Dissipation of chlorpyrifos in pakchoi-vegetated soil in a greenhouse

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Abstract: The dissipation of chlorpyrifos in pakchoi-vegetated soil was investigated in the summer and autumn in a greenhouse and field, respectively. The dissipation of chlorpyrifos in pakchoi-grown soil was comparatively described by fitting the residue data to seven models (1st-order, 1.5th-order, 2nd-order, RF 1st-order, RF 1.5th-order, RF 2nd-order, and bi-exponential or two-compartment models). Statistical analysis was performed using the SPSS 11.5 statistical package. The bi-exponential model was selected as the optimal model according to the coefficient of determination $r^2$. The dissipation half-lives ($DT_{10}$) of chlorpyrifos in pakchoi-vegetated soil at the recommended dose in the summer and autumn, calculated by the bi-exponential model, were 0.6 and 1.2 d in a greenhouse, 0.4 and 1.0 d in a field, respectively; the corresponding values at double dose were 1.2 and 2.1 d in a greenhouse, 0.5 and 1.3 d in a field, respectively. The kinetic data indicate the dissipation of chlorpyrifos in pakchoi-grown soil in a greenhouse is slower than that in a field, and dissipates slower in the autumn than in the summer.

Keywords: chlorpyrifos; dissipation; greenhouse; kinetic model; soil

Introduction

The warm, humid environment in the greenhouse provides favorable conditions for the development of insect pests and disease causal pathogens. The production of vegetables in greenhouses is associated with specific insect pest control problems that result in excessive application of pesticides. Compared to field conditions, the warm, humid and hermetic environmental conditions of greenhouses alter behaviors of pesticides on vegetables and in soil (Leistra et al., 1984; Cabras et al., 1985; Aguilera-del Real et al., 1997, 1999; Hernández Torres et al., 2002; Yu et al., 2005). A great deal of studies have been carried out on the dissipation of pesticides on vegetable plants in greenhouses (Egea Gonzalez et al., 1998; Martínez Vidal et al., 1998; Castillo-Sánchez et al., 2000; Arrebola Liébanas et al., 2001; Garau et al., 2002; Martínez Galera et al., 2003; Rial-óter et al., 2005).

Chlorpyrifos (o,o-diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) is a broad-spectrum organophosphate insecticide and acaricide widely used for insect pest control on grain, cotton, fruit, nut, and vegetable crops, as well as lawns and ornamental plants in China. Presently, chlorpyrifos is frequently applied in greenhouses for the control of insect pests on vegetables. The dissipation of chlorpyrifos in soil has been well investigated, its dissipation half-life greatly varied from less than 1 to more than 100 d depending on the soil type, soil microbial degradation, climatic conditions, and soil management practices (Wauchope et al., 1991; Redondo et al., 1997; Martínez Vidal et al., 1998; Laabs et al., 2000). However, little is known on soil dissipation of chlorpyrifos in pakchoi-soil system under greenhouse conditions.

In the present study, pakchoi was planted in a greenhouse and field, respectively. Chlorpyrifos was used as foliar spray for the control of insect pests on pakchoi. The dissipation of chlorpyrifos in pakchoi-planted soil was investigated in the summer and autumn, 2004. The objectives of this study were (1) to compare dissipation behaviors of chlorpyrifos in pakchoi-vegetated soil in a greenhouse and field; (2) to compare dissipation behaviors of chlorpyrifos in pakchoi-grown soil in the summer and autumn.

1 Materials and methods

1.1 Chemicals

Technical grade chlorpyrifos (≥99.5% purity) was purchased from the Institute for the Control of Agrochemicals, Ministry of Agriculture, China. Formulated chlorpyrifos (40% EC) was obtained from Xinnong Chemical Co., Zhejiang, China. Acetone and petroleum ether (60—90°) of analytical grade were purchased from Fangting Chemical Co., Zhejiang, China. The organic solvents were redistilled in full glass system before use.

