Sorption, Desorption and Mobility of Microencapsulated Chlorpyrifos in Two Typical Soils

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Abstract
The sorption, desorption, and mobility of microencapsulated chlorpyrifos (CPF-MC) in two typical soils, namely, silt loam and sandy, were investigated in this study. Sorption/desorption experiments were carried out by using the batch equilibration method. Results showed that the sorption isotherms of CPF-MC and emulsifiable concentrate of chlorpyrifos (CPF-EC) in silt loamy soil were similar. However, a considerable difference was observed in the sorption isotherms of two chlorpyrifos (CPF) formulations in sandy soil. The amounts of CPF desorbed from two soils in four desorption steps decreased sequentially in CPF-EC treatments, while the desorbed amounts remained stable in CPF-MC treatments. Hence, the sorption/desorption processes of CPF-EC were mainly controlled by soil affinity to CPF. However, these processes of CPF-MC were affected by the release rate of CPF from capsules. The mobility of two CPF formulations in soil was estimated in vertical columns packed with soils. Results showed that there was leaching of CPF-EC in silt loam column, whereas CPF-MC was not vertically mobile in silt loam column under the same leaching conditions. However, in column with sandy soil, the percentage of CPF-MC leaching from the column was 86.54%, which was higher than the 73.75% that leached from the column in the treatment with CPF-EC.

Microencapsulated technology, which involves entrapping active ingredient inside a hollow polymeric shell, has been applied to commercial pesticide manufacturing for many years (Frederiksen et al. 2002; Chen et al. 2009). Protection with a polymeric shell provides microencapsulated (MC) formulations with many advantages over the other conventional formulations, such as improved availability and decreased application dosage and toxicity to operators (Dailey and Dowler 1998; Alonso et al. 2014). Since the first product, parathion-methyl MC, was developed by Pennwalt Company in 1974, hundreds of MC pesticides have been applied in agriculture (Hua 2010; Hack et al. 2012).

By using MC, the environmental behaviors of pesticide are altered because of the shaping and entrapping by the polymeric shell (González-Pradas et al. 1999; Fernández-Pérez et al. 2000). Chen et al. (2014) found that the degradation curve of microencapsulated chlorpyrifos (CPF-MC) in soil does not follow the first-order kinetics model, and it differs from the degradation kinetics of the emulsifiable concentrate (EC) of CPF. Montemurro et al. (2002) found that the residue levels of CPF in MC treatments were almost constant to 65 days and then began to decrease. Another study by González-Pradas et al. (1999) showed that entrapping imidacloprid with alginate produced less vertical mobility of the active ingredient than the technical product. In the technical-grade product treatment, the total amount of imidacloprid leached from columns packed with soil was 82.3% of that applied, but the leached percentage was 44.7% in encapsulated formulation treatment. Similar results were obtained in the soil mobility test of alginate-based formulation and technical-grade isoproturon (Fernández-Pérez et al. 2000).

As an effective organophosphorous insecticide, CPF (O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl)phosphorothionate) is still widely used to control agricultural pests. MC was recently developed as an important formulation for CPF to improve the usage efficiency and reduce environmental pollution (Frederiksen et al. 2002; Zhu et al. 2010). Many studies on CPF-MC have been conducted in the past years, mostly on the product development and
efficacy evaluation, but few of them focused on the environmental risk assessment (Frederiksen et al. 2002; Montemurro et al. 2002; Llácer et al. 2010; Zhu et al. 2010; Guo et al. 2011).

Sorption/desorption and mobility are the key processes that regulate the distribution of a pesticide in soil and the contamination of this pesticide to soil or water (Welhouse and Bleam 1993; Hegeman et al. 1995; Friedman and Mualem 1999). The relationship between the environmental behaviors of CPF and its side effects on soil and water has been widely studied (Montemurro et al. 2002; Yu et al. 2006; Fang et al. 2009; Chen et al. 2014, 2015). However, there have been few studies of the environmental behavior of the MC formulations of CPF. The use of MC formulation has been encouraged for controlling the underground pests (Richards et al. 2015). Over 80 MC products containing CPF as active ingredient have been registered and applied in fields that vary in soil composition. It is essential to obtain information about environmental behavior of CPF-MC in soil to assess potential hazards to environment, especially for transport to surface waters and groundwater. In the present study, we used two typical types of soils to investigate the sorption/desorption and mobility of the CPF-MC in soils and compared the findings with the treatments with CPF-EC.

