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The decline of pesticide residues in the air of three rain shelter farms at Cameron Highlands

(Kajian susut sisa baki pestisid dalam udara tiga kebun berpelindung hujan di Cameron Highlands)

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Key words: pesticides, cypermethrin, chlorpyrifos, air

Abstract

Field experiments in three commercial farms in Cameron Highlands were conducted to study the decline in time in the concentration of pesticide residues in air for a non-volatile compound (cypermethrin) and a moderately volatile compound (chlorpyrifos). The concentrations of the compounds in air were monitored for three days (72 hours) after the pesticide application. The maximum concentration of chlorpyrifos found was 8.9 $\mu g/m^3$. Cypermethrin residue was not traceable throughout the studies. After a dissipation period of several hours, chlorpyrifos concentration in the air was rapidly decreased to more than 50% of its initial concentration. By using Single Factor ANOVA analysis, no significant differences in residue concentration were found between samples collected at 0.5 m and 1.6 m heights. Higher concentration of chlorpyrifos residues was observed in the farm with rain shelter and side netting.

Introduction

Pesticide input in the farm under conventional agriculture is inevitable due to its need to control pests and diseases. Pesticides that are applied on crops may contaminate other parts of the environment where they may pose adverse effects to non-target organisms including human. In Malaysia, pesticide contamination in the soils and water has been studied (Cheah et al. 1994; Ma et al. 2000; Ngan et al. 2002). However, study on pesticide pollution in the air has not been carried out and documented.

There are many factors affecting the distribution of pesticides in the air. These include management practices (i.e. crop selection, type of rain shelter and pesticide application technology), atmospheric temperature, wind speed and direction as well as pesticide properties (Burgoyne and Hites 1993; Wienhold and Gish 1994; Sofuoglu et al. 2001; Harrad and Mao 2004). Atmospheric temperature affects the transport of pesticides by influencing their vapour pressure and mixing heights (Manchester-Neesvig and Andren 1989). Wind direction may play a role in affecting the atmospheric concentration of pesticide; however the relationships are often not obvious, because winds tend to travel in different directions at different altitudes and source strength tends to be highly variable (Sweet and Vermite 1992). Pesticide volatility is found to be among the major factors affecting the concentrations in the air (Brouwer et al. 1992; Majewski et al. 1993; Hawthorne et al. 1996).

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Chlorpyrifos is a broad-spectrum organophosphate insecticide effective against cutworms, corn rootworms, flea beetles, flies, termites and lice. It acts on pests as contact poison and is commonly used on grain cotton, fruit, nut and vegetable crops (Kidd and James 1991). Cypermethrin is a synthetic pyrethroid used to control a wide range of insect pests, particularly lepidopterous pests in cereals, citrus, cotton, fruit and vegetables (Jin and Webster 1998). Cypermethrin has an α-cyano group in its structure which improves photostability and leads to a powerful and rapid debilitating effect on insects (Hassal 1990). Chlorpyrifos is moderately volatile while cypermethrin has a very low vapour pressure and is not readily volatized into the atmosphere *(Table 1).*

Cypermethrin is known to be a low toxicity pesticide which is rapidly eliminated from human body through body waste (Leachey 1985). Whereas, chlorpyrifos is classified as a moderately toxic pesticide and known to cause paralysis in high dosage (Racke 1992). Assessing pesticide exposure through inhalation forms part of complete farm's workers occupational health assessment. A farm worker's exposure to the pesticide through inhalation can be estimated based on residue level in air, duration of stay and respiration rate. The objective of this study was to determine the concentrations of pesticide in the air within the farm before and after the application of pesticide.

Materials and methods

Experimental plots and pesticide treatment

The experiments were conducted in three rain shelter farms grown with chrysanthemum, spinach and celery, and chilli respectively *(Table 2).* The plots were treated with a commercial product, namely *Nurelle 505,* which contains chlorpyrifos (45.9%) and cypermethrin (4.6%) active ingredients. The treatment rates of this product in the three plots were 140 ml/200 litres water, 92 ml/200 litres water and 200 ml/200 litres water respectively. This pesticide product was selected because it is commonly used in Cameron Highlands. The relative humidity and temperature of the farms during the experiments were recorded using a digital thermo-hydrometer (SELVISE TH 200, Jules Richard Instruments). The farms' location, structure and pesticide application rates were summarized *(Table 2).*

