

Sorption, Degradation and Leaching of Cypermethrin in Malaysian Soils

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Abstract : Cypermethrin is one the most extensively used insecticides in agriculture. Its increasing use has resulted in concerns regarding their potential effects on ecosystem and environment. Studies were conducted to characterize the sorption, degradation and leaching of cypermethrin in three common soils of Malaysia. Sorption was quantified using batch experiments. The sorption isotherms could be fitted by the Freundlich equation with K_F values of 33.9-87.0. The sorption decreased in the order of Tarat < Semongok < Balai Ringin soil. Degradation of cypermethrin in soils was quantified by applying 0.35 g m^{-2} commercial grade of cypermethrin to freshly tilled soils. Accelerated cypermethrin degradation was observed in soils especially on first day of cypermethrin application when the amount and intensity of sunlight were high. Cypermethrin was found to remain mostly in top 0-10 cm layer of three soils and only small amount were leached into the subsoils. Cypermethrin was detected in two subsoils at the deepest sampling depth monitored of 50 cm investigated with maximum concentrations of 0.54 mg kg^{-1} . Migration of cypermethrin which sorb strongly to soil organic matter to deeper layer was attributed to macropore transport with soil particles. The half-lives of cypermethrin in topsoils were 13.4-25 days. High dose of cypermethrin treatments for soil pests resulted in pronounced delays of its degradation and the transport of strongly sorbed cypermethrin into subsoils through preferential flow.

Keywords: sorption, degradation, leaching, cypermethrin, Malaysian soils

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Introduction

Cypermethrin [(RS)- α -cyano-3phenoxy benzyl(1RS)-cis,trans-3-(2,2-dichlorovinyl)2,2-dimethyl cyclopropane carboxylate] is a highly hydrophobic insecticide with low solubility of $4 \mu\text{g L}^{-1}$ in water. Cypermethrin has a corresponding high octanol-water partitioning coefficient ($\log K_{ow}$ of 6.6) indicating that it has a high affinity for sorption to soil organic matter (Tomlin, 1994). Even though it possesses relative non persistence in the environment, non-toxicity to mammals and comparatively low application rates for insect control, it is extremely toxic to fish and aquatic invertebrates (Bradbury and Coats, 1989). The sorption of pesticides in soil not only governs their bio-efficacy, but also influences their degradation and leaching. Sorption behaviour of pesticides is affected by soil properties and pesticide characteristics. Thus, the determination of partitioning characteristics of pesticides between soil and water phase is essential for the assessment of their environmental fate. The pesticide sorption properties have been extensively studied for temperate soils and climates (Liu *et al.*, 2009; Cook *et al.*, 2004). However, relatively sparse data are available on tropical soils (Parkpian *et al.*, 1998; Oliveira *et al.*, 2001). Sorption of pesticides on temperate soils have been reported for cypermethrin (Kumari and Singh, 1993).

Field studies on pesticides in humid tropical soils have been reported (Laabs *et al.*, 2000, 2002; Ciglasch *et al.*, 2006; Chai *et al.*, 2009a, b). Field dissipation of pesticides in humid tropical topsoils was rapid. For soil with no vegetation, half-lives of 0.4 to 20 days were reported for various types of pesticides (Laabs *et al.*, 2000, 2002; Chai *et al.*, 2009a). Shorter half-lives of 1.4 – 9.4 days were reported for soils with crops or vegetation, even though pesticides were applied repeatedly (Chai *et al.*, 2009b). Fast initial pesticide dissipation in humid tropical soils was attributed to surface losses through runoff, volatilisation, and photodegradation (Rudel, 1997). Slower disappearance thereafter was related to abiotic and microbial degradation in the soil (Wu and Nofziger, 1999). Higher precipitation and soil moisture also accelerated dissipation of pesticides in humid tropical soils (Laabs *et al.*, 2000). In laboratory studies, the half-lives for cypermethrin in soils were 17 days (Gu *et al.*, 2008). However, shorter field half-lives of 5 days were reported for other pyrethroid pesticides, λ -cyhalothrin in tropical soils (Laabs *et al.*, 2000). The aims of this study were to characterize the sorption, degradation and leaching of cypermethrin in three soils after high dosage application for pests control in soils.

Materials and methods

Reagents & chemicals

Cypermethrin standard (98 %) was obtained from Ehrenstorfer, Germany. Analytical grade sodium sulphate, acetone and n-hexane were purchased from J.T. Baker, USA.

