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Dissipation of Chlorfenapyr Residue in Pakchoi and Soil

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Chlorfenapyr[4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethylpyrrole-3- carbonitrile] is used as an insecticide and acaricide worldwide because of its excellent broad-spectrum insecticidal and acaricidal activity. The insecticide is known to be environmentally stable and of low toxicity to warm-blooded animals (Tomilin 1997). The major use of this insecticide is in vegetable and cotton crops, particularly for the control of those insect pests that became resistant to repeat application of the conventional insecticides such as organophosphates, carbamates and pyrethroids (Lovell 1990, Pei *et al* 2006, Tomilin 1997). It's particularly true for pakchoi (*Brassica chinesis* L.), a very important vegetable crop in the south part of China. The vegetable are heavily damaged by insect pests such as diamondback moth (*Plutella oxystella* L.), imported cabbageworm (*Pieris rapae* L.) and beet armyworm (*Spodoptera exigua* Hubner), and the farmers make liberal application of insecticides to control them. This has not only lead to higher resistant level of pests, but also leaves high levels of insecticide residues in vegetables for the consumer. Chlorfenapyr is now recommended for the control of a wide spectrum of insect pests in vegetables such as Chinese cabbage, pakchoi and cauliflower (Pei *et al* 2006). Residues of chlorfenapyr in Chinese cabbage were first analyzed and reported by Chen *et al* (2005) using high performance liquid chromatography. However, little information is available on the dissipation of chlorfenapyr residue in pakchoi crop and soil. Therefore, a supervised trial was conducted to study the dissipation dynamics of chlorfenapyr residues in the pakchoi and soil at Changsha, China.

MATERIALS AND METHODS

Chlorfenapyr was provided with a formulated insecticide 10% suspension concentrate and more than 99.5% analytical standard by American Cyanamide Corporation, USA. Field experiment was conducted in the vegetable field of Changsha, China in winter season of 2004 to 2005 to study the dissipation of chlorfenapyr in the pakchoi field ecosystem. The crop was raised according to the

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recommended agronomic practices. The treatments comprised two levels of 10% chlorfenapyr SC, viz. recommended dosage (75 g a.i./ha), double dosage (150 g a.i./ha) and an untreated control. The treatments were replicated three times in randomized block design. The soil has texture with a composition of 37.7 % clay, 24.5 % silt, 18.9 % sand, and 1.34 % organic carbon and pH of 7.6. The crop was sprayed with chlorfenapyr twice and thrice at application time interval of 7days. The crop and soil samples were collected at random from each plot (30 m^2) on 0 (2 h), 1, 3, 7, 10, 14 and 21days after application of chlorfenapyr. Part of sample (200 g) was drawn by quartering technique and kept in the refrigerator (-20℃) before extraction and analysis. The soil sample (20 g) was soaked overnight in a 500-mL conical flask with 100mL of acetone, and then 100mL deionized water was added and extracted with petroleum ether (100 mL+100 mL). The organic layer was separated and dried over anhydrous sodium sulfate (10 g) through a filter paper into a round-bottomed flask. The solvent was evaporated to dryness on a rotary evaporator at the temperature of 60℃. Residues were dissolved in 5 mL of petroleum ether prior to injection into GC.

The crop sample (50 g) was chopped and mixed, and then extracted with 100 mL of acetone in a high-speed bender for 2 min. The macerates were filtered with suction. The filter cake was reblended with 50 mL of acetone and filtered. Finally it was washed twice with 50 mL of acetone. The combined filtrate was taken in a 500 mL separatory funnel, 100 mL water was added, and contents were extracted with petroleum ether (100 mL+100 mL). The organic layer was passed over anhydrous sodium sulfate through a filter paper into a round-bottomed flask and rotary evaporated to dryness. For further cleanup, residues in petroleum ether were transferred to a glass column (180 mm×Φ15 mm) packed with Florisil (5 g) and Diatomite (1 g) overlayed with anhydrous sodium sulfate (1 cm), and eluted first with petroleum ether (25 mL) followed by 50 mL ethyl ether/petroleum ether mixture (4:6,V/V). The ethyl ether/petroleum ether fraction was evaporated on rotary evaporator at the temperature of 60℃ to dryness and volume made up in petroleum ether (5 mL) prior to analysis.

Residues were estimated on a gas chromatograph (HP-GC10A) using electron capture detector. Aliquots (2μL) of sample extracts were injected into GC with 500mm×Φ3.2mm glass column packed with 1.5% OV-17 and 2.0 % QF-1/Chromosorb W HP (80-100 mesh). Operation conditions were as follow: column temperature 21℃, injector temperature 250℃ and flow rate of nitrogen 60mL/min. Under these conditions, chlorfenapyr gave a sharp peak at a retention time of 3.25 min. Chlorfenapyr quantities were estimated according to the external reference method. The minimum detectable quantities of

chlorfenapyr were 2.5×10^{-11} g, and the actual minimum concentration detected in pakchoi and soil was 0.001 mg/kg and 0.003 mg/kg, respectively.

Recovery experiments were run on pakchoi and soil by spiking with known quantity of chlorfenapyr before the initial extraction and analyzing the residues by the method described above. Recoveries of chlorfenapyr were in the range of 88.21 %~97.67 % in pakchoi and 90.04 %~95.73 % in pakchoi at level of 0.1~1 mg/kg, respectively, indicating the acceptable range for the official method of pesticide residue analysis (Fan 1982).

