Concentration of Insecticides Cypermethrin Isomer in Total Suspended Particulate in Air of Cameron Highlands, Pahang, Malaysia
(Kepekatan Insektisid Isomer Cybermetrin pada Zarahan Termendap di Udara Cameron Highlands, Pahang, Malaysia)

NORELA SUUlAMAN, TOH LEE FONG, HAZZILA ABDUL SAMAT, ISMAIL SAHID, ROZALI OTHMAN & MAIMON ABDULLAH

ABSTRACT
This study was carried out to determine the concentrations of cypermethrin in total suspended particulate in air in several farming areas of Cameron Highlands. Samples of total suspended particulate were collected using a high volume air sampler (Model Graseby) from six different sampling sites around Cameron Highlands. Laboratory analysis of total suspended particulate was conducted by the standard method. High dosages of cypermethrin were used by farmers in the dry season. Results of the study showed that the concentrations of cypermethrin in total suspended particulate in the air samples were higher during the dry season (May-July 2004) compared to the rainy season (September-October 2004). There was a significant positive correlation between the concentrations of cypermethrin and total suspended particulate \( (p<0.05) \).

Keywords: Cypermethrin; suspended particulate in air

INTRODUCTION
Cameron Highlands supports some of the oldest commercial vegetable farms in Malaysia, producing mainly temperate vegetables, flowers and fruits such as crucifers, roses and strawberries. However, the high humidity and continuous planting season promote the proliferation of crop pests and diseases, thus, most of the farmers in Cameron Highlands use pesticides intensively to protect their crops. While modern agriculture is very productive, its adverse effects on the environment have become increasingly apparent, and are the result of practices aimed at reducing per unit cost of production. This has resulted in increased intensity and more specialized production, with increased emissions of substances that have detrimental effects upon the surrounding ecosystems (Vatn et al. 2006).

Pesticides are widely used to protect crops from pest, to reduce crop yield loss and to increase the comfort and safety of citizens. Although the use of pesticides has resulted in increased crop production and other benefits, there is much concern regarding the ultimate fate of the pesticides (Coupe et al. 2000). One potential path of off-site movement is through the atmosphere. Small amounts of pesticides can be transported over long distances through the atmosphere and deposited into aquatic and terrestrial ecosystems far from the point of application (Majewski & Capel 1995). It has long been recognized that pesticides can become potential air pollutants (Daines 1952). Once they are airborne, the pesticides can be carried by wind drift and deposited through wet or dry deposition processes in remote areas, or undergo atmospheric degradation (Tuduri et al. 2006).

Atmospheric transport can occur in the particulate phase when attached to dust particles, or a combination of both depending on the physical and chemical properties of the pesticide. Particulates comprise a wide range of materials which are solid or liquid in the air (Curtis et al. 2006). The sources of particulates are many and include dust from soil and roads, diesel exhaust, emissions from combustion and industrial processes; construction and
demolition, powdered pesticides, bio-aerosols and volcanic ash (Dickey 2000; Brook et al. 2004). After introduction into the atmosphere, pesticides can be degraded, transported, and redeposited (Coupe et al. 2000). Pesticides can revolatilize repeatedly (Majewski & Capel 1995; Gouin et al. 2004) and depending on their persistence in the environment, can travel over great distances (Shen et al. 2005). Particulates may travel thousands of kilometres in the air across oceans and become deposited upon other continents (Wilkening et al. 2000; Gyan et al. 2005). According to Harnly et al. (2005), pesticides and other volatile organic compounds (VOCs) can travel at significant distances in the air. During application, up to 30-50 percent of the amount applied can be lost into the air (Van den Berg et al. 1999) and this loss may constitute one of the many sources of atmospheric organic contamination (Samsonov et al. 1998).

