Dissipation Kinetics of Chlorpyrifos in Soils of a Vegetable Cropping System under Different Cultivation Conditions

Tengfei Liu¹, Daifeng Yang¹, Li Zhang², Mao Jian¹, Jun Fan¹

¹Jiangsu Taihu Area Institute of Agricultural Sciences, Suzhou, China
²College of Education and Humanity, Suzhou Vocational University, Suzhou, China

Email: bblutengfei@163.com

Abstract

Dissipation kinetics of chlorpyrifos in the near-neutral paddy soils of a vegetable cropping system under greenhouse, screenhouse and field conditions was studied using a rapid analytical method. The recoveries of chlorpyrifos were between 86.5% and 105.5% with relative standard deviations for repeatability between 6.6% and 9.1% at fortification levels of 0.01, 0.1 and 1 mg/kg in the soil. The limit of detection of the method was 0.004 mg/kg and the limit of quantification was found to be 0.01 mg/kg. The dissipation rates of chlorpyrifos followed the first-order kinetics and the half-life was 6.96, 6.04 and 5.20 days in the soil under greenhouse, screenhouse and field conditions, respectively. The dissipation rates of chlorpyrifos in the soil varied with different cultivation conditions. Chlorpyrifos in the soil dissipated slower in a greenhouse and screenhouse than in the open field, which was likely attributed to the hermetic environment in the greenhouse and screenhouse.

Keywords

Chlorpyrifos, Dissipation, Cultivation Condition, Soil

1. Introduction

Chlorpyrifos is an organophosphate broad spectrum insecticide, acaricide and termiticide, which has been commercially used since the 1960s. It has low solubility in water (0.002 g/L) and moderately high logKow and is preferential to partition from water to soil and plants [1]. Chlorpyrifos is widely used for the control of various soil, crop and household pests [2] [3]. Usually, it affects the
nervous system of the target insects by inhibiting the activity of acetylcholinesterase by phosphorylation, both at the synapse of neurons and in the plasma [4]. In China, an annual chlorpyrifos production of 200,000 t was estimated in 2015 [5]. However, excessive use and large scale synthesis of chlorpyrifos have led to the contamination of terrestrial ecosystems and increased the potential health risk for humans and non-target organisms, such as honeybees, silkworms, and earthworms [6]. It has been reported that exposure to chlorpyrifos may cause birth defects, nervous system disorders and increased rate of leukemia and immune system abnormalities [7] [8] [9] [10] [11]. As a result of these harmful effects, chlorpyrifos has been banned as a residential and field pesticide in many countries. Therefore, the evaluation on environmental behavior and effects of chlorpyrifos has received extensive attention.

In recent years, the dissipation of chlorpyrifos has already been studied in vegetables, rice, corn and tomato crop ecosystems at varied levels of field doses under different edaphoclimatic conditions by adopting unique analytical methods [12] [13] [14]. The dissipation of chlorpyrifos in soil has also been well investigated [15] [16] [17]. The half-life of chlorpyrifos varies from less than 1 to more than 100 days in the soil environment. This large variation in half-life has been attributed to different environmental factors, the most important of which are soil type, soil pH, climate conditions, organic carbon content and pesticide formulation [18]. However, little information is available on the dissipation kinetics of chlorpyrifos in the soils of vegetable cropping system under greenhouse, screenhouse and open field conditions. Therefore, the present work was conducted to study the dissipation kinetics of chlorpyrifos in soils and to compare dissipation behaviors of chlorpyrifos in the soil in a greenhouse, screenhouse and open field by employing a simple, sensitive and rapid analytical method.