Air sampler

XAD-4 trap resin method by Hall et al. (1997) was employed. Air was sampled with a pump (air volume sampler) attached with an adsorbent trap XAD-4 resin (Rohm and Haas, through Supelco, Bellefonte, PA), a macroreticular resin employed as the trapping medium. The adsorbent trap was mounted on a vertical iron stand in the centre of the farm at the height of 0.5 m and 1.6 m. The height at 0.5 m is the general height of nostril when the worker is squatting, whereas 1.6 m is the general height of nostril when the worker is standing. In most time, the farm workers are in these two postures (standing or squatting) when they are exposed to the pesticides.

Table 1. Physico-chemical and toxicological data of chlorpyrifos and cypermethrin

	Vapour pressure* (mm Hg)	Water solubility* (mg/litre)	ADI** (mg/kg/d)	Pesticide classification
Chlorpyrifos	1.87×10^{-5}	2.0	0.01	Organophosphate
Cypermethrin	1.3×10^{-9}	0.01–0.2	0.05	Pyrethroid

*At 20 °C
**Acceptable daily intake (Lu 1995)
Source: Lyman et al. (1982); Kidd and James (1991)

Table 2. Treatments and conditions of field trials in Cameron Highlands

Farm	Location	Farm description	Pesticide (commercial brand)	Active ingredient	Active ingredient (%)	*Dosage of pesticide
1	Kg. Raja	Rain shelter (chrysanthemum - medium height plant)	*Nurelle 505*	Chlorpyrifos Cypermethrin	45.9 4.6	140 ml/200 litres water
2	Kg. Raja	Rain shelter side netting (spinach & celery - low height plant)	*Nurelle 505*	Chlorpyrifos Cypermethrin	45.9 4.6	92 ml/200 litres water
3	Kuala Terla	Rain shelter (chilli - high height plant)	*Nurelle 505*	Chlorpyrifos Cypermethrin	45.9 4.6	200 ml/200 litres water

*Motorized sprayer

Preparation of the adsorbent trap

Glass wool was inserted into the glass column. A sample of 3 g XAD-4 resin was weighed and transferred into a glass column (length 100 mm and internal diameter 16 mm). The glass column was sealed with aluminum foil followed by parafilm.

Sampling of air

The aluminum and parafilm were unwrapped from the glass column containing resin. The glass column was fitted into air volume sampler. The air volume sampler was turned on for one hour at the rate of 10 litres air/min. At the termination of air sampling, the glass column was again wrapped with aluminum foil followed by parafilm. The glass column was then kept in an icebox and sent back to the laboratory for analysis. The first sampling period started before the application of pesticides (8–9 am), while the post-treatment samplings were carried out at three intervals, namely, 10–11 am or 9–10 am (second and third day), 2–3 pm and 6–7 pm intervals.

Extraction method

The extraction method was according to Hall et al. (1997). The resin on top and glass wool were transferred from glass column into a 250 ml conical flask. About 60 ml of acetone/toluene mixture (9:1) was added into the flask. The flask was then placed in an orbital shaker and shaken for one hour at 100 rpm. The extract was passed through a glass column (length 200 mm and internal diameter 30 mm) containing 30 g of Na_2SO_4. The Na_2SO_4 filtered extract was collected at the bottom of the glass column in a 250 ml conical flask. Another 20 ml of acetone was added into the glass column to flush out any remaining residue in Na_2SO_4. The collected extract was then concentrated to 1 ml by using a rotary evaporator before it was injected into a gas chromatography equipped with an electron capture detector for quantification.

Extraction efficiency

The glass columns packed with resin were spiked with the insecticides at the quantity of 10 mg and 1 mg. The solvent was allowed to evaporate to room temperature. After evaporation, the pesticides were extracted from the spiked samples using the same extraction method as described above. The pesticides recovered (% recovery) indicate the efficiency of the extracting method.

Trapping efficiency
Trapping efficiency indicates the effectiveness of the adsorbent (XAD-4 resin) in capturing pesticides from the air. A glass wool spiked with 10 mg of pesticides was placed 20 mm above the resin of the packed glass column. The glass column was then attached to the air volume sampler. The air volume sampler was switched on for 60 min at the flow rate of 10 litres air/min. After the sampling of air was done, the glass wool (above the resin) and resin were extracted separately.