Cypermethrin is a type II pyrethroid pesticide, widely used in agriculture and other environmental applications (Institoris et al. 1999). Pyrethroids are the synthetic analogues of natural compounds derived from the chrysanthemum flower. These compounds are among the most effective and safe natural insecticides known because of their selective activity on insects and low toxicity for mammals and birds (Dent 2000). The insecticidal character of pyrethroids is due to the chrysanthemic acid group in their structure (Mak et al. 2005). Pyrethroids are considered as contact poisons, affecting the insect nervous system, opening the sodium channels and polarizing the neuronal membranes. These pyrethroids are now being used worldwide as insecticides in agriculture, forestry, public health and household application because of their selective insecticidal activity, rapid biotransformation and excretion by the mammalian catabolic system and their non-persistence in the environment. Despite the fact that the most recent pyrethroids are also the most stable, they are still photodegraded and biodegraded considerably faster than the persistent chlorinated insecticides (Galera et al. 1996). Persistence and transport of a pesticide in the atmosphere may facilitate exposure to target animals. It is important therefore, to measure pesticide concentrations in air and precipitation so that this pathway can be evaluated (Tuduri et al. 2006).

The objective of this study is to determine the concentrations of cypermethrin in total suspended particulate in air sampled from several farming areas of Cameron Highlands. Data obtained in this study were also compared between the dry season and rainy seasons.

METHODOLOGY

The study area comprised several zones in the agricultural areas of Cameron Highlands. The selected sampling areas are divided into three zones, namely the south zone (Ringlet and Lembah Bertam), central zone (Kea Farm and Kuala Terla) and north zone (Kampung Raja and Blue Valley). (Table 1 & Figure 1)

<table>
<thead>
<tr>
<th>Station</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Altitude (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ringlet</td>
<td>04°24'36 N</td>
<td>101°22'06 E</td>
<td>1200</td>
</tr>
<tr>
<td>Lembah Bertam</td>
<td>04°24'58 N</td>
<td>101°23'45 E</td>
<td>1350</td>
</tr>
<tr>
<td>Kea Farm</td>
<td>04°30'11 N</td>
<td>101°24'42 E</td>
<td>1650</td>
</tr>
<tr>
<td>Kuala Terla</td>
<td>04°32'39 N</td>
<td>101°25'21 E</td>
<td>1320</td>
</tr>
<tr>
<td>Kampung Raja</td>
<td>04°34'02 N</td>
<td>101°25'47 E</td>
<td>1400</td>
</tr>
<tr>
<td>Blue Valley</td>
<td>04°35'05 U</td>
<td>101°25'09 E</td>
<td>1350</td>
</tr>
</tbody>
</table>

Sampling areas are located in the valley floor surrounded by terraced vegetable and flower farms, thus aerial sprayings of the pesticides would tend to be trapped within the vicinity of the area. Thus, the topography of the area in conjunction with air circulation apparently plays an important role in influencing the distribution of the pesticide residues in the air. Air sampling was done in each station for three days using a high volume sampler (HVS) model Graseby continuously in 24 hours at the air rate of 1.13 m³/minute. Sampling was carried out in dry season (May-July 2004) and in rainy season (Aug-Oct 2004). This HVS was equipped with a fibreglass filter paper with 20.4 x 28.1 cm².

After the sampling was done, the filter paper was cut into small pieces with a pair of scissors, then transferred to a 250 mL conical flask. Organic solvent (mixture 90 mL acetone and 10mL toluene in 9:1 ratio) was prepared and poured into the sample flask which was then shaken for 1 hour using Ultrasonic Brunsonik Shaker Model 15. The sample was then filtered through a 0.45µm filter paper and rinsed twice with 20 mL acetone. The sample was filtered again through chromatography column containing 40 g sodium sulphate (dried at 550 °C) and was rinsed twice with 20 mL acetone. The volume of sample was reduced to 5 mL with rotary evaporator. Finally the filtered sample was rinsed twice with 1 mL acetone, and then reduced to 1 mL with a gentle flow of nitrogen. All the prepared samples were analysed for cypermethrin isomer by gas chromatography.