2. Methods and Materials

2.1. Chemicals

Chlorpyrifos emulsifiable concentrates at 48% were provided by Jiangsu Kuaida Co., Ltd (Nantong, China). Chlorpyrifos standard (1000 mg/L) was purchased from the Institute of Environmental Protection Monitoring, China Ministry of Agriculture (Tianjin, China). Primary secondary amine (PSA, 40 - 60 μm) and octadecyl silane bonded silica (C18, 40 - 60 μm) were obtained from Agela Technologies, Inc (Tianjin, China) and Sepax technologies, Inc (Delaware, USA). n-hexane (HPLC grade) was purchased from Oceanpak Alexative chemical., Ltd (Gothenburg, Sweden). Analytical grade acetonitrile, acetic acid, anhydrous sodium acetate, anhydrous MgSO4 were procured from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Working standard solutions of chlorpyrifos were prepared by serial dilution with n-hexane and all standard solutions were stored in amber bottles (10 mL) at

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2.2. Experimental Design

The experiment was carried out at an experimental farm, where pakchoi cabbages (*Brassica chinensis* L.) were planted, of Jiangsu Taihu Area Institute of Agricultural Sciences in Suzhou, China during May-June 2015. We performed the experiment under three cultivation conditions (greenhouse, screenhouse and open field) and replicated three times in the separate plots (3 × 5 m, with 1-m buffer area between plots) in each cultivation condition. The greenhouse is constructed of steel frame and covered with polyethylene film and is approximately 8.1 m by 31.0 m in size. The cross section of the greenhouse is shown in Figure 1. The chlorpyrifos residues in the soil of greenhouse, screenhouse and open field were undetected before the experiment. The soil in the plots was clay loam in texture, with soil properties of pH 6.8, organic matter 2.15%, total nitrogen 16.12 g/kg and cationic exchange capacity 11.5 cmol/kg.

We sprayed chlorpyrifos 48% EC once at the dosage of 1152 g a.i/ha (double the highest recommended dosage of the pesticide producer) on each plot and detected chlorpyrifos residue after 0 (2 h after application), 1, 3, 5, 7, 10, 14, 21, 28 and 35 days. Approximately 1 kg of soil was sampled at 8 to 10 points in each plot using a tube auger at a depth of about 10 cm beneath the surface, air dried, sieved through a 0.25-mm mesh, and mixed by stirring. From the mixture, 5.0 g soil was subsampled for the determination of chlorpyrifos. This approach was conducted according to the “Guideline on Pesticide Residue Trials” (NY/T 788-2004) issued by Ministry of Agriculture of the People’s Republic of China [19].

2.3. Weather Conditions

The daily mean maximum/minimum temperature under greenhouse, screenhouse and open field throughout the experiment were 14°C - 49°C, 14°C - 47°C and 15°C - 37°C, respectively. It rained only a little during the experiment period. Average daily temperature, average daily illumination intensity and precipitation during the experiment period are shown in Figures 2-4, respectively.

Figure 1. The cross section of experimental greenhouse.
Figure 2. Average daily temperature during the experiment period.

Figure 3. Average daily illumination intensity during the experiment period.

Figure 4. Daily rainfall during the experiment period.
2.4. Sample Extraction and Cleanup
Chlorpyrifos was extracted from the soil samples and cleaned up according to Jiang’s methods [20] with minor modifications. Briefly, 5.0 g soil samples were weighed into 50 mL centrifuge tubes. Then 10 mL acetic acid-acetonitrile solution (volume ratio, 1:99) and 2 g anhydrous sodium acetate were added into the tube following ultrasonic extraction for 15 min. Next, 2 g anhydrous MgSO₄ was added to the sample tube and vortexed for 2 min. Afterwards, the extract was centrifuged at 9056 g for 4 min at room temperature. An aliquot of 4 mL was transferred from the supernatant to a new clean 10-mL centrifuge tube and cleaned up by dispersive solid phase extraction with 150 mg of C18, 150 mg of PSA and 300 mg of anhydrous MgSO₄. Centrifugation was then carried out as described above. Subsequently, 2 mL of the supernatant were taken and evaporated to dryness at 50˚C. The residues were redissolved in 1 mL of n-hexane and were then filtered through a 0.2-μm membrane.

