with different concentrations of PLA-MPs, and the subsequent impacts on soil P bioavailability. Results show that the half-life of CPF ranged from 11.0 to 14.8 d, and that PLA-MPs inhibited the degradation rate of CPF only when the PLA-MP addition level was relatively high and CPF application level was low. The dynamic changes to soil available P fractions were similar to that of the TCP content, which first increased during the first 3–7 d of incubation, and then decreased to a level similar to the initial condition by the end of incubation. Statistical analyses show that the soil P composition was mainly affected by PLA-MPs at early periods, whereas effects at later stages were mainly due to CPF. These findings imply that the degradation of CPF leads to a transient increase in P bioavailability in MPs-contaminated soils. Therefore, further research focusing on P response (transformation, utilization and balance) to organophosphorus pesticide application in MPs contaminated soil is urgently needed.

## CRediT authorship contribution statement

**Hui Ju:** Writing – review & editing. **Sha Xue:** Writing – review & editing, Resources. **Darrell W.S. Tang:** Writing – review & editing. **Xiaomei Yang:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Violette Geissen:** Writing – review & editing, Supervision. **Yan Wang:** Writing – review & editing. **Lingling Ding:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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