The GC study was carried out using the Agilent Technologies 6890 gas chromatograph equipped with micro electron captured detector (µ-ECD) and the Hp-5 capillary column (30.0 m length, 0.32 µm I.D and 0.25 µm of film thickness). The injection port temperature was set to 90 °C and the detector temperature was set to 290 °C. Carrier gas flow was 1.6 ml/min nitrogen (99%). The oven temperature programme was ramped from 95 °C to final 270 °C (30 °C min-1). The injection volume was 0.4 µL.

RESULTS AND DISCUSSION

The insecticide cypermethrin includes four isomers, cypermethrin I, cypermethrin II, cypermethrin III and cypermethrin IV. Figure 2 shows the calibration curve for all the isomers, while Figure 3 shows the chromatogram of standard solution for cypermethrin (0.1 ppm). There
FIGURE 1. Location of the sampling stations in Cameron Highlands

FIGURE 2. Calibration curve of (a) Cypermethrin 1

\[ y = 18.274x - 0.5517 \]

\[ R^2 = 0.9991 \]
are only three peaks visible in the figure, probably the result of a combination of cypermethrin III and cypermethrin IV peaks at minute 14.896. The retention times of cypermethrin I and cypermethrin II are 14.582 minutes and 14.747 minutes respectively (Figure 3). Study on cypermethrin by Mazlinda (2002) using gas chromatography also showed that there were only three peaks of cypermethrin.

Table 2 and 3 show the concentrations of cypermethrin isomers in total suspended particulate at the sampling stations during the dry and rainy seasons. In the dry season, the range of the concentrations of total cypermethrin, cypermethrin I, cypermethrin II and cypermethrin III in total suspended particulate are 0.737-3.740 ng/m³, 0.177-1.367 ng/m³, 0.181-1.137 ng/m³ and 0.380-1.440 ng/m³ respectively (Table 2), while in the rainy season the concentration ranges are 0.139-2.610 ng/m³, 0.041-1.171 ng/m³, 0.031-0.757 ng/m³ and 0.049-0.682 ng/m³ respectively (Table 3). The highest concentration of cypermethrin I was at Ringlet (1.367±0.307 ng/m³ for the dry season and 1.171±0.537 ng/m³ for the rainy season); whilst the lowest was at Blue Valley (0.177±0.020 ng/m³ for the dry season and 0.041±0.004 ng/m³ for the rainy season) (Table 2 and Table 3).

![FIGURE 2. Calibration curve of (b) Cypermethrin II (c) Cypermethrin III](image)

![FIGURE 3. Chromatogram of the standard solution of Cypermethrin (0.1 ppm)](image)
The concentration of Cypermethrin II in total suspended particulate during the dry season was highest at Ringlet (1.171±0.263 ng/m²) and lowest at Blue Valley (0.177±0.020 ng/m²). Cypermethrin II was also detected at only three sampling stations during the rainy season, namely Ringlet (0.547±0.045 ng/m²), Lembah Bertam (0.362 ng/m²) and Kuala Terla (0.175±0.015 ng/m²). The frequency of detection of cypermethrin II in total suspended particulate was also lower than obtained for the other isomers. Furthermore, the concentration of cypermethrin III during the dry season was highest at Kuala Terla (1.440±0.139 ng/m²) and lowest at Lembah Bertam (0.041±0.004 ng/m²), while the concentration of cypermethrin III during the rainy season was highest at Ringlet (0.682±0.333 ng/m²) and lowest at Lembah Bertam (0.049±0.003 ng/m²) respectively.

