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Dissipation of chlorpyrifos and residue analysis in rice, soil and water under paddy field conditions

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ABSTRACT

The analytical method for the residues of chlorpyrifos in rice plants, water and soil was developed and dissipation of chlorpyrifos under field conditions was studied. The limit of detection (LOD) of chlorpyrifos was 0.006 mg kg^{-1} and the limit of quantification (LOQ) was found to be 0.04 mg kg^{-1} in rice plant (water) and 0.02 mg kg^{-1} in the other substrates, respectively. The results showed that the initial residues of chlorpyrifos in Nanjing and Guangxi were 4.99 and 6.05 mg kg^{-1} (rice plant), 1.35 and 1.58 mg kg^{-1} (water) and 0.51 and 0.63 mg kg^{-1} (soil), respectively. The half-lives of chlorpyrifos in rice plant, water and soil from Nanjing were 4.28 , 0.58 and 1.35 day, respectively, and the half-lives of those from Guangxi were 3.86 , 0.52 and 1.21 day, respectively. The husked rice, rice hull and straw samples were found to contain chlorpyrifos well below the maximum residue limit (MRL) following the recommended dosage, the residues of chlorpyrifos in soil were undetectable under all application levels and frequencies after 28 day of applications.

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1. Introduction

Rice (*Oryza sativa* L.) consumption has increased worldwide over recent decades, as it has become one of the most common foods (Lucía et al., 2010). In China, rice is the main food and planting area accounts for about 23% of that of world and total production accounts for more than 30%, ranking the first in the world (Zhang, 2007). Rice is often attacked by various insects during its growing period. For example, the losses caused by insects are from 2.0% to 31.5% worldwide annually (Jiang et al., 2010). Thus, spraying insecticides is one of effective insect-control techniques, and has applied in agriculture for a long time.

Chlorpyrifos [*o,o*-diethyl-*o*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate - $\text{C}_9\text{H}_{11}\text{Cl}_3\text{NO}_3\text{PS}$] is one of organophosphorus (OPPs) insecticides, which are the most important and widely used classes of agricultural pesticides (Pope et al., 2005). Because of its intensive use, a wide range of terrestrial ecosystems are contaminated by chlorpyrifos and public concerns on safety have been increased. Therefore, the evaluation on environmental behavior and effects of chlorpyrifos has researchers' attention (Fang et al., 2009). Dissipation (Redondo et al., 1997), absorption (Van Emmerik et al., 2007), photolysis (Graebing and Chib, 2004) and biodegradation (Singh et al., 2006) of chlorpyrifos

in ecosystems have been reported. Zhang et al. (2010) studied the degradation of chlorpyrifos in rice from farm to fork and risk assessment and concluded that the risks may be controlled after human health risk assessment data being refined and updated. The results of the research can help to establish the maximum residue level (MRL) value and determine pre-harvest interval. However, in the literature, little work is available on the impact of chlorpyrifos under paddy field conditions.

In our study, the effects of chlorpyrifos on pesticide residues in the rice were investigated by analyzing the chlorpyrifos residues in rice, water and soil matrix substrates using gas chromatography (GC). The residual dissipation and final residue of chlorpyrifos in the rice crops and the soil is determined to provide evaluation for safe use chlorpyrifos.

2. Materials and methods

2.1. Chemical materials

Pure grade chlorpyrifos (99.5% of purity) was purchased from the Institute for the Control of Agrochemicals, Ministry of Agriculture, Beijing, China. Chlorpyrifos 20% EC (Dursban 20 EC) was procured from Shanghai Hui Kwang Chemical Co., Ltd (Shanghai, China). Organic solvents including acetone, acetonitrile, dichloromethane and n-hexane were chemical pure grade, purchased from Merck (Darmstadt, Germany). Analytical grade anhydrous sodium sulfate was obtained from China National Medicines Corporation Ltd (Beijing, China). Florisil was

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purchased from Beijing Chemistry Reagent Company (Beijing, China) and activated by heating at 130 °C for 12 h. Activated charcoal was cleaned with HCl and washed free of HCl residue with water. A stock solution of chlorpyrifos was prepared at 100 mg kg⁻¹ in acetonitrile in a volumetric flask and conducted at 4 °C before use.