2.5. Instrumental Determination
Chlorpyrifos contents were determined using an 7890A gas chromatograph with an electron capture detector (GC-ECD) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Nitrogen (purity ≥ 99.999%) was used as carrier gas with a flow rate of 1 mL/min. The injector and ECD temperature were 260˚C and 300˚C, respectively. The oven temperature was programmed as follows: 120˚C (hold 2 min) increased to 280˚C at 20˚C/min and held for 10 min. The injection volume was 1 μL in splitless mode.

2.6. Data Processing and Statistical Analysis
The degradation of chlorpyrifos followed the first-order kinetics equation, and the residue concentrations against time is provided by the general equation, which can be calculated as

\[ C_t = C_0 e^{-kt} \]  

where \( C_t \) is the concentration (mg/kg) at time \( t \) (days) after application, \( C_0 \) is the initial concentration (mg/kg) [21]. The dissipation half-life (\( t_{1/2} \)) was determined from the equation

\[ t_{1/2} = \frac{\ln 2}{k} \]  

which was obtained from Equation (1), where \( k \) is the first-order rate constant (day⁻¹).

All statistically analysis was performed in SPSS20.0 software. The level of statistical significance was defined at \( p < 0.05 \).

3. Results
3.1. Evaluation of Determination Method
A calibration curve was calculated by plotting peak area versus the correspond-
ing concentration (mg/L) of five gradient standard solutions. A good linearity ($y = 103.650x - 2541$) was achieved for the target analyte between 0.005 and 2.00 mg/L with a correlation coefficient of 0.9988. Recoveries of chlorpyrifos at 0.01, 0.1 and 1.0 mg/kg in the soil were determined in five replicates to evaluate the accuracy and precision of the method.

The obtained recoveries are given in Table 1 and ranged from 86.5% to 105.5%. The relative standard deviation (RSD) of the method for repeatability ranged from 6.6% to 9.1%. Both the recoveries and relative standard deviation were within acceptable range [22]. The limit of detection (LOD) and limit of quantification (LOQ) of the method were determined at signal-to-noise ratios of 3:1 and 10:1, respectively, for chlorpyrifos in soil. The LOD and LOQ were 0.004 and 0.01 mg/kg, respectively. Figure 5 and Figure 6 show the gas chromatograms of blank and chlorpyrifos fortified soil. These data are generally considered to be satisfactory for chlorpyrifos residue analysis.

Table 1. Recoveries and relative standard deviations of chlorpyrifos from spiked soil ($n = 5$).

<table>
<thead>
<tr>
<th>Sample Matrix</th>
<th>Sample Weight (g)</th>
<th>Fortified Level (mg/kg)</th>
<th>Average Recovery (%)</th>
<th>RSD(1) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>soil</td>
<td>5.0</td>
<td>0.1</td>
<td>96.3</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>86.5</td>
<td>8.8</td>
</tr>
</tbody>
</table>

(1) RSD = relative standard deviation.
3.2. Dissipation of Chlorpyrifos in Soil

The dissipation trends of chlorpyrifos in the soil are shown in Table 2. The residue amount of chlorpyrifos diminished rapidly at first and slowly at a later stage. The initial deposits of chlorpyrifos in the soil 2 h after application were 0.830, 0.866 and 0.474 mg/kg under greenhouse, screenhouse and open field conditions, respectively. This high difference in initial deposits might be caused by environmental differences such as temperature, rainfall and solar radiation in the three cultivation types. The dissipation rate of chlorpyrifos increased with the increase of temperature and solar radiation [23] [24]. In the present study, the temperatures inside greenhouse and screenhouse are frequently higher than in open field (Figure 2). The higher temperature would accelerate evaporation and thermodegradation of chlorpyrifos. However, the hermetic environment in greenhouse and screenhouse may reduce the loss of chlorpyrifos by evaporation. The enhancement in dissipation of chlorpyrifos should, therefore, be very limited. On the other hand, the greenhouse cover and screenhouse net could decrease the effect of solar radiation on degradation of chlorpyrifos. The reduced solar radiations were significantly responsible for the decrease in dissipation of chlorpyrifos [25]. In general, the initial deposits in the soil were significantly different under the three cultivation conditions.