Materials and Methods

Chemicals and Soils

The CPF-EC formulation, Dursban 48 was supplied by DOW Chemical Co., USA. CPF-MC (36%, m/m) with urea–formaldehyde resins as capsule material was prepared in our laboratory using the process of in-situ polymerization. The properties of CPF microcapsules were measured under wet condition by using a microscope. The average size of microcapsules was 8 µm, and the microcapsules have smooth surface and spherical shape. Certified analytical standard CPF (99.5%) was supplied by Shanghai Pesticide Research Institute, China.

Two types of soils were used in this study. One was collected from farmland surface (0–20 cm in depth) in Zhejiang Academy of Agricultural Sciences, Hangzhou, China and labeled as “S-1”, while the other one was obtained from the market and labeled as “S-2”. Two soils were air dried and sieved with 2-mm sieve, and then characterized using standard protocols (Yu 1979). Based on the soil characteristics, S-1 and S-2 were classified as silt loam and sandy soil, respectively. Physical and chemical characteristics of the two soils are listed in Table 1.

| Physical and chemical characters | S-1 | S-2 |
|---------------------------------|-----|-----|
| Sand (%)                        | 20.8| 98.8|
| Silt (%)                        | 74.3| 0.2 |
| Clay (%)                        | 8.0 | –   |
| Organic matter (%)              | 3.23| 0.4 |
| Cationic exchange capacity (cmol/kg) | 9.6 | –   |
| Total nitrogen (%)              | 0.18| –   |
| pH                              | 6.8 | 7.1 |
| Soil type                       | Silt loam | Sand |

Sorption/Desorption Studies

Sorption and desorption studies were carried out using the standard batch equilibration method (US EPA 1998). Serial dilutions of EC and MC formulations containing initial CPF concentrations (C₀) between 2 and 29 mg/L were prepared using 0.01 mol/L CaCl₂ aqueous solution. Then, 25 mL of each dilution was added to 3 g S-1/S-2. The soil-aqueous suspensions were transferred into 50-mL polypropylene centrifuge tubes and sealed with screw caps. Suspensions were centrifuged (10 min, 9000×g, 25 °C) after being agitated on a shaker for 24 h at 25 ± 1 °C to achieve equilibrium. The supernatants were transferred into 250-mL separatory funnels and extracted three times with petroleum ether (50 mL for each time). After dehydration with anhydrous sodium sulfate, the combined extracts were concentrated to near dryness and then re-dissolved with 10 mL of acetonitrile. All trials were conducted in triplicate. The same processes without CPF served as the control. The amount of CPF adsorbed by the soil was calculated based on the difference in CPF concentrations between the initial and equilibrium solutions.

Three treatments with initial CPF concentrations of 11, 17, and 23 mg/L were immediately used in the desorption experiments. After removing the supernatants, 25 mL of 0.01 mol/L CaCl₂ aqueous solution was added into each tube. The centrifuge tubes were agitated to disperse the soil chunks. Then, the processes of centrifugation, extraction, concentration, and re-dissolution were conducted as described in sorption experiment. Each sample was desorbed by 25 mL of 0.01 mol/L CaCl₂ aqueous solution for four times.

Mobility Studies

Mobility studies of two CPF formulations in soil were carried out in accordance with the Organization for Economic Co-operation and Development (OECD) guidelines.
Glass leaching columns with inner diameter of 4 cm and 40 cm in height were used. The columns were packed with 30 cm-deep untreated S1/S2, then the soils were saturated with 0.01 mol/L CaCl₂ aqueous solution and then mixed with 1 g of untreated soil thoroughly. The mixtures were scattered evenly over the surface of the soil columns and covered by a round filter paper. A total volume of 1.2 L 0.01 mol/L CaCl₂ aqueous solution was added to each soil column dropwise at a rate of 8 mL/h through a dropping funnel and every 150 mL of eluent was collected. After leaching and leaving the column to drain for 48 h, each soil column was sectioned into five segments. All soil segments were air dried in low light to a constant weight. Each trial was replicated three times.