2.2. Field study

Field experiments were conducted in Nanjing (32°-04' north latitudes and 118°-78' east longitudes) and Nanning in Guangxi province (23°-32' north latitudes and 108°-51' east longitudes) of China during summer season in 2009 and 2010. The field treatments included the dissipation experiment and final residue experiment; each treatment consisted of one control and three replicates of treated samples with an area of 30 m² and separated by irrigation channels. For control treatment, no pesticide was sprayed and samples were collected as experimental treatment.

2.3. Chlorpyrifos dissipation

In dissipation experiments, chlorpyrifos (EC, 25%) was dissolved in water and sprayed onto the surface of rice plants by manual sprayer (PS16-7, 40.5 cm × 17 cm × 57 cm, 16 L volume, max. pressure 1.0 mPa) at an application dosage of 843.75 g ai ha⁻¹ (the highest recommended dosage of the pesticide producer), then rice plants (about 500 g), soil (0–10 cm, about 200 g) and water (depth of water keep in 5 cm approximately 200 mL) were sampled randomly from each plot at 0.083 (2 h after application), 1, 3, 7, 10, 14, 21, 30, 45 and 60 day after application. Water samples were stored at 4 °C and other samples were at –20 °C until analyzed.

2.4. Final residues in rice and soil

The growth period of the rice plants used in this experiment, which was harvested in October, was 60 day after application. To study the effect of chlorpyrifos dosage, frequency on the residues, two dosages were used, higher dosages at 843.75 g ai ha⁻¹ and lower dosages at 562.5 g ai ha⁻¹. Both high and low application rates were used in two or three applications (7 day interval each), and the last spray was applied 14, 21 or 28 day before harvest.

2.5. Analytical procedure

2.5.1. Sample preparation

Rice plants and straws were cut into small pieces (about 0.5 cm × 0.5 cm) before analysis. Water samples were collected in the plastic bottles randomly from each plot and filtered. Soil samples were measured on a dry matter basis after having been dried in the shade and sifted through a 40-mesh sieve. At harvest, soil, straws and rice samples were collected for final residue analyses. Rice was air-dried at room temperature and shelled into rice hull and husked rice. Husked rice and rice hull were all ground to powder.

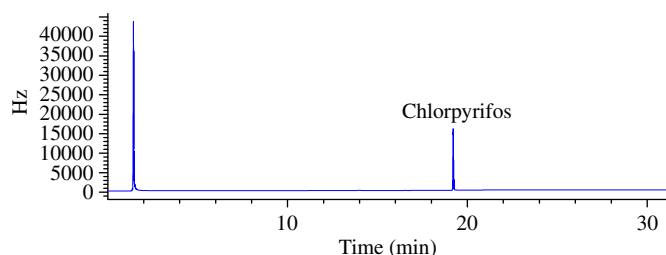


Fig. 1. Typical GC chromatograph of a standard solution of chlorpyrifos (1 mg kg⁻¹). The relative retention times for was about 19.2 min.

Table 1

Average recovery and relative standard deviation (\pm RSD) of different samples^a.

Fortified level (mg kg ⁻¹)	Rice plants (%)	Water (%)	Soils (%)	Straws (%)	Rice hull (%)	Husked rice (%)
0.01	96.47 \pm 2.67	88.13 \pm 5.26				
0.05	104.73 \pm 2.51	96.33 \pm 3.01	105.40 \pm 3.45	91.53 \pm 4.24	96.51 \pm 4.26	94.07 \pm 4.29
0.1	102.40 \pm 3.42	89.54 \pm 4.99	96.27 \pm 3.24	95.20 \pm 1.56	94.50 \pm 3.53	94.50 \pm 2.60
0.2			98.57 \pm 2.65	103.67 \pm 4.65	102.57 \pm 5.23	98.12 \pm 5.45

^a Values are average of triplicate analysis at each fortification level.

2.5.2. Extraction

Rice plant (5.00 g) and straw samples (5.00 g) were extracted with 30 mL acetone by a homogenizer (ULTRA TURRAX) for 30 s; then, 0.3 g of activated charcoal powder was added followed by shaking the contents for 1 h on a mechanical shaker. The contents were then filtered and the filtrate was dried with 10 g anhydrous sodium sulfate. Soil samples (15.00 g) were extracted with 40 mL of acetone and the contents were shaken for 4 h on the mechanical shaker; then the sample was filtered, the organic solvent was evaporated; the residue were dissolved in 1.00 mL of acetonitrile followed by going through a 0.22 μ m polypropylene filter for GC analysis. Water samples (30.0 mL) were extracted with two portions of 15 mL of dichloromethane; then, the organic layers were combined, and the organic solvent was evaporated, and the residues were dissolved as described above. Powdered rice hull (5.00 g) or husked rice (10.00 g) samples were extracted with 40 mL of acetone; the further process was then the same manner as the described above.

