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Dissipation of chlorpyrifos on pakchoi inside and outside greenhouse

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Abstract: The dissipation of chlorpyrifos on pakchoi inside and outside greenhouse was studied. The decline curve of chlorpyrifos on pakchoi could be described as first-order kinetic. The experimental data showed that both the hermetic environment of greenhouse and season affected dissipation rates of chlorpyrifos on pakchoi. Chlorpyrifos declined faster outside greenhouse than inside greenhouse. Chlorpyrifos residues at pre-harvest time were below the maximum residue limits (MRLs) fixed in China, whereas the values inside greenhouse were higher than those outside greenhouse by almost 50%. The recommended pre-harvest time established under conditions of open field might not always fit to greenhouse production.

Keywords: chlorpyrifos; residue; dissipation; pakchoi; greenhouse

Introduction

Greenhouse production of vegetables has been developed rapidly, greenhouse provides more favorable climate for fast reproduction of pests and diseases, which require extensive application of pesticides for their control (van Lenteren, 2000). On the other hand, the hermetic environment in greenhouse alters dissipation behavior of pesticides in both crop plants and soil. Therefore, extensive application of pesticides in greenhouse may result in accumulation of residues at levels considerably higher than those in open field. In the recent years, increasing concern on the safety of pesticide application in greenhouse and residual level in the crops has been a major focus for the community in China and elsewhere (Martinez, 2003; Garau, 2002; Heunandez, 2002; Aguilera-del, 1999; Martínez, 1998). Although studies have been carried out for assessing levels of pesticide residues in greenhouse products, the difference between dissipations of pesticides inside and outside greenhouse is largely unknown yet.

Chlorpyrifos [O, O-diethyl-O-(3, 5, 6-trichloro-2-pyridinyl) phosphorothioate], an organophosphorus pesticide, acts as an insecticide-acaricide through ingestion, contact, and inhalation. It has been widely used for control of aphids, white fly, and other insects in a number of crops, including corn, fruits, and vegetables. Usually, chlorpyrifos is applied through soil-incorporated/directed use, bark treatment, and foliar treatment. Similar to other organophosphorous insecticides, chlorpyrifos is a cholinesterase inhibitor, which may cause potential toxicity in human (Oliver, 2000). Due to its broad-spectrum activity, chlorpyrifos is presently regarded as an ideal chemical to replace other high toxic organophosphorous insecticides and used widely and frequently for the control of pests in greenhouse production of vegetables in China. With the increasing use of chlorpyrifos, studies are needed to evaluate dissipation behavior in vegetables under greenhouse environment. The dissipation of chlorpyrifos in orange fruit (Martínez, 1998), tomatoes and green beans (Montemurro, 2002) has been reported previously. However, little is known about dissipation of chlorpyrifos on pakchoi, which is one of main leaf vegetables in China. Chlorpyrifos has been used widely for the control of pests on pakchoi and the safety of its application and dissipation behaviors need to be evaluated in detail. The objectives of this study were to analyze dissipation of chlorpyrifos on pakchoi inside and outside greenhouse, and to evaluate the difference of chlorpyrifos dissipation under two climatic conditions.

1 Materials and methods

1.1 Chemicals

Commercial chlorpyrifos 40% EC used in this study was supplied by Xinnong Chemical Co., Zhejiang, China. Chlorpyrifos standard (≥ 99.5%) was purchased from the Institute for the Control of Agrochemicals, Ministry of Agriculture, China. Petroleum ether (60—90℃) was of analytical reagent grade and was redistilled before use.

1.2 Field trials

Chlorpyrifos applications were conducted in open field and greenhouses, respectively, with surface area of 90 m^2 in size. The greenhouse was constructed of polyethylene, with a lateral window (0.5 m × 25 m) covered with a fine netting. The cross section of the greenhouse is shown in Fig. 1. Chlorpyrifos was applied by spraying at the rate of 2500 L/hm^2 at dosages of 0.84 and 0.42 kg/hm^2 of active ingredient, corresponding to the normal and double dosages, respectively, as recommended by the manufacturer for application on such crops in open fields. All experiments were triplicated for each treatment.