Apparatus and Instrumentation

An orbital Shaker (Lab-line Instruments Inc., USA) was used for shaking the soil suspensions during extraction. A Rotavapor RE 111 rotary evaporator (Switzerland) coupled to a Buchi 461 water bath (Switzerland) and a refrigerated cooler (Polyscience, USA) was used to concentrate extracts. An Agilent Model 6890 gas chromatograph (GC) equipped with an electron capture detector (ECD) was used for the determination of cypermethrin.

Batch equilibrium studies

Cypermethrin solutions ($0.1 - 5.0 \text{ mg L}^{-1}$) were added to 2 g dried soils in a 50 mL teflon tube and left for 20 min for the solvent to evaporate. Twenty mL of calcium chloride solution (0.01 M) was then added and the soil solutions were shaken on an orbital shaker at 150 rpm for 24 hr to achieve equilibrium. The contents were centrifuged at $10,000 \times g$ for 20 min. Ten mL of supernatant solution was taken and extracted twice with 50 mL dichloromethane in a separating funnel. The extracts were combined, dried with 10 g sodium sulphate, preconcentrated and the cypermethrin was determined by GC-ECD. The emptied flasks were rinsed twice with 20 mL n-hexane to remove the remaining cypermethrin adhered to the wall and the extracts were concentrated and determined separately to account for cypermethrin sorption on flasks.

Degradation studies

Soils

The experiments were conducted at three sites, namely, Balai Ringin (N $01^{\circ} 02' 48.9''$, E $110^{\circ} 48' 21.7''$), Tarat (N $01^{\circ} 12' 01.9''$, E $110^{\circ} 31' 15.3''$) and Semongok (N $01^{\circ} 23' 05.9''$, E $110^{\circ} 19' 44.7''$) located in Kuching, Sarawak. The experimental sites were situated 140, 36 and 1 km from the laboratory, respectively. The respective soils are classified as a Typic Kandiodult (fine, mixed, isohyperthermic), a Typic Udorthent (clayey, siliceous, isohyperthermic), and a Typic Paleudult (very fine, mixed, isohyperthermic) according to Soil Taxonomy (Soil Survey Staff, 1999).

Climate

The mean air-surface temperatures at the experimental sites were $23.8 - 28.9^{\circ}\text{C}$. The precipitation recorded (Rimco Tipping Bucket, Australia) at Balai Ringin (79 mm, July; 209 mm,

August; 190 mm, September) and Tarat (213 mm, October; 265 mm, November; 654 mm, December) was lower than that at Semongok (370 mm, November; 601 mm, December; 603 mm, January). Precipitation intensities were very variable with highest intensity of 120 mm d^{-1} . Sunshine hours differed among the sites with the highest number of hours recorded at Balai Ringin (average of 6.7, 5.7 and 3.0 h for July, August and September), while Tarat (average of 2.5, 3.9 and 4.0 h for October, November, December), and Semongok (average of 4.0, 4.0 and 2.3 h for November, December, January) had less sunshine.

Experimental design and cypermethrin treatment

A commercial grade of Agent 505 (cypermethrin, 4.59 % w/w; Hextar Chemical, EC) was used in the present investigation. All vegetations were removed from the plots and the top 20 cm of soil was ploughed manually using a hoe following farmers' practice 1 week before spraying. Fifteen liters of diluted Agent 505 (5 mL L^{-1} ; density 1.1 g mL^{-1}) solutions were sprayed evenly onto three plots of soil, with each plot measuring $1.2 \text{ m} \times 3 \text{ m}$, using a knapsack sprayer with a cone nozzle (Knapsack, Malaysia). Due to travel distances from the laboratory, spraying was carried out at 11:00, 10:00 and 09:00 am at Balai Ringin, Tarat and Semongok, respectively. The cypermethrin treatments resulted in the addition of 0.35 g m^{-2} . The experiments were conducted using randomized block designs with three replicates for each cypermethrin treatment and a further control treatment. Buffer strips of 1.0 m were planted with maize to prevent pesticide spray drift.