2.5.3. Clean-up

A portion of 10 mL acetone extract was evaporated to dryness in a nitrogen evaporator with a water bath at 60 \pm 1 °C. The dry extract was dissolved in 5 mL of n-hexane, followed by cleaned up using a pre-activated Florisil cartridge by eluting a portion of 5 mL of acetone/n-hexane (1:9, V/V) and 5 mL of n-hexane. The chlorpyrifos were absorbed on the Florisil cartridge and eluted off the cartridge with 10 mL of acetone/n-hexane (1:9, V/V). The solvent of the eluate was evaporated to dryness in a nitrogen evaporator with a water bath at 60 \pm 1 °C. The residues were dissolved in 1 mL of acetonitrile and analyzed by GC-ECD.

2.5.4. Instruments and analytical conditions

The samples were analyzed by GC (Agilent 6890, USA) equipped with electron capture detector (ECD). The column was HP-5 (0.25 μ m film thickness, 30 m length, 0.25 mm i.d., J&W Scientific, USA) for chlorpyrifos determination. The instrument conditions are as follows: inlet temperature 250 °C, initial oven temperature 120 °C for 1 min; temperature was then increased from 20 °C min⁻¹ to 260 °C and held for 8 min. Ultra-pure quality nitrogen was used as carrier gas and injections were carried out in splitless mode using 1 μ L injection volumes. The relative retention time for chlorpyrifos was about 19.2 \pm 0.2 min (Fig. 1).

2.5.5. Limit of detection (LOD)

Recoveries experiments were conducted to confirm the validity of the methods. Different known concentrations of chlorpyrifos (0.01, 0.02, 0.1, 0.2, 0.5 and 1 mg L⁻¹) were prepared by diluting the stock solution with acetonitrile. The injection volume was 1 μ L and the peak area observed was plotted against the standard concentrations to obtain a calibration linear curve. The limit of detection (LOD) was determined based on the lowest level of standard concentration detected and limit of quantification (LOQ) was the quantification limit at which can significantly distinguish two different values of residues.

2.5.6. Degradation of chlorpyrifos

The degradation of chlorpyrifos was described by the model of the first-order function ($C_t = C_0 \times e^{-kt}$). The degradation half-life ($t_{1/2}$) of chlorpyrifos in each experiment was obtained by the function $t_{1/2} = \ln 2/k$, where C_t is the concentration (mg kg⁻¹) at time t (days) after application, C_0 is the initial concentration (mg kg⁻¹) and k is the first-order rate constant (day⁻¹).

3. Results

3.1. Recovery and detection limits

A standard calibration curve of chlorpyrifos was constructed by plotting analyte concentrations against peak areas. A good linearity ($y = 40452.75x - 644.92$) was achieved between the range of 0.01–1 mg L⁻¹ with a correlation coefficient of $R^2 = 0.9995$. It is suggested that chlorpyrifos can be detected with good precision

provided the extraction procedure adopted gives good recoveries. The recovery study was conducted for different substrates. At three different fortification levels (0.01, 0.05, 0.1 or 0.2 mg kg⁻¹), the average recoveries from fortified samples in three replicated experiments for each matrix were in the range of 88.13–105.40% and the relative standard deviation (RSD) ranged from 1.56% to 5.45% (Table 1). The LOD of chlorpyrifos was 0.006 mg kg⁻¹. The LOQ was 0.04 mg kg⁻¹ in rice plant (water) and 0.02 mg kg⁻¹ in the other substrates, respectively.

3.2. Dissipation of chlorpyrifos under paddy conditions

3.2.1. Dissipation of chlorpyrifos in rice plants

The initial concentration of chlorpyrifos in rice plants 2 h after treatment was found to be 4.991 mg kg⁻¹ at Nanjing and 6.052 mg kg⁻¹ at Guangxi. As can be seen in Fig. 2, there was a steady decrease in the residue content from Nanjing and Guangxi. The residues of chlorpyrifos were 0.057 mg kg⁻¹ on the 45th days

Table 2

First-order kinetic equations and half-life for chlorpyrifos dissipation under the paddy field conditions.