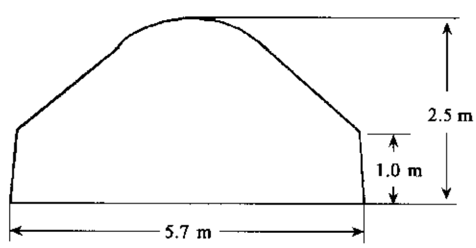

Fig. 1 The cross section of experimental greenhouse

1.3 Sampling and preparation

Pakchoi samples inside and outside greenhouse were collected randomly on 0, 1, 3, 5, 7, 10, 15 and 25 d after application of chlorpyrifos. The samples were placed into individual polyethylene bags and transported immediately to

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the laboratory and treated within a few hours by chopping and dividing into four sub-samples (25 g). All sub-samples were stored in individual polyethylene bags at −20℃ until extraction.

1.4 Extraction of chlorpyrifos

Twenty-five grams of pakchoi were homogenized in a glass jar with 80 ml of petroleum ether (60—90℃) and 80 g of anhydrous sodium sulfate at high-speed of 10000 r/min for 2 min. The mixture was decanted and filtered through a 7 cm buchner funnel with 10 g of anhydrous sodium sulfate, and the filter cake was washed successively 3 times with 25 ml of redistilled petroleum ether. The filtrates were combined in a 250 ml flat-bottom flask, and concentrated to almost dry and then just to the point of dryness with a slight N_2 stream. Redistilled petroleum ether was added to dissolve chlorpyrifos and the volume was adjusted to 5 ml for the determination by GC-FPD.

1.5 Determination of chlorpyrifos by GC

Quantitative analysis of chlorpyrifos was performed with a Fuli GC9790 gas chromatography, which was equipped with flame photometric detector (FPD) and a phosphorus filter. A fused silica capillary column (Pesticide Residue-Ⅱ, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China) (30 m length, 0.32 mm internal diameter, and 0.25 μm film thickness) was employed for the separation in GC. Operating conditions were as follows: injector port temperature, 230℃; column temperature, 230℃; detector temperature, 250℃; carrier gas, nitrogen, 50 ml/min; air, 80 ml/min; hydrogen, 125 ml/min.

1.6 Recovery study

Three replicate analyses were performed at different spiking levels to assess recoveries of the extraction method. 25 g of fresh pakchoi samples that were not applied with the insecticide were spiked with 10 mg/kg, 1.0 mg/kg and 0.1 mg/kg of chlorpyrifos. The extraction and detection of chlorpyrifos were performed as described above.

2 Results and discussion

2.1 Recovery study

The extraction procedure described above was assessed for its recovery of chlorpyrifos at three different spiking levels of 10 mg/kg, 1.0 mg/kg and 0.1 mg/kg, respectively. The average recoveries of chlorpyrifos fortified in pakchoi are shown in Table 1. In all cases, the recoveries of chlorpyrifos were > 90% with coefficients of variation not exceeding 6.0%. The results suggest that the extraction procedure used in this study is efficient in extracting chlorpyrifos residues from pakchoi samples. Fig. 2 shows the chromatograms of blank and chlorpyrifos fortified samples. These data are generally considered to be satisfactory for residue determinations.

Table 1 Recoveries of the analytical method used for chlorpyrifos in pakchoi

Fortification level, mg/kg	Recovery, %	*RSD* (*n* = 3)
10.00	92.5	3.2
1.00	94.2	3.1
0.10	101.8	6.0

2.2 Dissipation of chlorpyrifos on pakchoi inside and outside greenhouse

Fig.3 shows the residual data obtained in the dissipation studies of chlorpyrifos on pakchoi inside and outside greenhouse. These data were subjected to statistic analysis by first-order function $R = R_0 e^{-kt}$, which is frequently used in behavior study of pesticide residues on crops prior to harvest. The dissipation half-lives of chlorpyrifos were calculated from the equation $t_{1/2} = \ln 2/k$. The statistical chlorpyrifos dissipation parameters are summarized in Table 2.