The trapping efficiency of the resin was determined from this formula:

$$\text{Trapping efficiency} = \frac{\text{Pesticides recovered from resin}}{\text{Pesticides spiked} - \text{pesticides recovered from glass wool}} \times 100$$

Residue determination by gas chromatography (GC)
The final extracts were analysed by gas chromatographs (Hewlett Packard 6890) equipped with Electron Capture Detector (ECD). For GC-ECD, a HP-5 capillary column (length 30 m, internal diameter 0.32 mm and film thickness 0.25 mm) was employed. An initial column temperature of 50 °C was retained for 3 min and raised to 200 °C at a rate of 50 °C per minute. Injector and detector temperatures were maintained at 250 °C and 350 °C respectively. Helium (99.9% purity) was used as carrier gas with a flow rate of 1.5 ml/min. The make up gas was nitrogen (99.9% purity) at a flow rate of 60 ml/min.

Statistical analysis
Single Factor ANOVA analysis was used to determine whether the residue concentrations at the height of 0.5 m and 1.6 m are significantly different from each other.

Results and discussion
Extraction and trapping efficiency
The recoveries for the extraction efficiency ranged from 78.6–125.3% with relative standard deviation less than 14% indicating the extraction method was effective *(Table 3).* Trapping efficiency of chlorpyrifos at the spiked rate of 10 μg was 93.4% with relative standard deviation of 4.5%. Trapping efficiency of cypermethrin was not assessed due to the non-volatility of the compound. Cypermethrin was found to be in the same amount in the glass wool even at the end of the experiment. This demonstrates the non-volatility of cypermethrin. Therefore it was hard to determine trapping efficiency of cypermethrin in this study. The limit of quantification for both chlorpyrifos and cypermethrin was 0.1 $\mu g/m^3$.

Field trial
For all three experimental farms, pesticide concentration levels in air before the application were below the limit of quantification (<0.1 $\mu g/m^3$). After the application, the chlorpyrifos concentrations in the air were found to range from 0.1 to 8.9 $\mu g/m^3$ *(Figure 1).* Higher residue of chlorpyrifos (2.4–8.9 $\mu g/m^3$) was detected in the samples collected immediately after the application. The residue levels were,

Table 3. Extraction efficiency of chlorpyrifos and cypermethrin

Spiked rate (mg)	R1 (%)	R2 (%)	R3 (%)	Average (%)	SD	%RSD
Chlorpyrifos						
10	101.5	79.3	82.5	87.8	12.0	13.7
1	120.2	113.1	109.7	114.3	5.4	7.2
Cypermethrin						
10	98.2	78.6	82.7	86.5	10.4	12.0
1	125.3	117.3	121.2	121.3	4.0	3.3