The total amount of cypermethrin in total suspended particulate was highest at Ringlet (3.740±0.115 ng/m²) and lowest at Blue Valley (0.320±0.046 ng/m²) in the dry season, but was highest at Ringlet (2.610±0.264 ng/m²) and lowest at Lembah Bertam (0.142±0.016 ng/m²) in the rainy season (Table 2 and 3). NIOSH did not have standardized guidelines pertaining to cypermethrin levels in air. The total amount of cypermethrin in total suspended particulate was highest at Ringlet probably because Ringlet was located in the valley floor surrounded by terraced vegetable and flower farms, thus aerial sprayings of the pesticides would tend to be trapped within the vicinity of the area. Thus, the topography of the area in conjunction with air circulation apparently plays an important role in influencing the distribution of the pesticide residues in the air. During night, air bearing pollutants would move towards the valley, while during day it would move towards the escarpment of the mountain. This phenomenon is due to differences in the cooling gradients of the atmosphere (Perkin 1974; Williamson 1973). However, since the downward drift of the air during night is faster than its upward drift during the day, the result is that the pollutants are not well-distributed and will tend to be trapped in the valley if the pollutants are produced from the surrounding areas (Perkin 1974; Sham 1987).

Statistical test showed there are significant differences (p<0.05) between the concentrations of cypermethrin I in the total suspended particulate sampled from Ringlet, Kampong Raja and Blue Valley areas in the dry season. The concentrations of cypermethrin II showed significant differences (p<0.05) between Ringlet and Blue Valley and between Lembah Bertam and Kampong Raja during the same period. Likewise, the concentrations of cypermethrin III also showed significant differences between Blue Valley

### Table 2. Concentration of cypermethrin (ng/m³) in total suspended particulate during the dry season

<table>
<thead>
<tr>
<th>Station</th>
<th>Cypermethrin I ± Standard deviation</th>
<th>Cypermethrin II ± Standard deviation</th>
<th>Cypermethrin III ± Standard deviation</th>
<th>Σ Cypermethrin ± Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ringlet</td>
<td>1.367±0.307</td>
<td>1.137±0.263</td>
<td>1.237±0.240</td>
<td>3.740±0.115</td>
</tr>
<tr>
<td>L. Bertam</td>
<td>0.863±0.268</td>
<td>0.671±0.192</td>
<td>1.040±0.410</td>
<td>2.573±0.185</td>
</tr>
<tr>
<td>Kea Farm</td>
<td>0.759±0.217</td>
<td>0.695±0.213</td>
<td>1.436±0.292</td>
<td>3.689±0.411</td>
</tr>
<tr>
<td>K. Terla</td>
<td>1.047±0.181</td>
<td>0.979±0.146</td>
<td>1.440±0.139</td>
<td>3.464±0.249</td>
</tr>
<tr>
<td>Kg. Raja</td>
<td>0.547±0.045</td>
<td>0.544±0.039</td>
<td>1.094±0.082</td>
<td>2.186±0.317</td>
</tr>
<tr>
<td>Blue Valley</td>
<td>0.177±0.020</td>
<td>0.181±0.015</td>
<td>0.380±0.046</td>
<td>0.737±0.116</td>
</tr>
<tr>
<td>LSD0.05</td>
<td>0.362</td>
<td>0.303</td>
<td>0.423</td>
<td>0.362</td>
</tr>
</tbody>
</table>

Note:   
- L. Bertam = Lembah Bertam, K. Terla = Kuala Terla, Kg. Raja = Kampong Raja
- The same alphabet in same column indicates no significant difference (LSD0.05)