Soil sampling and pesticide analysis

Soils were sampled (1 kg) at depths of 0 – 10, 10 – 20, 20 – 30, and 30 – 50 cm starting from day 0 (2 hours after spray) to 98 for cypermethrin residue analysis. For each plot, 3 samples were taken using a core sampler (Ejikelkamp, The Netherlands). The soil samples from different plots were combined, mixed and three composite samples were taken for analysis. For the analysis of cypermethrin in soil, soil samples (10 g) were weighed into a 500 mL shaking glass flask. Double deionized water (10 mL) and hexane:acetone (1:1) (150 mL) were added to the flask and the resulting mixture was shaken for one hour on an orbital shaker at 300 rpm. The extract was left to settle and then filtered through a glass filter paper (Whatman GF/C, $1.2 \mu\text{m}$) into a receiving flask. The filtrate was evaporated to almost dryness on a rotary evaporator at 40°C and made up with n-hexane (10 mL). The final extract ($2 \mu\text{L}$) was injected into GC-ECD for determination of cypermethrin. Good recoveries of 80.0 – 101.2 % with standard

deviation of less than 8.3 % were obtained for the cypermethrin in the three soils (Chai *et al.*, 2007).

Data Analysis

The sorbed amount of cypermethrin (q) to soil was calculated as the difference between the initial (C_o) and final (C_e) solution concentrations:

$$q = (C_o - C_e) (V/M) \quad (1)$$

Where, q is given in units of mg kg^{-1} , while solution concentrations are in units of mg L^{-1} . V is the volume of solution (mL), and M is the mass of soil (kg). The sorption data were fitted to the following Freundlich equation:

$$q = K_f C_e^{1/n} \quad (2)$$

Where, K_f is Freundlich sorption parameters with unit $\text{mg}^{(1-n)} \text{kg}^{-1} \text{L}^n$. $1/n$ is dimensionless. Absorption isotherms were calculated using the linearized form of Freundlich equation. The distribution coefficient (K_d) for pesticide was calculated based on the following equation:

$$K_d = q / C_e \quad (3)$$

To determine the sorption affinity of pesticide to organic matter in soil, the K_d value was normalized to the organic carbon content of each soil using the following formula:

$$K_{oc} = (K_d / \% \text{OC}) \times 100 \quad (4)$$

Analysis of variance was performed using a generalized linear model at $p < 0.05$ level (SAS Institute, 1999).

The pesticide dissipation was modeled using first-order kinetics; $C_t = C_o e^{-kt}$, where C_t is the concentration at time t , C_o is the initial concentration and k is the rate constant. Curve fitting was performed using a non-linear least squares regression analysis of residue

concentration against time using TableCurve (Systat Software Limited, U.S.A).

Results

Soil characteristics

The three soils used in this investigation were all acidic soils with pH of 4.8 – 5.6 (data not shown). There was not much difference in the contents of carbon in organic matter (OM) among the three soils (1.4 – 2.2 %). Balai Ringin soil has comparatively lower cation exchange capacity (2-3 times) and clay content (2-4 times), compared to Tarat and Semongok soils. The clay fraction is dominated by kaolinite and a vermicullitic phase; in addition the less weathered Tarat soil contains illite.

Sorption isotherms

Recoveries of cypermethrin in soils were $89.13 \pm 3.67 \%$ (data not shown). The sorption of cypermethrin to three soils was in accordance with the Freundlich sorption equation with r^2 values > 0.93 (Table 1). The K_f values calculated for the soils were in agreement with the K_d values. The Freundlich constant, n , was unity for Semongok soil, indicating that the sorption isotherms were linear. Non-linearity was observed for Balai Ringin and Tarat soils. K_f and K_d values for cypermethrin were two times higher for Balai Ringin and Semongok than Tarat soil. After normalizing the K_d values with their organic carbon (OC) content, the K_{oc} for cypermethrin in Balai Ringin and Semongok soils were 2-2.5 times higher than Tarat soils. This indicated that other factors other than organic carbon were responsible for the sorption of cypermethrin to the soils. Linearity of cypermethrin sorption isotherms over the range studied in three soils suggested that sorption sites were not saturated (data not shown). The amount of cypermethrin sorbed continued to increase in the solution.

Table 1 : Distribution coefficient (K_d), Freundlich coefficients (K_f) and coefficient of determination (r^2) for sorption of cypermethrin in soils at 25 °C.