More than 50% of chlorpyrifos was degraded in the samples by 5 days after application for all three cultivation conditions. By 21 days after application, chlorpyrifos was dissipated by 90.5% in a greenhouse, 92.7% in a screenhouse

Table 2. Dissipation of chlorpyrifos residues in soil under different cultivation conditions.

<table>
<thead>
<tr>
<th>Days After Application</th>
<th>Greenhouse (mg/kg)</th>
<th>Dissipation (%)</th>
<th>Screenhouse (mg/kg)</th>
<th>Dissipation (%)</th>
<th>Open Field (mg/kg)</th>
<th>Dissipation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.830 ± 0.004</td>
<td>-</td>
<td>0.866 ± 0.003</td>
<td>-</td>
<td>0.474 ± 0.007</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.549 ± 0.011</td>
<td>33.9</td>
<td>0.568 ± 0.010</td>
<td>34.4</td>
<td>0.273 ± 0.005</td>
<td>42.4</td>
</tr>
<tr>
<td>3</td>
<td>0.491 ± 0.007</td>
<td>40.8</td>
<td>0.431 ± 0.008</td>
<td>50.2</td>
<td>0.231 ± 0.012</td>
<td>51.2</td>
</tr>
<tr>
<td>5</td>
<td>0.411 ± 0.006</td>
<td>50.5</td>
<td>0.349 ± 0.010</td>
<td>59.7</td>
<td>0.209 ± 0.010</td>
<td>56.0</td>
</tr>
<tr>
<td>7</td>
<td>0.333 ± 0.012</td>
<td>59.9</td>
<td>0.235 ± 0.006</td>
<td>72.9</td>
<td>0.195 ± 0.015</td>
<td>58.8</td>
</tr>
<tr>
<td>10</td>
<td>0.278 ± 0.003</td>
<td>66.5</td>
<td>0.171 ± 0.006</td>
<td>80.3</td>
<td>0.132 ± 0.010</td>
<td>72.2</td>
</tr>
<tr>
<td>14</td>
<td>0.170 ± 0.011</td>
<td>79.5</td>
<td>0.131 ± 0.008</td>
<td>84.8</td>
<td>0.091 ± 0.010</td>
<td>80.8</td>
</tr>
<tr>
<td>17</td>
<td>0.109 ± 0.010</td>
<td>86.9</td>
<td>0.102 ± 0.009</td>
<td>88.2</td>
<td>0.045 ± 0.003</td>
<td>90.5</td>
</tr>
<tr>
<td>21</td>
<td>0.079 ± 0.003</td>
<td>90.5</td>
<td>0.063 ± 0.004</td>
<td>92.7</td>
<td>0.018 ± 0.001</td>
<td>96.3</td>
</tr>
<tr>
<td>28</td>
<td>0.048 ± 0.002</td>
<td>94.2</td>
<td>0.026 ± 0.002</td>
<td>97.0</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>BDL</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
<td>BDL</td>
<td>-</td>
</tr>
</tbody>
</table>

(1)Data are mean ± SD of three independent determinations. (2)Below determination limit of 0.01 mg/kg. In a column, residue values followed by a commom letter are not significantly different (P < 0.05) by Duncan’s multiple range test.
and 96.3% in the open field. The residues reached below LOQ of 0.01 mg/kg at 35 days after application irrespective of the cultivation conditions. The dissipation of chlorpyrifos in soil occurred with an initial rapid disappearance on the soil surface which might be due to its high volatilization (vapor pressure, 2.49 mPa at 25˚C), high sorption coefficient (849 mL/g), photolysis and physical loss, followed by a slower decline related to steady microbial and chemical degradation in the soil body [4] [26].

Table 3 demonstrated the dissipation kinetics of chlorpyrifos in the soil under different cultivation conditions by plotting residue concentration versus time after application. The dissipation pattern of chlorpyrifos follows the first-order kinetics with a good fit (Figure 7). The half-lives of chlorpyrifos in the soil during the period under study were 6.96, 6.04 and 5.20 days under greenhouse, screenhouse and open field conditions, respectively. Compared with the open field, the half-life of chlorpyrifos was much longer in a greenhouse and screenhouse.