1.2 Soil

The soil, used for recovery test, was collected from the field prior to the first application of chlorpyrifos, and contained no detectable amount of chlorpyrifos residues from previous years. The physico-chemical properties of the soil were determined at the Institute of Environmental Resource and Soil Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou, China and are summarized in Table 1. The soil was classified as loam soil (Soil Physics Lab in Institute of Soil Science, Academia Sinica, Nanjing, 1978).

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Table 1 Properties of the soil matrix

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand, %</td>
<td>21.50</td>
<td>Organic matter, %</td>
<td>3.05</td>
</tr>
<tr>
<td>Silt, %</td>
<td>71.12</td>
<td>Total nitrogen, %</td>
<td>0.14</td>
</tr>
<tr>
<td>Clay, %</td>
<td>7.38</td>
<td>CEC, cmol/kg</td>
<td>10.60</td>
</tr>
<tr>
<td>Soil pH</td>
<td>6.77</td>
<td>Texture</td>
<td>Loam</td>
</tr>
</tbody>
</table>

Note: CEC, cationic exchange capacity

1.3 Field trial

The experiments were conducted on a farm located at Huajiachi Campus, Zhejiang University (Zhejiang, China) in a field (60 m²) and rectangular greenhouse: 90 m² surface, constructed of polyethylene (200 μm thickness), with a flat roof and a lateral window (25 m × 0.5 m) and covered with fine netting. Pakchoi (Brassica chinensis L.) was grown in a greenhouse and field incorporating 4000 and 1600 plants, respectively. Chlorpyrifos (40% EC) was applied in the summer and autumn, 2004 with a knapsack sprayer at the rate of 2500 L/ha at two doses: 0.42 and 0.84 kg of active ingredient per ha, corresponding to the full and double dose, respectively, as recommended on the label for such crops. Triplicates were carried out for each treatment. During the experimental period, climate conditions were monitored and registered by Hangzhou Meteorological Administration, Zhejiang, China.

1.4 Sampling and preparation

Soil samples were taken randomly from a 20-cm depth at 1, 3, 5, 10, 15, and 25 d after application of chlorpyrifos. Soil samples were collected in polyethylene bags and transport to laboratory immediately. After removal of pieces of stones and plants, the soil samples were air-dried at room temperature, homogenized, sieved (2 mm) and stored at -20°C until analysis. Three replicates were performed for each soil sample.

1.5 Weather conditions

Average daily temperature and precipitation throughout the experiments are shown in Figs. 1 and 2, respectively. The daily mean maximum/minimum temperatures outside and inside the greenhouses throughout the study were 29.0—20.1 and 29.7—24.5°C in the summer, 25.6—14.4 and 26.7—17.3°C in the autumn, respectively. The rainfall volume is 26 mm and 32.4 mm in summer and autumn throughout the experiments, respectively.

1.6 Extraction of chlorpyrifos

Soil sample (50 g) was weighed into a 250-ml Erlenmeyer flask, 20 ml of distilled water and 50 ml of acetone were successively added, and then shaken for 2 h at 150 r/min on a rotary shaker. The soil mixture was filtered through Buchner funnel, the filter cake was washed thrice with 25 ml of acetone for each. All filtrates were collected in a 250-ml flat-bottom flask and evaporated on a vacuum rotary evaporator to remove acetone, transferred into a 250-ml separating funnel and extracted thrice with 50 ml of petroleum ether for each. The organic phase was dried through anhydrous sodium sulphate and concentrated to almost dryness with a slight N2 stream, then diluted to 5 ml with redistilled petroleum ether for determination by gas chromatography (GC).

1.7 GC assays

The GC analyses were performed using a GC-9790 gas chromatograph (Fuli Analysis Apparatus Co., China), equipped with a flame photometric detector (FPD). A fused silica capillary column (Pesticide Residue-II, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China) (column length 30 m, column ID 0.32 mm, film thickness 0.25 μm) was employed. Nitrogen (N2) was used as carrier gas at a constant flow rate of 50 ml/min, hydrogen was used at a flow rate of 120 ml/min and air at 80 ml/min. The oven temperature was maintained at 230°C with injector temperature at 240°C and detector temperature at 250°C.