Soil	K_f	n	r^2	K_d	r^2	K_{oc}
Balai Ringin	87.1 ^a	0.8	0.99	76.4 ^a	0.98	3473 ^a
Tarat	33.9 ^b	1.4	0.97	34.5 ^b	0.93	1917 ^b
Semongok	72.0 ^a	1.0	0.98	68.5 ^a	0.96	4893 ^a

K_d K_{oc} mL g^{-1} ; K_f $\text{mg}^{(1-n)} \text{kg}^{-1} \text{L}^n$; *Different letters in superscript indicate the coefficients are significantly different ($p < 0.05$)

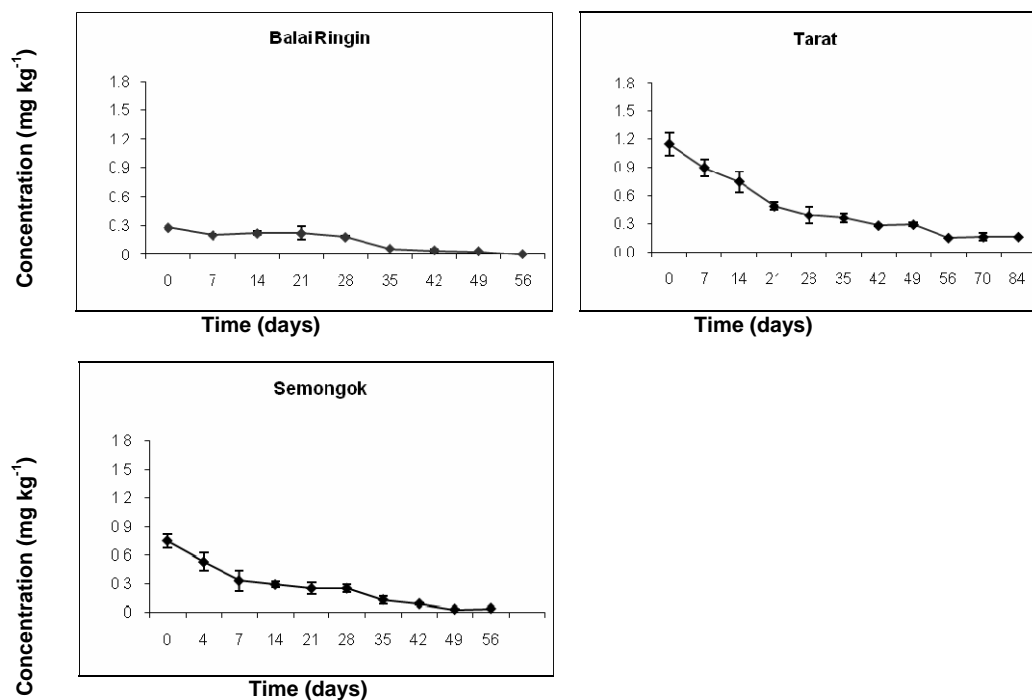


Figure 2 : Dissipation of cypermethrin in Balai Ringin, Tarat and Semongok topsoil (0-10 cm) soil profile. Points are linked with straight line. Vertical bars indicate standard deviation ($n = 3$).

Pesticide Degradation

Cypermethrin was found mostly in the top soil (0-10 cm) of Balai Ringin, Tarat and Semongok soils (Figure 2). The cypermethrin concentrations found in top soils were low (0.22-1.15 mg kg⁻¹) but persisted in soil. The cypermethrin residue disappeared from the top soils of Balai Ringin, Tarat and Semongok soils at day 63, 98 and 63, respectively. Cypermethrin concentration found at day 0 in Tarat soil was 1.15 mg kg⁻¹; about one to five times higher than Semongok and Balai Ringin soils. For Balai Ringin soil, cypermethrin in the range of 0.18 – 0.32 mg kg⁻¹ persisted in soil from day 0 to day 28. Distinct cypermethrin degradation was only observed after day 28 onwards. At day 42, only 27.3 % (0.06 mg kg⁻¹) of the initial residue remained in the soil. For Tarat and Semongok, cypermethrin also degraded gradually from its initial concentrations. At day 28, 27.7 % (0.39 mg kg⁻¹) and 24.5 % (0.13 mg kg⁻¹) of the cypermethrin remained in the two soils, respectively.

Lower amount of cypermethrin (0.01-0.54 mg kg⁻¹) were found in the subsoils (data not shown). In subsoils, cypermethrin was detected from the first sampling at day 0 (two hours after pesticide application) down to 50 cm depth for Balai Ringin and Tarat soils but only until 30 cm depth for Semongok soil. Cypermethrin was only detected in subsoil until day 49 for Balai Ringin and Tarat soils but shorter periods of 35 days for Semongok soil. Higher cypermethrin concentration in Tarat topsoils resulted in higher cypermethrin concentration in Tarat soil (0.01-0.54 mg kg⁻¹) compared to Balai Ringin (0.01-0.22 mg kg⁻¹) and Semongok soils (0.01-0.22 mg kg⁻¹). Cypermethrin was only found at day 0, 7, 28, and 35 until 30 cm in Tarat soil.