Matrix	Locality	Kinetic equation	Coefficient (R ²)	Half-life (day)
Rice plant	Nanjing	$C_t = 4.9905e^{-0.1616t}$	0.9764	4.32
	Guangxi	$C_t = 6.0515e^{-0.1733t}$	0.9461	3.86
Water	Nanjing	$C_t = 1.3485e^{-1.0138t}$	0.9429	0.58
	Guangxi	$C_t = 1.5855e^{-1.0583t}$	0.9263	0.52
Soil	Nanjing	$C_t = 0.5345e^{-0.5677t}$	0.9872	1.35
	Guangxi	$C_t = 0.6291e^{-0.6122t}$	0.9608	1.21

of Nanjing, thereafter no residue was found in rice plants in Nanjing. However there was no residue found in rice plants in Guangxi after the 30th day. The half-lives and other statistical parameters of the chlorpyrifos residue dissipation were calculated from the experimental data and were summarized in Table 2. The half-lives were found to be 4.32 and 3.86 day for Nanjing and Guangxi locations, respectively.

3.2.2. Dissipation of chlorpyrifos in water

The initial concentration of chlorpyrifos in water 2 h after treatment was 1.349 mg kg⁻¹ in Nanjing and 1.586 mg kg⁻¹ in Guangxi, respectively. From Fig. 2, it can be seen that the residues of chlorpyrifos in water were 0.045 mg kg⁻¹ at the 21th day of Nanjing, and then decreased to no residue (< LOQ) in Nanjing. In the contrast, the residue was non-detectable (< LOQ), found in water in Guangxi after 14 day of application. The half-lives were similar, 0.58 and 0.52 day for Nanjing and Guangxi locations, respectively.

3.2.3. Dissipation of chlorpyrifos in soil

The initial concentration of chlorpyrifos in soil was 0.5345 and 0.6291 mg kg⁻¹ in Nanjing and Guangxi, respectively. The residue decreased from day 1 to day 14 and at day 14, the residues were at 0.016 mg kg⁻¹ and 0.013 mg kg⁻¹ levels in Nanjing and Guangxi soil. After 14 day, no residue was found in soils in Nanjing and Guangxi. Fig. 2 shows the dissipation curve of chlorpyrifos in soil under natural field conditions. The half-lives were 1.35 and 1.21 day for Nanjing and Guangxi, respectively.

3.3. Final residue analysis

Residues of chlorpyrifos in rice straw, soil, husked rice and rice hull after applying different dosage and frequencies of 25% Chlorpyrifos EC were presented in Tables 3 and 4. The residue levels in husked rice were 0.049–0.385 mg kg⁻¹ at 14 day after spraying; 0.026–0.196 mg kg⁻¹ at 21 day; 0.013–0.067 mg kg⁻¹ at 28 day after application. The residue levels in rice hull were 0.854–3.899 mg kg⁻¹ at 14 day; 0.435–1.850 mg kg⁻¹ at 21 day; 0.127–0.742 mg kg⁻¹ at 28 day. The residue levels in straw were 1.109–3.774 mg kg⁻¹ at 14 day; 0.763–1.734 mg kg⁻¹ at 21 day; 0.338–0.894 mg kg⁻¹ at 28 day. The residues of chlorpyrifos in soil were undetectable under all application levels and frequencies of application after 28 day.

4. Discussion

The data of fortification showed good recoveries in the type of matrices, demonstrating the analytical method was robust and reliable. The recoveries were observed to be slightly greater than 100% (except for water and husked rice samples) indicating the matrices may play a role affecting the recovery. It should note