1.8 Recovery study

The recovery study was carried out by spiking chlorpyrifos with 50 g of soil that had not been treated with the insecticide. The validation of the method was assessed at four spiking levels: 0.01, 0.1, 1.0, and 10 mg/kg, respectively. The samples were extracted and analyzed as described above. Three replicate analyses were performed for each spiking level and corre-
sponding blank sample.

2 Results and discussion

2.1 Evaluation of recovery

The average recoveries of chlorpyrifos from pakchoi field soil are presented in Table 2. The recoveries ranged from 92.0% to 105.4% of the spiked amount, with relative standard deviation less than 7.0%. The minimum detection limit was calculated to be 0.005 μg/g of soil. No substrate interferences were observed as evidenced by the control sample analysis. Fig.3 shows gas chromatograms of blank and chlorpyrifos fortified soil. These data indicate that the extraction method is considered to be satisfactory for requirements of chlorpyrifos residues analysis.

<table>
<thead>
<tr>
<th>Table 2 Recovery of chlorpyrifos from spiked soil</th>
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<tbody>
<tr>
<td>Fortification level, mg/kg</td>
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<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>0.10</td>
</tr>
<tr>
<td>1.00</td>
</tr>
<tr>
<td>10.00</td>
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Notes: * Each value is a mean of three replicates; RSD, relative standard deviation

![Fig.3 Gas chromatograms of blank and chlorpyrifos fortified soil](image)

2.2 Dissipation of chlorpyrifos in soil

The disappearance curves of chlorpyrifos in pakchoi-vegetated soil in a greenhouse and field are shown in Fig.4. Levels of chlorpyrifos residues could not be well interpreted by the use of a 1st-order model, which allowed a linearization of data by plotting the logarithms of the residues versus time, because the residues diminished quicker at first and much more slowly at a later stage in comparison with the 1st-order model (Fig.4). Statistical analysis was carried out according to the formal approaches to study the dissipation of chlorpyrifos and determine the statistical parameters which describe such behavior (Timme et al., 1986; Aguilera-del Real et al., 1997, 1999). The disappearance of chlorpyrifos in pakchoi-vegetated soil was described using 1st-order, 1.5th-order, 2nd-order, RF 1st-order, RF 1.5th-order, RF 2nd-order, and bi-exponential models (two-compartment model; Seow et al., 1986; Nose, 1987) by means of nonlinear regression (SPSS statistical package, V.11.5), respectively. Table 3 shows the equations of the decline curves that fit the experimental data, as well as the coefficients of determination $r^2$. Their corresponding coefficients of determination $r^2$ were used to select the optimal models (maximum value of $r^2$). As it is well known, $0 < r^2 \leq 1$ and, the bigger this coefficient is, the better the curve fits the experimental data. Optimal models for the dissipation of chlorpyrifos in pakchoi-grown soil were the bi-exponential models in most cases, except for the 2nd-order model (summer, greenhouse) at double dose and the RF 1st-order model (autumn, field) at double dose (Table 3). However, coefficients of determination $r^2$ of the bi-exponential models in the latter cases were very close to those of the optimal models. It was, therefore, reasonable to regard the bi-exponential models as the optimal models for all cases. The data for each case were simulated with the bi-exponential model.