The degradation rate constants, half-lives and regression coefficients for cypermethrin in Balai Ringin, Tarat and Semongok top soils are shown in Table 2. The cypermethrin degradation followed first-order kinetics ($r^2 > 0.83$). The half-lives for cypermethrin in Balai Ringin, Tarat and Semongok soils were 25.0, 20.4 and 13.4 days, respectively.

Table 2 : Degradation rate constants (k), half-lives ($t_{1/2}$), and regression coefficients (r^2) for cypermethrin in three soils

Soils	Regression coefficient, r^2	Rate constant, k (days ⁻¹)	Half-life, $t_{1/2}$ (day)	$t_{1/2}$ 95 % cl (day)
Balai Ringin	0.83	0.028±0.006	25.0	20.7-31.5
Tarat	0.97	0.034±0.002	20.4	19.1-21.9
Semongok	0.92	0.052±0.008	13.4	11.6-15.8

Discussion

The K_f values of 33.9-87.0 and K_d value of 34.5-76.4 L kg⁻¹ for cypermethrin obtained in our studies were consistent with results reported by Kumari and Singh (1993). The later reported K_f values for cypermethrin were 33.1 – 66.1 at 30°C in four different soils with OM of 0.52 – 1.84 % and pH of 6.3 – 9.0. However, lower K_d values of 9.4 and 16.2 L kg⁻¹ were reported for cypermethrin in Red soil and Black soils, respectively (Liu *et al.*, 2009). The amount of OM of soils was not reported. Different sorption of other pyrethroid pesticides has also been reported. Zhou and Rowland (1997) reported K_d values of 2100-2600 for permethrin on estuarine sediments with 2.1-3.2 % OC. In contrast, Cooke *et al.* (2004) reported K_d values of 26-91 for permethrin in agricultural soils with 1.8-3.5 % OC. Ismail and Kalithasan (2004) reported K_f values of 11.1-51.8 for permethrin in six soils with OM of 1.0-3.2%.

Higher air temperature and intensity of solar radiation resulted in lower initial cypermethrin concentrations (0.32 mg kg⁻¹) in the top layer of the Balai Ringin soil when compared to the Tarat and Semongok soils, which had initial concentrations of 1.15 mg kg⁻¹ and 0.75 mg kg⁻¹, respectively. The mean air surface temperature on day 0 at Balai Ringin was higher (28°C) when compared to the Tarat (26°C) and Semongok (25.2°C) soils. The intensity of solar radiation at the three experimental sites was likely to be highest at Balai Ringin and lowest at Semongok, as spraying was carried out at 11:00, 10:00 and 09:00 hour at Balai Ringin, Tarat and Semongok, respectively. Furthermore, the number of hours with sunshine on day 0 differed greatly at the three experimental sites with 6.7, 1.5 and 2.6 h for Balai Ringin, Tarat, and Semongok, respectively (data not shown). The amount of cypermethrin applied to the soils on day 0 was 0.35 g m⁻². The estimated amounts of cypermethrin detected in the 0 – 50 cm depth of the soils at Balai Ringin, Tarat, and Semongok at day 0 were 0.06, 0.39 and 0.1 g, respectively. Hence, the mass balance of cypermethrin shows that a high percentage of cypermethrin had initially evaporated or photodegraded in the Balai Ringin (82%) and Semongok soils (71%) compared with the Tarat soil (0%).

Many pesticides are susceptible to photodegradation and volatilization (Rudel, 1997). Volatilization losses also increase with increasing temperature and relative humidity (Grass *et al.*, 1994), which are typically around 25 – 28°C and about 80% at the experimental sites. Even though, cypermethrin has low vapour pressures of 8.7×10^{-4} mPa at 25°C, photochemical decomposition of cypermethrin has been reported in the laboratory studies (Worthing and Hance, 1991). Due to higher concentration at Tarat soil, cypermethrin only

dissipated completely in 98 days compared to 63 days for Semongok and Balai Ringin soils. Relative low concentrations of cypermethrin detected on day 0 (<1.15 mg kg⁻¹) were due to the lower active ingredient in its formulation (4.59%).