Air-dried soil samples were transferred into Erlenmeyer flasks containing 50 mL of acetone-petroleum ether (1:1, V/V). The flask was successively agitated on a reciprocating shaker at 25 ± 2 °C for 2 h and then sonicated in an ultrasonic bath for 5 min. After a successive procedure of filtration, washing with 3% sodium sulfate, dehydration with anhydrous sodium sulfate, concentrating on a rotary evaporator and dissolution by 10.0 mL acetonitrile, the extracts were prepared and ready for gas chromatography (GC) analysis.

**GC Analysis**

CPF concentration was determined on Shimadzu GC-2010 (Shimadzu Corp., Japan) equipped with a Ni⁶³ electron capture detector and fused silica capillary column (HP-5, Supelco, USA, 30-m length, 0.32-mm internal diameter, and 0.33-µm film thickness). The operating conditions were as follows: injector port temperature, 280 °C; detector temperature, 300 °C; column temperature, 240 °C; carrier gas (N₂) flow rate, 50 mL/min; injection volume, 2 µL. The peak area was used to calculate the concentration of CPF. CPF-certified standard was used for external calibration.

**Statistical Analysis**

The data were presented as means ± standard errors (n = 3). The figures were generated using Microsoft Excel (Microsoft, USA). Data were statistically analyzed with the SPSS for Windows software (V13, IBM, USA). Differences in sample concentrations, sorption amounts, desorption amounts, distribution in soils were analyzed for significance by a one-way analysis of variance (ANOVA) at the level of P < 0.05.
a concentration sufficient to be effective for the control of insect pests. Therefore, the rate of controlled release, the soil characteristics, and effective concentration of a pesticide on the target organism should be considered when verifying the recommended dosage of an MC pesticide. Otherwise, it may not be possible to achieve the desired level of pest control and only increase the risk of the pest developing resistance to the pesticide.

A significant difference was found between the adsorption isotherms of CPF-MC and CPF-EC in S-2 (Fig. 1). The maximum adsorption amount was not reached with the CPF concentration range of 2–29 mg/L for CPF-MC. As shown in Fig. 1, the CPF amounts released from the MC to the aqueous phase did not reach the level of saturation for the adsorption of CPF by S-2; therefore, the adsorption isotherms of CPF-MC by S-2 were of linear type. It should be noted that the calculated adsorption amount of CPF was not the actual amount of adsorption by the soil but the total amount of CPF in the capsules and adsorbed in the soil.

After the adsorption experiment, three treatments \( C_0 = 11, 17, 23 \) mg/L were carried out for the desorption experiment immediately. The desorption amount of CPF from S-1 in EC treatment was positively correlated with \( C_0 \), and the desorption amount decreased successively with desorption time (Fig. 2A). Hence, hysteresis exists in the adsorption/desorption of CPF by S-1, thus confirming previous results (Laabs and Amelung 2005). Yu et al. (2006) also found the desorption constant \( K_{df} \) is greater than the adsorption constant \( K_{af} \) for CPF. The desorption of the MC formulation in S-1, however, differed from that of the EC formulation (Fig. 2C). The CPF in the capsules was released rapidly into the water at the beginning of the desorption test because of the large concentration difference inside and outside of the capsules (Frederiksen et al. 2002; Elbahri and Taverdet 2005). Then, the released CPF was absorbed by the soil. Considering the strong affinity of the soil for CPF, the release-adsorption–desorption could not reach equilibrium within 24 h. Thus, the desorption amounts determined during the test reflected the overall CPF flux that occurred through the processes of releasing from the microcapsules, adsorption to soil and subsequent desorption. Previous study showed that release rate of CPF from the capsules in mineral salt solution was also affected by the change in inner capsule vapor pressure, the microcystic swelling after external moisture invasion, and the ion exchange inside and outside the capsules (Fan and Singh 1989). In addition, some MCs may be ruptured with friction between the soil and capsules during agitation. Thus, the determined desorption amounts of four repeats were not stable. Desorption results indicated that the MC formulation had an excellent controlled-release property. CPF-MC could normally extend the effective period of control on pests compared with traditional formulations (Chen et al. 2015). The unextractable amount (bound residue) or bioavailability of pesticides is affected

![Fig. 2 Desorption amounts of CPF from soils (n=3). A: CPF-EC from S-1; B: CPF-MC from S-1; C: CPF-EC from S-2; and D: CPF-MC from S-2.](image-url)
by the residence time or “aging” of residue in soil (Gevao et al. 2000). The desorption amounts of CPF from the soil in the four cycles under EC treatment decreased successively, indicating that the bound residue of CPF in the soil increased with time. In contrast, the “aging” process of CPF in soil might be slowed down by microencapsulation because CPF was separated from the soil by the capsule wall.