The dissipation rate of chlorpyrifos under open field conditions was faster than that under greenhouse and screenhouse conditions and the dissipation or-

![Figure 7. Dissipation pattern of chlorpyrifos residues in soil under different cultivation conditions.](image)

**Table 3.** First-order kinetic equations of dynamics of chlorpyrifos in soil under different cultivation conditions.

<table>
<thead>
<tr>
<th>Cultivation Condition</th>
<th>Kinetic Equation</th>
<th>Coefficient (R²)</th>
<th>Rate Constant ( k ) (day⁻¹)</th>
<th>Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenhouse</td>
<td>( C_t = 0.6857e^{-0.0999t} )</td>
<td>0.9860</td>
<td>0.0999¹</td>
<td>6.96³</td>
</tr>
<tr>
<td>Screenhouse</td>
<td>( C_t = 0.6450e^{-0.1147t} )</td>
<td>0.9814</td>
<td>0.1147¹</td>
<td>6.04⁴</td>
</tr>
<tr>
<td>Open field</td>
<td>( C_t = 0.4176e^{-0.1331t} )</td>
<td>0.9455</td>
<td>0.1331¹</td>
<td>5.20⁸</td>
</tr>
</tbody>
</table>

In a column, values followed by a common letter are not significantly different (\( P < 0.05 \)) by Duncan’s multiple range test.
order was as follows: open field > screenhouse > greenhouse. The results demonstrated that the half-life and dissipation of chlorpyrifos were closely related to the cultivation conditions, which agreed with the findings of Fang et al. (2006) who showed that the dissipation of chlorpyrifos in pakchoi-grown soil in a greenhouse was slower than that in a field [27]. It was well documented that the dissipation of chlorpyrifos in soil is closely related to microorganisms and climatic conditions, including temperature, rainfall and solar radiation [28] [29]. In the present study, the greenhouse cover and screenhouse net could decrease the degradation of chlorpyrifos by solar radiation. Furthermore, the greenhouse and screenhouse walls reduced chlorpyrifos loss to the atmosphere via airflow. In addition, the rainfall can also play an important role in the dissipation rate of pesticides. The high rainfall can result in leaching and runoff of pesticides in soil [27]. However, it rained only a little throughout experimental period (Figure 4) and no precipitations occurred during the first week after application of chlorpyrifos. Therefore, precipitation had almost no effect on the dissipation of chlorpyrifos in soil in this study. In general, chlorpyrifos in the soil dissipated slower in a greenhouse and screenhouse than in the open field, which was likely attributed to the hermetic environment in the greenhouse and screenhouse. There was no significant difference in the dissipation rate of chlorpyrifos between greenhouse and screenhouse conditions, probably due to similar temperature and solar radiation (Figure 2 and Figure 3).

4. Conclusion

Our findings provide an insight into the dissipation kinetics of chlorpyrifos in the soil of vegetable cropping system under greenhouse, screenhouse and open field conditions. Acetonitrile (containing 1% acetic acid) was selected as the extraction solvent and PSA and C18 were used as sorbents for removal of matrices. The chlorpyrifos levels within the samples were detected by GC-ECD and no impurities affected the accuracy of this method. The proposed method has been shown to facilitate rapid determination of chlorpyrifos in soils. The LOD and LOQ of the method were 0.004 mg/kg and 0.01 mg/kg, respectively. The half-lives of chlorpyrifos in the soil under greenhouse, screenhouse and open field conditions were 6.96, 6.04 and 5.20 days, respectively. The slower chlorpyrifos dissipation in soil under greenhouse and screenhouse conditions than under field condition was probably due to the hermetic environment in the greenhouse and screenhouse. The slower dissipation of chlorpyrifos in a greenhouse and a screenhouse may result in an accumulation of its residues in soil, which should be further examined in the future to minimize the detrimental effects on succeeding crops and promote the sustainable development of soil.

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