Cypermethrin was less affected by precipitation. This was evidenced from little differences in the rates of cypermethrin dissipation at the three sites. This is consistent with its lower water solubility and higher octanol-water partitioning coefficient resulting in strong bonding of cypermethrin to soil organic matter (Wauchope *et al.*, 1992). The amount of precipitation and its distribution over time differed at the three experimental sites. At Balai Ringin, only 3 mm of precipitation was recorded from day 0 to 16, followed by 22.5 mm at day 17. On the contrary, high rainfall occurred close to day 0 at Tarat (day 2, 55 mm) and Semongok (day 1, 61 mm), when cypermethrin concentrations at top soils were at their highest.

Although cypermethrin is strongly sorbed and has low solubility, it was detected in subsoil of Balai Ringin and Tarat down to a depth of 50 cm, but only down to a depth of 30 cm for Semongok soil. Small amounts of cypermethrin were detected in the subsoils only a few hours after the high volume of pesticide application corresponding to 1.4 mm of precipitation. All top soils had high moisture contents during pesticide application and this may have induced macropore flow, even though ponding infiltration did not take place. Similar observation was also reported (Gjettermann *et al.*, 1997). Thus, the application of high volume of cypermethrin may cause the transport of cypermethrin with particulate materials such as organic matters into the subsoils via macropores flow paths resulted in the detection of cypermethrin at a depth of 50 cm. Similar results have been reported for chlorpyrifos which also has high K_d value (Chai *et al.*, 2009a). Cracks, root channels, earth worm burrows and macropores were present throughout the soil profiles down to 1 m (Chai *et al.*, 2009a). In addition, tilling using a hoe down to 20 cm which is the usual farmers' practice may create cracks and pores especially in the top soil which could further facilitate pesticide migration in solution or as sorbed to particles. Heavy rainfall and loose top soils causes dispersion of soil material in the topsoils and cypermethrin may be transported with particulate materials such as soil organic matter to deeper soil layers.

Konda and Pasztor (2001) observed fast vertical movement of pesticide during and immediately after rainfall in particular at higher pesticide loadings. Fast migration in soils may take place due to colloidal transport in macropores mediated by dissolved organic matter and other particles. In addition surfactants added to the pesticide spraying formulation may

contribute to increased solubility and leaching (de Jonge *et al.*, 1998). The type of soils and preferential flow can contribute to the leaching of pesticides with low solubility such as the pyrethroid pesticides. Deltamethrin was reported to leach down to 40 cm in a clayey soil due to pronounced preferential flow which facilitate particulate-facilitated transport in macropores contribute to enhanced vertical translocation (Laabs *et al.*, 2002). In another study, 80 cm of rain that fell immediately after the application of pesticides moved small fractions of all cypermethrin to a depth of at least 55 cm (Ciglasch *et al.*, 2005). The fast leaching of cypermethrin was due to solute transport resulting from commercial formulation of cypermethrin which contained chemical solubilizers; colloidal transport specific to pyrethroid. Tariq *et al.* (2006) reported preferential flow resulted in small amount of γ -cyhalothrin moved into the 10-30 layer soils.

The half-lives of cypermethrin obtained from our studies were 13.4-25 days. In laboratory studies, the half-lives of cypermethrin in red and sandy soils were 17.1 and 8.1 days, respectively (Gu *et al.* 2008; Liu *et al.* 2007). The half-lives of cypermethrin in soils planted with crop were 5-7 days (Chai *et al.* 2009b). For other pyrethroid pesticides, the average field half-lives of lambda-cyhalothrin and deltamethrin in soils were 5-11 days (Laabs *et al.*, 2000; 2002). Half-lives of cyfluthrin in alluvial soils were 19.3 days (Gupta *et al.*, 2002).

Conclusion

The sorption behaviour of cypermethrin varied among soils. The isotherms could be fitted by Freundlich equation. The cypermethrin remained mostly in the top 0-10 cm of the three soils studied despite the difference in the properties of the soils and high amount of cypermethrin applied. Only small amount of cypermethrin was leached downwards into the subsoils due to particulate transport. The amount and intensity of the sunlight played a crucial role in the photo degradation and volatilization of the cypermethrin applied initially. Degradation was slower when the intensity of the sunlight was reduced. The half-lives of cypermethrin in three soils were Semongok < Balai Ringin < Tarat. For effective pest control in soil, cypermethrin should be applied when there is less sunlight.

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