The desorption processes of the two CPF formulations in S-2 are shown in Fig. 2B and Fig. 2D, respectively. The desorption amounts of the three treatments \( (C_0 = 23, 17, 11 \text{ mg/L}) \) of the EC formulation in the first and second cycles were higher than those of the third and fourth cycles, especially in the high-concentration treatments. At the early stage of the test, CPF was desorbed from S-2 to the aqueous phase rapidly because of the concentration difference between solid and water. Thereafter, the desorption was stable because of the low affinity of S-2 for CPF. The desorption amount in CPF-MC treatment reflected the released amount of CPF from the MC to the aqueous phase. The concentration of CPF in-capsule was considerably higher than that of out-capsule. Thus, the released amounts in each cycle were stable.

S-1 and S-2 are two typical soils in which CPF-MC may be used in agricultural application. Hence, the balance of release rate and sorption/desorption should be considered when an MC product is developed and applied in field. Otherwise, the MC product may decrease the effectiveness for control of the target pest and may result in more persistent contamination of the soil.

**Leaching Behavior in Soils of Two CPF Formulations**

The leaching behaviors of the two CPF formulations in the two soil samples were estimated by conventional breakthrough experiments in vertical columns. As shown in Fig. 3A, both CPF formulations were immobile in S-1. In the EC treatment, CPF was not detected in the leachate until the artificial rainfall volume reached 600 mL. An average of 0.051 mg CPF was eventually eluted out of the column, which was about 5% of the total amount added. This result supports the assumption that the immobility of CPF in soil is attributed to the adsorption of the pesticide to the organic material and clay components of the soil (Li et al. 2007; Xue et al. 2017). An average of 0.015 mg CPF (about 1.5% of total added amount) was eventually eluted out of the column in the MC treatment, and this amount is significantly lower than that in the EC treatment. The distributions of CPF in the column after the elution also differed between the two treatments (Fig. 3C). Almost 90% of the initial CPF amount remained in the first segment (0–6 cm) in the MC treatment, whereas about 70% of the initial amount had moved to the second (6–12 cm) and
third (12–18 cm) segments in the EC treatment. Hence, the MC formulation caused less vertical mobility of the CPF compared with EC. Most of the CPF remained encapsulated and the movement of CPF was generally dependent on the mobility of MCs in the soil. Since soil porosity decreases with the increase in organic matter and clay contents, the immobility of MC formulation in soil may be caused by the resistance to the filtration of MCs through the soils, so most of the MCs were ob structed at the top of the column (Fernández-Pérez et al. 2000; González-Prasad et al. 1999; Hack et al. 2012). Friedman and Mualem (1999) also found that filtration was the main obstruction to the mobility of MCs in the soil column. These results suggested that the MC formulation could reduce the runoff of pesticides to surface waters.

Under the same test condition, the CPF in both formulations was mobile in the S-2 column (Figs. 3B and D). Approximately, 0.865 and 0.738 mg of CPF were eventually eluted out of the column in the EC and MC treatments, respectively. Most CPF residues in the columns were also concentrated at the bottom segment of the columns. With lower organic matter and clay content in S-2, the soil porosity increased and the affinity of the soil for CPF decreased. When the speed of water flow was not considered, the mobility of MC in soil was mainly affected by some product texture in terms of shape, size, and qualities of coating surface (Friedman and Mualem 1999). The increase in soil void facilitated the transport of MC in S-2. Hence, if MC formulations are applied in sandy soil, the risks of transport to surface waters should be a priority for assessment.

CPF-MC formulations are now widely applied in China to control soil pests. The results of this study showed that the mobility of MCs in soil is mainly dependent on the soil porosity. In the field, soil contains not only void volumes, but also cracks and fissures and the burrows of soil organisms that could facilitate the passage of MCs through soils. Therefore, although microencapsulated pesticides can increase the efficiency of pests control and reduce environmental contamination, care must be taken when using MC formulations of pesticides in coarse granular soils, and especially in areas close to rivers and reservoirs.

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**Availability of data and material** The raw data are stored in a data repository at the Zhejiang Academy of Agricultural Sciences and can be made available upon request to the author (zwsclz@163.com).

**Declarations**

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical Approval** Not applicable.

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