The differences of the dissipation for chlorpyrifos in pakchoi-vegetated soil in a greenhouse and field were observed (Fig.4). 25 d after chlorpyrifos application, it was dissipated in pakchoi-grown soil in the summer and autumn by 98.7% and 96.6% in a greenhouse, 98.7% and 97.6% in a field at the recommended dose, respectively; the corresponding values were 96.3% and 94.3% in a greenhouse, 98.6% and 95.9% in a field at double dose, respectively. The kinetic data of chlorpyrifos dissipation calculated with the optimal model and the 1st-order model are summarized in Table 4. The disappearance time for 50% of the initial amount of chlorpyrifos obtained using the optimal model was much shorter than that obtained from the 1st-order model. A similar result has been observed in an Oxisol (Laabs et al., 2000). The DT$_{50}$ of chlorpyrifos in pakchoi-vegetated soil at the recommended dose in the summer and autumn, calculated by the optimal model, were 0.6 and 1.2 d in a greenhouse, 0.4 and 1.0 d in a field, respectively; the corresponding values at double dose were 1.2 and 2.1 d in a greenhouse, 0.5 and 1.3 d in a field, respectively. Compared with field, the DT$_{50}$ of chlorpyrifos in pakchoi-vegetated soil was much longer in a greenhouse. Furthermore, chlorpyrifos dissipated more rapidly in the summer than in the autumn.

The initial rapid dissipation of chlorpyrifos in soil during the first 0 to 5 d was followed by a slower second phase decline, as can be observed in Fig.4. The dissipation of chlorpyrifos in soil occurred in two distinct phases, with an initial rapid disappearance on the soil surface, 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 second phase decline related to steady microbial and chemical degradation in the soil body (Laabs et al., 2000). The dissipation of chlorpyrifos in soil was closely related to climatic conditions (temperature, solar radiations, rainfall etc). The dissipation rate increases with the increase of temperature and solar radiations (Hill and Inaba, 1991; Vail et al., 1995; Rüdel, 1997; Wu and
Noziger, 1999). The rainfall also plays an important role on the dissipation rate of pesticides. The high rainfall can result in leaching and runoff of pesticides in soil. It rained only a little throughout experimental period (26 mm in the summer, 32.4 mm in the autumn). Furthermore, no rainfall event happened in the first week after application of chlorpyrifos. Thus, the rainfall had almost no effect on the dissipation of chlorpyrifos in soil in this case. The greenhouse cover could also decrease the effect of solar radiations on degradation of chlorpyrifos. The reduced solar radiations caused by glass screen were significantly
responsible for the decrease in dissipation of pesticides on vegetables (Garau et al., 2002; Yu et al., 2005). In the present case, the polyethylene cover would decrease more solar radiation and hence decreases the photodegradation rate of chlorpyrifos. Compared to field, the temperature is often much higher in a greenhouse and hence increases the dissipation rate of chlorpyrifos. Moreover, the greenhouse walls reduced chlorpyrifos loss to the atmosphere via airflow (Siebers and Mattusch, 1996; El Hadiri et al., 2003). In general, chlorpyrifos in pakchoi-vegetated soil dissipated slower in a greenhouse as comparison with a field, which might be attributed to the hermetic environment in the greenhouse. The changes of seasons could also alter the dissipation behaviors of chlorpyrifos in soil. In fact, the seasonal effect on the dissipation of pesticides was mainly caused by changes in temperature (Hill and Schaanje, 1985). Of course, the solar radiations and rainfall are also important factors affecting the dissipation of pesticides. Compared with the autumn, the temperature and solar radiations are often much higher in the summer. During this experiment, the rainfall volume was small and almost same in the summer and autumn. Therefore, chlorpyrifos in soil dissipated more rapidly in the summer than in the autumn.

3 Conclusions

The dissipation of chlorpyrifos in pakchoi-vegetated soil could be best described by the bi-exponential model. The chlorpyrifos in pakchoi-grown soil dissipated slower in a greenhouse than in a field mainly due to the hermetic environment in the greenhouse, and dissipated slower in the autumn than in the summer mainly due to changes of temperature. The dissipation data of chlorpyrifos in a field soil may not be valid for the assessment of its behavior in a greenhouse. The slower dissipation of chlorpyrifos in a greenhouse may result in an accumulation of their residues in soil, which is considered to be detrimental to succeeding crops and sustainable development of soil.

References:


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