All replicates were used for calculation of mean values at a confidence level (α) of 0.05. Degradation rate of chlorfenapyr over time was estimated by first-order linear regression analysis. Linear regression analysis was performed on the data using the DPS® 2000 data processing system (Tang and Feng 2002). Half-life ($T_{1/2}$) was calculated from the formula $\ln 2/k$, where k is the degradation rate constant.

RESULTS AND DISCUSSION

The residue data and percentage dissipation of chlorfenapyr in pakchoi and soil were presented in Table1. As evident from the analytical data (Table1), the average initial deposit of chlorfenapyr on pakchoi at the rate of 150 g a.i./ha was found to be 0.688 mg/kg on 0 (2 h) day, which dissipated to 0.337 mg/kg, 0.182 mg/kg, 0.045 mg/kg, 0.053 mg/kg and 0.012 mg/kg in 1, 3, 7, 10 and 14 days after the application, respectively. The percentage dissipation recorded in this period was 51.02 %, 73.55 %, 93.46 %, 92.3 % and 98.26 %, respectively. In 21 days after application, the residue was in the undetectable level with almost 100 % dissipation. The average initial deposit in soil was 0.149 mg/kg on 0 (2 h) day, which dissipated to 0.107 mg/kg, 0.113 mg/kg, 0.063 mg/kg, 0.059 mg/kg and 0.036 mg/kg in 1, 3, 7, 10 and 14 days after the application, respectively. The percentage dissipation recorded in this period was 28.19 %, 24.16 %, 57.72 %, 60.40 % and 75.84 %, respectively. The percentage dissipation was 92.62 % in 21 days after application and the corresponding average residue was 0.011 mg/kg.

The average residue data were subjected to DPS statistical analysis of Tang and Feng (2002) to elucidate the decline of chlorfenapyr residue as a function of time and to determine the kinetics parameters that described this process. As evident from Table 2, dissipation of chlorfenapyr residue in pakchoi and soil could be described very well by pseudo-first order kinetics equation, and its correlation coefficient (R) was 0.9864 and 0.9749, respectively. The half-life

($T_{1/2}$) of chlorfenapyr was 1.37 days in pakchoi and 6.98 days in soil.

Table1 Residues of chlorfenapyr in pakchoi and soil at the dose of 150 g a.i./ha.

Days after application (days)	Pakchoi		Soil	
	Residue level ±SD (mg/kg)	Dissipation (%)	Residue level ±SD (mg/kg)	Dissipation (%)
0	0.688±0.041	--	0.149±0.053	--
1	0.337±0.055	51.02	0.107±0.034	28.19
3	0.182±0.092	73.55	0.113±0.041	24.16
7	0.045±0.039	93.46	0.063±0.022	57.72
10	0.053±0.046	92.30	0.059±0.015	60.40
14	0.012±0.024	98.26	0.036±0.070	75.84
21	UD	100	0.011±0.005	92.62

*Average of three replicates; Ud means undetectable.

Table 2 Dissipation equation of 10 % chlorfenapyr SC residue in pakchoi and soil

Samples	$T_{1/2}$ (d)	Regression equation $Ct=C_0 \cdot e^{-kt}$	R	F test	Significant level P
Pakchoi	1.37	$Ct=0.6633e^{-0.5184t}$	0.9864	144.6	2.74×10^{-4}
Soil	6.98	$Ct=0.1388e^{-0.0992t}$	0.9749	96.0	1.88×10^{-4}

Table 3 Final residue of 10 % chlorfenapyr SC in pakchoi and soil

Dosage (g a.i./ha)	Application times	Harvest time from final application (days)	Residue* (mg/kg)	
			Pakchoi	Soil
75	2	7	0.387	0.164
		14	0.164	0.087
	3	7	0.413	0.377
		14	0.055	0.104
150	2	7	1.068	0.465
		14	0.519	0.409
	3	7	1.095	0.581
		14	1.041	0.343

*Average of three replicates.

As evident from final residue levels of chlorfenapyr in pakchoi and soil (Table3), when chlorfenapyr was sprayed twice at the recommended dose (75 g a.i./ha), the residue levels of chlorfenapyr was 0.38 mg/kg and 0.164 mg/kg in pakchoi and 0.164 mg/kg and 0.087 mg/kg in soil, respectively, at 7 days and 14 days

from the final application. When sprayed thrice at the same dosage, the final residue level was 0.413 mg/kg and 0.055 mg/kg in pakchoi and 0.377 mg/kg and 0.104 mg/kg in soil, respectively, at 7 days and 14 days from the final application. When sprayed twice at the doubled dose (150 g a.i./ha), the final residue level was 1.068 mg/kg and 0.519 mg/kg in pakchoi and 0.465 mg/kg and 0.409 mg/kg in soil, respectively, at 7 days and 14 days from the ultimate application. When sprayed thrice at the doubled dosage, the final residue level was 1.095 mg/kg and 1.041 mg/kg in pakchoi and 0.581 mg/kg and 0.343 mg/kg in soil, respectively, at 7 days and 14 days from the ultimate application.

In conclusion, chlorfenapyr was used to control the insect pests such as diamondback moth and beet armyworms *et al* at 75 g a.i./ha twice at the growth season with time interval of 7 days. At 7 and 14 days from the final application, the residue level of chlorfenapyr was not more than 0.5 mg/kg in pakchoi and 0.4 mg/kg in soil, and was within the range of US EPA's and Australian MRL of 0.5 mg/kg of chlorfenapyr in crops (ICAMA 2001). Therefore, a dosage of 75 g a.i./ha of chlorfenapyr in pakchoi was suggested, which can be considered to be safe to human beings and animals.

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