### Table 3. Concentration of cypermethrin (ng/m³) in total suspended particulate during the rainy season

<table>
<thead>
<tr>
<th>Station</th>
<th>Cypermethrin I ± Standard deviation</th>
<th>Cypermethrin II ± Standard deviation</th>
<th>Cypermethrin III ± Standard deviation</th>
<th>Σ Cypermethrin ± Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ringlet</td>
<td>1.171±0.537</td>
<td>0.757±0.382</td>
<td>0.682±0.333</td>
<td>2.610±0.264</td>
</tr>
<tr>
<td>L. Bertam</td>
<td>0.062±0.000</td>
<td>0.031±0.005</td>
<td>0.049±0.003</td>
<td>0.142±0.016</td>
</tr>
<tr>
<td>Kea Farm</td>
<td>0.087±0.000</td>
<td>0.000±0.000</td>
<td>0.091±0.014</td>
<td>0.178±0.003</td>
</tr>
<tr>
<td>K. Terla</td>
<td>0.085±0.000</td>
<td>0.041±0.000</td>
<td>0.101±0.072</td>
<td>0.227±0.031</td>
</tr>
<tr>
<td>Kg. Raja</td>
<td>0.053±0.004</td>
<td>0.000±0.000</td>
<td>0.086±0.005</td>
<td>0.139±0.023</td>
</tr>
<tr>
<td>Blue Valley</td>
<td>0.041±0.004</td>
<td>0.000±0.000</td>
<td>0.151±0.028</td>
<td>0.192±0.078</td>
</tr>
<tr>
<td>LSD0.05</td>
<td>0.305</td>
<td>0.224</td>
<td>0.205</td>
<td>0.730</td>
</tr>
</tbody>
</table>

Note:   
- L. Bertam = Lembah Bertam, K. Terla = Kuala Terla, Kg. Raja = Kampong Raja
- The same alphabet in same column indicates no significant difference (LSD0.05)
and the other stations during the dry season (p<0.05) (Table2). There are significantly higher concentrations of cypermethrin I, cypermethrin II and cypermethrin III in total suspended particulate from Ringlet during the rainy season (p<0.05) when compared with the other sampling stations in other areas (Table 3).

The concentrations of cypermethrin I, cypermethrin II and cypermethrin III in total suspended particulate were higher during the dry season compared to the rainy season, possibly because it was an active ingredient of most of the pesticides used by the farmers in the dry season (Sivapragasam et al. 1992). The concentration of cypermethrin in the total suspended particulate formed in the atmosphere (Sham 1987), thus accounting for its low values in the rainy season. According to Klingman & Ashton (1982), vaporization of air pollutants would increase with the increase in ambient temperature. The number of days recording high temperatures (> 19 °C) during the dry season was 26/92 days (28.26 %) compared with 1/92 day (1.09 %) during the rainy season, and this could have affected the rates of the pesticide evaporation from soil, water or contaminated vegetation, thus resulting in more cypermethrin molecules being vapourized into the atmosphere (Klingman & Ashton, 1982). The concentration of cypermethrin in the total suspended particulate was higher during the dry season compared to the rainy season, possibly because it was an active ingredient of most of the pesticides used by the farmers in the dry season (Sivapragasam et al. 1992).

**CONCLUSION**

The results of the study showed that the concentration of cypermethrin in total suspended particulate was higher during the dry season compared with rainy season. However, meteorological factors such as volume and frequencies of rainfall also influence the concentration of the pesticides in the farming areas of Cameron Highlands. In addition, the topography of the sampling stations would also influence the levels of cypermethrin in the atmosphere. In addition, further research should be conducted to study the behaviour of new generations of pesticides coming into the market, which are considered to be more effective and biodegradable in the environment.

**TABLE 4. Meteorological data for the dry and rainy seasons**

<table>
<thead>
<tr>
<th></th>
<th>Dry season (May- July)</th>
<th>Rainy season (Aug - Oct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average temperature/day (°C)</td>
<td>18.3±0.6</td>
<td>17.7±0.2</td>
</tr>
<tr>
<td>Average rain/day (mm)</td>
<td>6.0±3.1</td>
<td>10.2±4.8</td>
</tr>
<tr>
<td>Amounts rain/month (mm)</td>
<td>551.6</td>
<td>929.7</td>
</tr>
<tr>
<td>Wind speed/day (m/s)</td>
<td>1.4±0.6</td>
<td>1.5±0.4</td>
</tr>
</tbody>
</table>

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Norela Sulaiman, Toh Lee Fong, Hazzila Abdul Samat, Ismail Sahid & Maimon Abdullah School of Environment and Natural Resources Sciences Faculty Science and Technology Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor Malaysia

Mohd. Rozali Othman School of Chemical Sciences and Food Technology Faculty Science and Technology Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor Malaysia

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