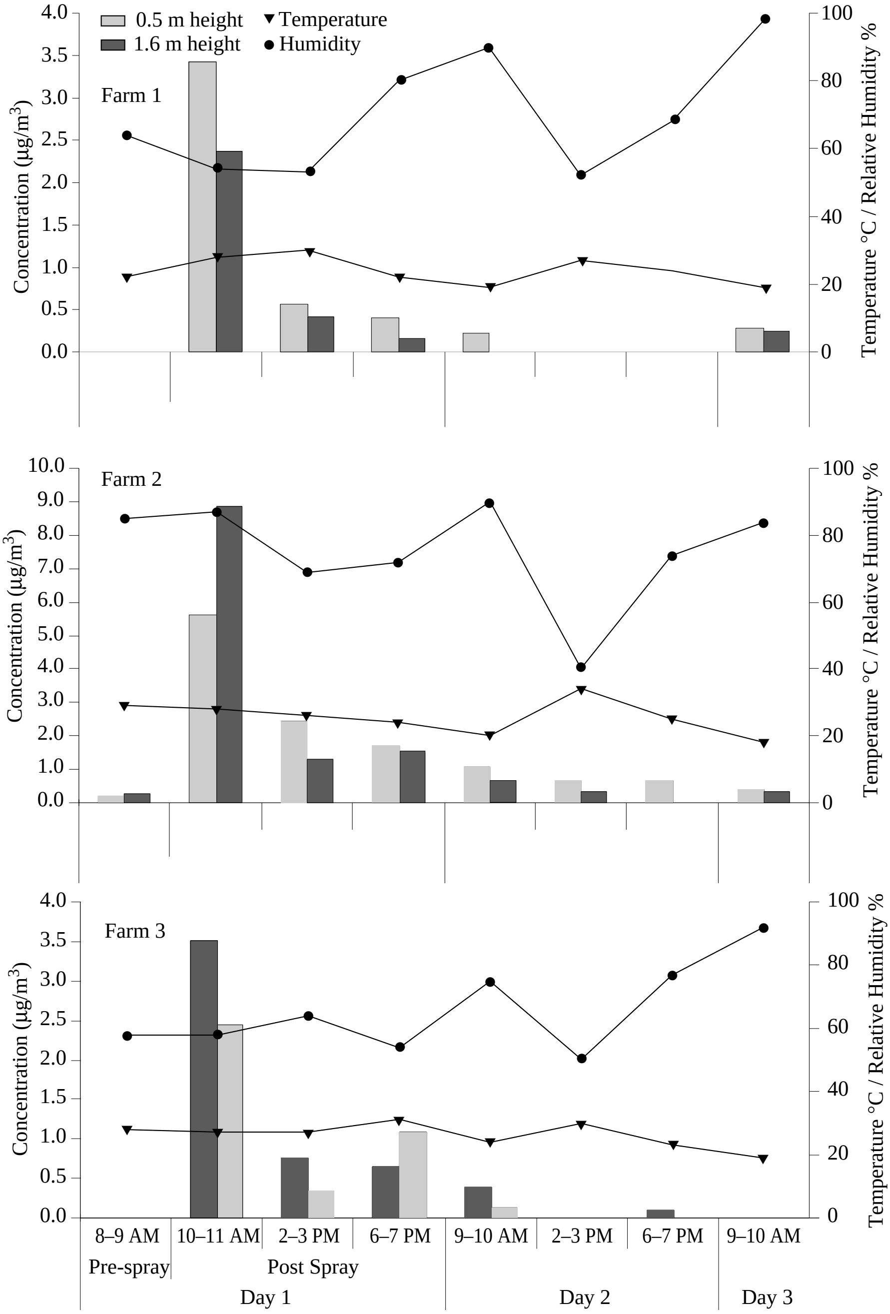

Figure 1. Chlorpyrifos residue in Farm 1, 2 and 3

however, rapidly decreased to more than 50% within four hours after application. At the second day after the application, the observed chlorpyrifos residues ranged from 1.1 μg/m^3 to less than limits of quantification. The decline of the residue concentrations in air was probably due to the dissipation effects by air flow and wind factor.

Cypermethrin residue was not detected in all the samples collected from the trials. The absence of cypermethrin in air may be attributed to its low volatility. This is in line with the finding of other researchers (Siebers and Mattusch 1996), in which cypermethrin concentrations in the air of greenhouses were found to be less than limit of quantification for the day of application and the following days. Experimental results of Bacci et al. (1987) suggested that cypermethrin did not volatize from the contaminated soil to the surrounding air.

Single Factor ANOVA analysis indicated no significant difference (p >0.05) in concentration between samples collected at 0.5 m and 1.6 m heights for all three experimental farms. The p values were 0.67, 0.96 and 0.73 for Farm 1, 2 and 3 respectively. The recorded relative humidity of the farms ranged from 52% in the morning to 98% at night and the temperature varied from 18–34 °C. However, neither relative humidity nor temperature shows obvious correlation with the residue levels.

Figure 2 shows the comparison of average concentration of chlorpyrifos residues at 0.5 m and 1.6 m heights among different farms. No obvious difference in concentrations between Farm 1 and Farm 3 was noticed. However, chlorpyrifos concentrations in Farm 2 were comparatively higher than the others, suggesting that side netting in Farm 2 could have reduced the dissipation effects of pesticide residues in the air due to the limitation of airflow. Efforts in studying the efficacy of pesticide in rain shelter farm may be initiated in order to assess the suitability of spray volume and effectiveness of sprayer, since such information could be used to reduce exposure risk and cost.