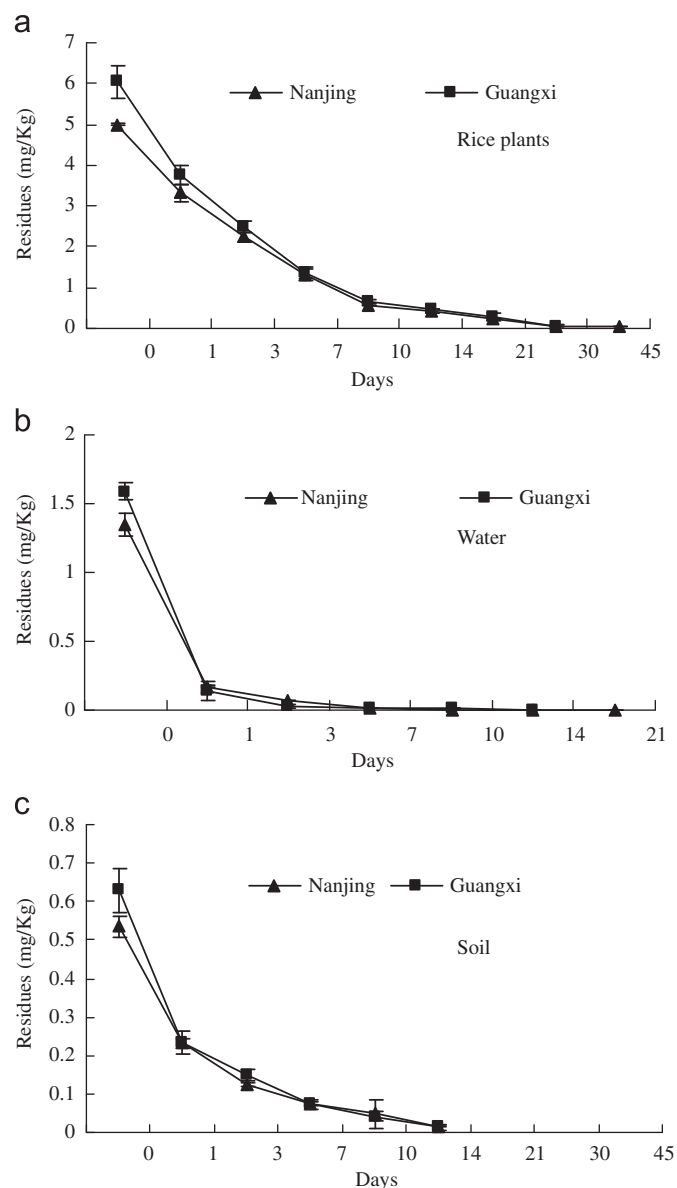


Fig. 2. Dissipation of chlorpyrifos residues under natural field conditions in rice plants, water and soil in 2009 (▲: Nanjing and ■: Guangxi). Error bars represent the standard deviation ($n=3$).

Table 3

Final residues of chlorpyrifos in husked rice, rice hull, straw and soil in Nanjing and Guangxi, China in 2009.

Days after spraying	Number of times sprayed	Dosage (g ai ha ⁻¹)	Residue (mg kg ⁻¹) (Mean ± SD, n=3)							
			Nanjing				Guangxi			
			Husked rice	Rice hull	Straw	Soil	Husked rice	Rice hull	Straw	Soil
14	2	562.50	0.049 ± 0.008	0.950 ± 0.305	1.109 ± 0.425	0.035 ± 0.015	0.052 ± 0.035	0.854 ± 0.076	1.279 ± 0.067	0.023 ± 0.035
		843.75	0.230 ± 0.002	2.146 ± 0.012	1.907 ± 0.065	0.052 ± 0.008	0.280 ± 0.005	1.228 ± 0.032	2.130 ± 0.125	0.042 ± 0.045
	3	562.50	0.128 ± 0.003	1.548 ± 0.031	1.548 ± 0.105	0.043 ± 0.105	0.208 ± 0.102	1.241 ± 0.114	1.241 ± 0.007	0.036 ± 0.155
		843.75	0.353 ± 0.021	3.832 ± 0.212	3.291 ± 0.015	0.054 ± 0.035	0.385 ± 0.045	2.529 ± 0.023	3.723 ± 0.001	0.056 ± 0.215
21	2	562.50	0.038 ± 0.004	0.746 ± 0.145	0.844 ± 0.025	< 0.02	0.031 ± 0.218	0.435 ± 0.022	0.763 ± 0.058	< 0.02
		843.75	0.092 ± 0.005	1.046 ± 0.045	0.918 ± 0.005	0.025 ± 0.115	0.079 ± 0.035	0.673 ± 0.156	0.963 ± 0.009	< 0.02
	3	562.50	0.063 ± 0.002	1.345 ± 0.029	1.072 ± 0.255	< 0.02	0.063 ± 0.305	0.444 ± 0.358	0.963 ± 0.036	< 0.02
		843.75	0.107 ± 0.013	1.846 ± 0.052	1.531 ± 0.065	0.026 ± 0.235	0.178 ± 0.046	0.711 ± 0.004	1.496 ± 0.250	0.021 ± 0.055
28	2	562.50	0.026 ± 0.025	0.368 ± 0.002	0.338 ± 0.125	< 0.02	0.017 ± 0.007	0.144 ± 0.009	0.351 ± 0.047	< 0.02
		843.75	0.062 ± 0.022	0.644 ± 0.013	0.686 ± 0.035	< 0.02	0.052 ± 0.011	0.225 ± 0.109	0.717 ± 0.065	< 0.02
	3	562.50	0.052 ± 0.008	0.437 ± 0.009	0.474 ± 0.065	< 0.02	0.043 ± 0.206	0.131 ± 0.022	0.504 ± 0.005	< 0.02
		843.75	0.077 ± 0.011	0.742 ± 0.011	0.816 ± 0.055	< 0.02	0.065 ± 0.018	0.316 ± 0.042	0.763 ± 0.065	< 0.02