In summer, the half-lives of chlorpyrifos at levels of full and double dosages on vegetable inside greenhouse obtained from first-order function were 1.84 and 1.96 d,

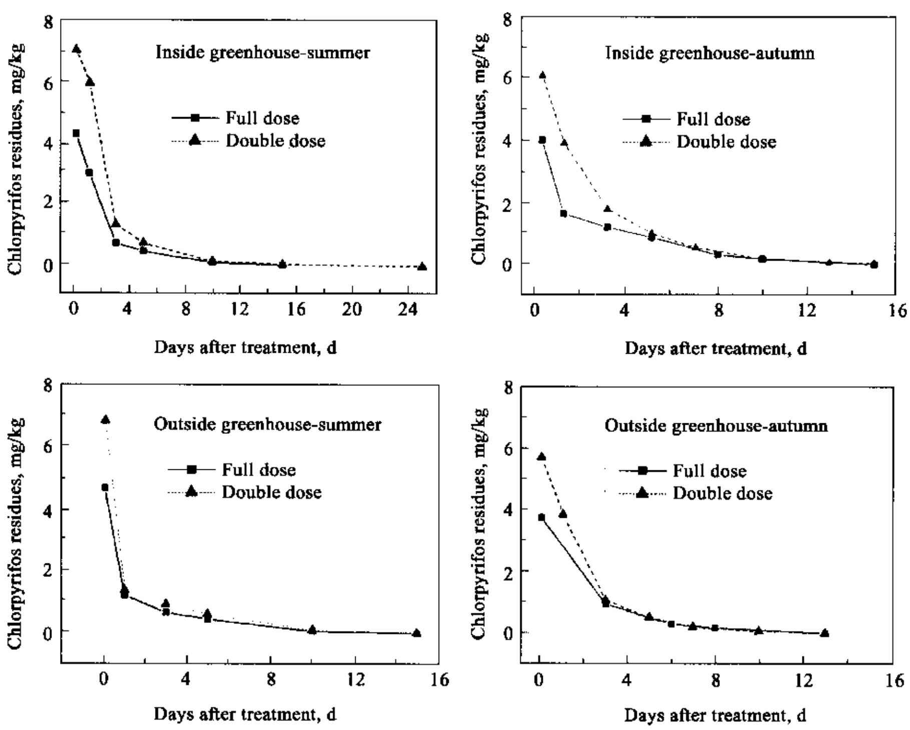

Fig.3 Dissipation of chlorpyrifos on pakchoi inside and outside greenhouse, values given are mean of results obtained from three replicates

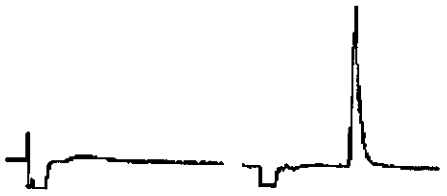

Fig.2 Chromatograms of blank and chlorpyrifos fortified pakchoi

respectively. The corresponding values outside greenhouse were 1.46 and 1.77 d, respectively. These data indicate that chlorpyrifos declines a little inside greenhouse comparing with outside greenhouse. A similar difference between chlorpyrifos dissipation on the vegetable inside and outside greenhouse in autumn was also observed (Table 2). The half-lives of chlorpyrifos at levels of full and double dosages in autumn outside greenhouse were 2.13 and 1.85 d, whereas the corresponding values inside greenhouse were 2.27 and 2.14 d respectively. These data indicate that the hermetic environment alters dissipation rates of chlorpyrifos on pakchoi. Moreover, the dissipation rates were also affected by the change of season. In the cases of autumn, the half-lives were greater than those in the cases of summer.