In order to estimate the exposure risk of the workers in the farms, a calculation method based on BBA-guideline I, 3-3 (Siebers and Mattusch 1996) on the operator safety resulted in admissible concentrations was used. The observed residue data was

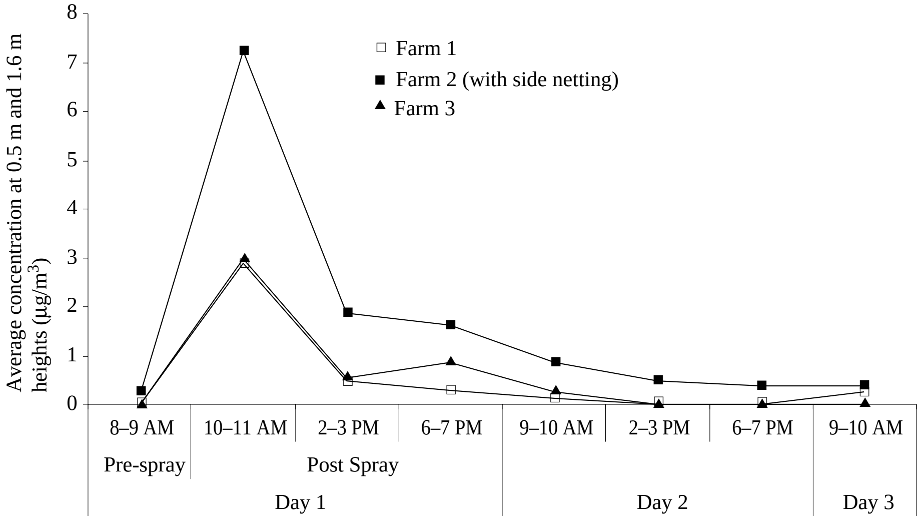

Figure 2. Average concentration of chlorpyrifos residue in air (Comparison between farms)

compared with acceptable daily intake (ADI). Assuming 10 m^3 (Siebers and Mattusch 1993) as respiration rate per working day (8 hours) and using the highest average concentration of chlorpyrifos found in a day (7.24 $\mu g/m^3$), the inhalation per working day is 72.4 μg of chlorpyrifos. As the ADI of chlorpyrifos is 0.01 mg/kg/d *(Table 1)*, a worker with 60 kg body weight will be able to sustain 600 μg of chlorpyrifos in a day without any harmful effects. This acceptable concentration (600 μg) is far higher than the estimated inhalation (72.4 μg). Although this calculation predicts the exposure risk of the worker, it does not reflect worst-case situation and other toxic effects like dermal irritation. A thorough toxicological assessment has to be conducted in order to determine the actual health risk due to the exposure. However, it is recommended that pesticide with low volatility be used, and less dosage of pesticide be applied in enclosed areas such as greenhouses or rain shelters with side netting only after the efficacy of the relevant pesticides has been properly assessed.

Conclusion

A farm with rain shelter with side netting tends to retain higher concentration of pesticide for a longer time as compared to farms with rain shelter only. Chlorpyrifos with moderate volatility was detected in the air during the experiment while cypermethrin with low volatility was not detected. In order to reduce the risk of pesticide exposure especially among the farm workers, it is recommended that pesticides with low volatility be used.

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Abstrak

Kepekatan sisa baki pestisid di udara telah dikaji di tiga kebun di Cameron Highlands. Pestisid yang dikaji terdiri daripada pestisid dengan kadar pemeruapan rendah (cypermethrin) dan kadar pemeruapan sederhana (chlorpyrifos). Kepekatan pestisid tersebut dipantau selama tiga hari selepas penyemburan pestisid dengan menggunakan penyembur berkuasa motor. Kepekatan tertinggi chlorpyrifos yang dijumpai ialah 8.9 $\mu g/m^3$. Sisa baki cypermethrin didapati berada di bawah had kuantifikasi sepanjang kajian. Beberapa jam selepas penyemburan pestisid, kepekatan sisa baki chlorpyrifos berkurangan >50% daripada kepekatan awalnya. Dengan menggunakan analisis ANOVA, tiada perbezaan signifikan dalam kepekatan sisa baki antara sampel yang diambil pada ketinggian 0.5 m dan 1.6 m. Kepekatan sisa baki chlorpyrifos lebih tinggi di kebun pelindung hujan yang dikelilingi dengan jaring.

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