The limit of quantification (LOQ).

Table 4

Final residues of chlorpyrifos in husked rice, rice hull, straw and soil in Nanjing and Guangxi, China in 2010.

Days after spraying	Number of times sprayed	Dosage (g ai ha ⁻¹)	Residue (mg kg ⁻¹) (Mean ± SD, n=3)							
			Nanjing				Guangxi			
			Husked rice	Rice hull	Straw	Soil	Husked rice	Rice hull	Straw	Soil
14	2	562.50	0.055 ± 0.025	0.948 ± 0.055	1.200 ± 0.085	0.040 ± 0.002	0.053 ± 0.022	0.856 ± 0.009	1.330 ± 0.045	0.022 ± 0.042
		843.75	0.225 ± 0.006	2.106 ± 0.125	2.099 ± 0.005	0.051 ± 0.034	0.278 ± 0.036	1.336 ± 0.043	2.163 ± 0.008	0.053 ± 0.104
	3	562.50	0.143 ± 0.035	1.499 ± 0.405	1.711 ± 0.035	0.042 ± 0.007	0.220 ± 0.076	1.232 ± 0.065	1.723 ± 0.005	0.031 ± 0.226
		843.75	0.365 ± 0.125	3.899 ± 0.305	3.755 ± 0.115	0.057 ± 0.025	0.374 ± 0.109	1.994 ± 0.011	3.774 ± 0.202	0.068 ± 0.038
21	2	562.50	0.036 ± 0.065	0.793 ± 0.005	0.939 ± 0.305	< 0.02	0.033 ± 0.212	0.444 ± 0.093	0.853 ± 0.340	< 0.02
		843.75	0.094 ± 0.009	1.056 ± 0.055	1.082 ± 0.045	0.022 ± 0.085	0.078 ± 0.009	0.685 ± 0.062	0.877 ± 0.066	0.025 ± 0.123
	3	562.50	0.073 ± 0.215	1.850 ± 0.115	1.128 ± 0.009	< 0.02	0.073 ± 0.043	0.517 ± 0.135	0.938 ± 0.005	0.021 ± 0.098
		843.75	0.192 ± 0.065	1.850 ± 0.065	1.734 ± 0.004	0.035 ± 0.005	0.196 ± 0.065	0.790 ± 0.054	1.564 ± 0.156	0.036 ± 0.065
28	2	562.50	0.027 ± 0.125	0.362 ± 0.075	0.435 ± 0.002	< 0.02	0.013 ± 0.310	0.127 ± 0.084	0.422 ± 0.042	< 0.02
		843.75	0.062 ± 0.252	0.632 ± 0.215	0.726 ± 0.045	< 0.02	0.050 ± 0.008	0.217 ± 0.012	0.709 ± 0.122	< 0.02
	3	562.50	0.058 ± 0.115	0.468 ± 0.135	0.525 ± 0.115	< 0.02	0.040 ± 0.006	0.137 ± 0.045	0.422 ± 0.052	< 0.02
		843.75	0.069 ± 0.075	0.695 ± 0.154	0.894 ± 0.315	< 0.02	0.066 ± 0.056	0.303 ± 0.005	0.719 ± 0.152	< 0.02

The limit of quantification (LOQ).

that the effect varies with the nature of pesticide, matrix type, analytical system and the concentration (Ajay et al., 2004).