Table 2 Statistic data of chlorpyrifos dissipation on pakchoi inside and outside greenhouse

Site	Level	Season	Kinetic data	r^2	$t_{1/2}$, d	R_7, mg/kg
IG	FD	Summer	$R = 3.45e^{-0.376t}$	0.9853	1.84	0.25
IG	DD	Summer	$R = 5.65e^{-0.354t}$	0.9720	1.96	0.47
IG	FD	Autumn	$R = 3.15e^{-0.304t}$	0.9700	2.27	0.38
IG	DD	Autumn	$R = 4.83e^{-0.294t}$	0.9863	2.14	0.61
OG	FD	Summer	$R = 3.22e^{-0.473t}$	0.9782	1.46	0.12
OG	DD	Summer	$R = 3.59e^{-0.391t}$	0.9673	1.77	0.23
OG	FD	Autumn	$R = 2.83e^{-0.325t}$	0.9677	2.13	0.29
OG	DD	Autumn	$R = 4.22e^{-0.374t}$	0.9791	1.85	0.31

Notes: IG. inside greenhouse; OG. outside greenhouse; FD. full dose; DD. double dose

Chlorpyrifos residue in pakchoi at recommended pre-harvest time (7 d, established by China), calculated from first-order function, ranged from 0.12 to 0.61 mg/kg (R_7, Table 2). The chlorpyrifos residues inside greenhouse were generally higher than those outside greenhouse due to the slower dissipation inside greenhouse. The residual values were all lower than the corresponding MRLs of China (1.0 mg/kg), and also lower than EU MRLs (0.5 mg/kg, 2003) except for the treatment with double dosage of chlorpyrifos in autumn. However, it should be noted that the values of chlorpyrifos residue on pakchoi inside greenhouse were higher than those outside greenhouse by almost 50%.

Pesticide residues on vegetable usually decrease on account of vegetable growing, evaporation, codistillation, thermodegradation, and photodegradation. The temperatures inside greenhouse are frequently higher than outside greenhouse. Fig. 4 shows the average daily temperatures inside and outside greenhouse during the experiment period. The higher temperatures would accelerate evaporation, codistillation as well as thermodegradation of pesticides. However, the hermetic environment in the greenhouse may reduce the loss of pesticide by evaporation and codistillation. The enhancement in dissipation of pesticide should, therefore, be very limited. On the other hand, the greenhouse cover could decrease the effect of solar radiations on degradation of pesticides. The reduced solar radiations caused by glass screen were significantly responsible for the decrease in dissipation of pesticides on vegetable (Garau, 2002). In the present case, the polyethylene cover would decrease more solar radiations and hence decrease the photodegradation rates. In general, the hermetic environment of greenhouse would decrease the dissipation of pesticides.

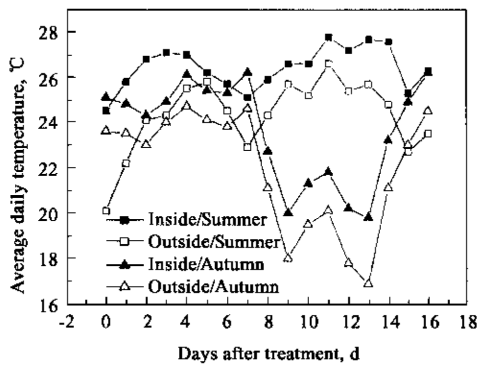

Fig.4 Average daily temperature throughout the experiments

The results obtained in this study suggest that actual residual levels of pesticides inside greenhouse may higher than those in open field. The recommended pre-harvest time, established under conditions of open field, might not always fit to greenhouse production.

3 Conclusions

Dissipation of chlorpyrifos on pakchoi inside and outside greenhouse could be described as first-order kinetic. The experimental data showed that both the hermetic environment of greenhouse and season affected dissipation rates of chlorpyrifos on pakchoi. Compared with inside greenhouse, chlorpyrifos declines faster outside greenhouse. Although chlorpyrifos residues at pre-harvest time were lower than the MRLs, the values inside greenhouse were higher than those outside greenhouse by almost 50%.

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