Based on the dissipation data, the initial residue of chlorpyrifos in rice plants grown in Guangxi was 6.052 mg kg⁻¹, which was higher than the initial residue level of 4.991 mg kg⁻¹ in Nanjing. It may be due to the local climate conditions (for example, generally the summer is hotter and more humid in Nanjing than in Guangxi) affecting the initial concentration of chlorpyrifos in rice plants and other factors including soil pH, moisture and growth dilution might have played a significant role (Dhananjay et al., 2005). Furthermore, the influence of cropping system might have influence the dissipation. Kidd and James (1991) in their work revealed that the chlorpyrifos has low solubility in water, it will be explained the high initial concentration of chlorpyrifos in water (1.349 mg kg⁻¹ in Nanjing and 1.586 mg kg⁻¹ in Guangxi, respectively). Because aquatic macrophytes can absorb chlorpyrifos to help remove the residue from the aqueous environment (Karen et al., 1998), the residues of chlorpyrifos in the water of Nanjing and Guangxi were undetectable after 21 day. Compared with the initial residues in rice plants, the initial residue level of chlorpyrifos in soil was considerably low, which was 0.5345 mg kg⁻¹ in Nanjing and 0.6291 mg kg⁻¹ in Guangxi. The difference in half-life of chlorpyrifos in soil between the two sites was similar (1.35 and 1.21 day), indicating that chlorpyrifos rapidly dissipated in soil. Chlorpyrifos persists in soil

with degradation being primarily due to soil type, soil microorganisms and climatic condition (Singh et al., 2002a; Singh et al., 2002b).

After application of chlorpyrifos in paddy field, it persisted mainly on rice straw and rice hull. Fresh or processed rice straw and rice hull are used as feeds for ruminants in many regions of China. Thus, the persistence of pesticide residues is a potential risk. The MRLs of chlorpyrifos on rice straw and rice hull have not been well established yet, but it set as 2.0 mg kg⁻¹ on rice forage by Environment Protein Agency (USA, 2007). As can be seen in this work, high residues of chlorpyrifos greater than 2.0 mg kg⁻¹ were observed in rice straw and rice hull samples at day 14 after the last application. However, the final residues of chlorpyrifos in rice straw and rice hull samples were below the MRL under all application levels and frequencies after 21 day. According to the findings of this work, the rice straw and rice hull may be safely used as animal feeds. Pesticide residues in soil raise a number of potential harmfulness, such as adverse impact on subsequent crop and contamination of the ground water. However, the residues of chlorpyrifos in soil were undetectable under the application levels and frequencies after 28 day. These results showed that chlorpyrifos appeared to be safe for the environment.

In some countries, the MRLs for chlorpyrifos in some crops have been established. In China, the MRL of chlorpyrifos (GB2763, 2005) in rice grain was 0.1 mg kg⁻¹. As indicated in Tables 3 and

4, the residues of chlorpyrifos exceeding 0.1 mg kg^{-1} were observed in husked rice samples at 14 day after the last application and the residues of some husked rice samples from high dosage fields also greater than 0.1 mg kg^{-1} at day 21. The residues in the husked rice samples from the low application rate did not exceed 0.1 mg kg^{-1} at 21 day after application of chlorpyrifos. The results provide a quantitative basis for revising the guidelines for the application of this pesticide to rice. The data suggest that rice not be sprayed no more than twice with chlorpyrifos (EC, 25%) at a recommended rate not exceeding $562.5 \text{ g ai ha}^{-1}$ with an interval of at least 7 day between each application. There should be a withholding period of at least 21 day between the last application and harvest. Comparing the residue levels of chlorpyrifos in 2009 with the data in 2010 (Tables 3 and 4), it was observed that the residue levels in 2010 were relatively higher than those in 2009. The temperature, humidity and wind may be affecting the dissipation of chlorpyrifos in the growing periods (Guo et al., 2010), and the differences in residues of different locations suggest that local soil characteristics and climate may affect the dissipation of chlorpyrifos (Li et al., 2008).

5. Conclusion

The dissipation rates of chlorpyrifos at the two experimental sites were different, suggesting that degradation of chlorpyrifos was affected by local conditions such as soil chemistry, climates, etc. From the dissipation and final residue data, the authors recommend that for the rice crops, a better application of chlorpyrifos should be chlorpyrifos (EC, 25%) with two applications at the rate of $562.5 \text{ g ai ha}^{-1}$, and a Pre-Harvest Interval (PHI) of at least 21 day. Low residues of chlorpyrifos at the harvest time showed that chlorpyrifos is safe for the paddy field environment and the crops planted the following years.

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