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Research article

ADSORPTION, DESORPTION AND MOBILITY OF CYPERMETHRIN AND DELTAMETHRIN IN MALAYSIAN SOILS

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ABSTRACT: Laboratory studies were conducted to determine the adsorption, desorption and mobility of cypermethrin and deltamethrin in peat and silt clay soils. Adsorption studies showed that adsorption of cypermethrin and deltamethrin into soil fit the Freundlich adsorption isotherm. The higher Freundlich adsorption distribution coefficients [K_{ads}] for peat soil (205 1/kg: cypermethrin, 431 1/kg: deltamethrin) than silt clay soil (140 1/kg: cypermethrin, 346 1/kg: deltamethrin) indicated that cypermethrin and deltamethrin were more easily adsorbed in peat soil. The observed K_{oc} values of deltamethrin were 539 (peat soil) and 4061 (silt clay soil) while K_{oc} values of cypermethrin were 256 (peat soil) and 1643 (silt clay soil). In the desorption studies, results indicated that desorption of these insecticides was higher in silt clay soil than in peat soil. In the mobility study, the results showed that mobility of these insecticides was greater in peat soil than silt clay soil.
Keywords: Adsorption, cypermethrin, deltamethrin, mobility, soils

INTRODUCTION

The behaviour of pesticides in the soil depends on factors such as the physico-chemical characteristics of the pesticide, the active surface of the soil mineral and organic components, and the amount of the pesticide applied [1]. Adsorption of pesticides by soils has frequently been found to be correlated with organic matter and clay contents. Adsorption is the binding of the chemical to the soil. Pesticides that are strongly adsorbed tend not to leach, but rather are lost with the soil through soil erosion processes. Pesticides that are weakly adsorbed are lost mainly in surface runoff water and percolation. Adsorption of pesticides, therefore, is basic to understanding the behavior of pesticides in soil. In the environment, pyrethroids are usually degraded by one or more biotic and abiotic processes i.e. metabolic degradation by plants, animals and microorganisms and degradation by light (photolysis). There are three main routes of degradation by light in pyrethroids i.e. ester cleavage (splitting the molecule where a carbon atom and an oxygen atom are connected with a double bond), reductive dehalogenation (removal of chlorine, flourine, on bromine atoms) and isomerization (conversion from one isomer to another). Brings et al. [2] reports that cypermethrin has a life-time of 30 days [2]. The degradation of cypermethrin in the soil environment was primarily by microbial action with the principal pathway being cleavage of the ester linkage [3, 4]. Protecting groundwater from pesticide contamination is a high priority. Leaching of herbicides and other pesticides can occur as rainfall or irrigation water moves down through the soil. Leaching potential of various herbicides depends on factors just discussed, solubility, amount and frequency of rainfall, soil adsorption, persistence, and soil texture and structure. These pore spaces are key to water retention and movement through the soil. Organic matter content is the most important variable affecting sorption of pesticides onto soil particles [5]. Soil organic matter also influences how much water the soil can hold before movement occurs. Cypermethrin (RS)-α-cyano-3-phenoxybenzyl (1RS, 3RS, 3SR)-3-(2,2-dichlorovcy)-2,2-dimethilcyclopropanecarboxylate is a synthetic pyrethroid insecticide that has been proven to be effective against pests in cotton, top fruit and vegetables. Its behaviour, bioefficacy, sorption, movement, persistence and degradation in soil, sediment and water have been widely studied [6, 7, 8].

Deltamethrin S- α –cyno-3- phenolxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethilcyclopropanecarboxylate is active against a wide range of insects that attack crops and animals and has been recommended for foliar application on various vegetable and field crops [9]. Its behaviour, bioefficacy, sorption, movement, persistence and degradation in soil, sediment and water have been widely studied [10, 11, 12, 13]. Understanding the adsorption, desorption and mobility of pesticide metabolites is an important aspect of assessing the environmental fate of pesticides. Therefore, this study was carried out to investigate the adsorption, desorption and mobility of cypermethrin and deltamethrin in two different Malaysian soils.

MATERIAL AND METHODS

Cypermethrin and Deltamethrin

Commercial grade of cypermethrin (Kencis® 38.75 g a.i /l) and deltamethrin (Dencis® 12.35 g a.i /l) obtained from AGREVO Sdn. Bhd. was used. Stock solution of 100 µg /ml was prepared by diluting the commercial grade with distilled water. For the calibration curve, the analytical grade cypermethrin (39% trans and 59% cis) and deltamethrin (99.9%) purity were obtained from Chem Service (SUPELCO). Working standard solutions containing 2.0 – 10.0 µg/ml were prepared by appropriate dilution of the standard stock solution of 100 µg/ml with hexane (HPLC grade).

Soil Collection and Analysis

Two different soil types were selected from different locations. The peat soil samples were from an agriculture plot located near Kuala Selangor Agriculture Department, Selangor and silt clay soil samples were collected from a vegetable farm in Kampung Yu, Selangor. The soils were analyzed and classified at the Soil Testing Laboratory of the Department of Geology, UKM. The physico-chemical properties of each soil are given in Table 1. All the samples were collected from a depth of 0-10 cm, air-dried and sieved through a (≤ 2 mm) mesh. The samples were placed in labelled black polyethylene bags, and stored at -4ºC.

Table 1. Physicochemical properties of soil

Physicochemical properties	Peat soil	Silt clay soil
pH	4.16	5.4
% Organic matter	79.96	8.52
CEC (meq/100 g)	33.82	202.6
Sand (%)	3.00	2.85
Silt (%)	-	46.10
Clay (%)	-	51.05
% Water content	52	29.1

Extraction of soil samples

The method used to extract cypermethrin from the soils was based on the technique suggested by Kumari and Singh with minor modifications [14]. The soil sample (20 g) was weighed and then put into a 250 ml conical flask, shaken on an orbital shaker (240 rpm) with distilled water and acetonitrile (150 ml, water:acetonitrile, 1:2) for 30 min. The experiment was replicated thrice. The sample was left to settle for about 1 hr and then transferred into a separatory funnel where 20 ml hexane was added. The sample was then shaken for about 1 min. Then, 50 ml of 4% NaCl was added to the extract. The hexane layer was filtered through 40 g of $NaSO_4$ in a glass column. The sample of the supernatant was collected and filtered through an RC membrane (pore size 0.45 µm) to remove particulates. Finally the extract was evaporated to dryness under a stream of nitrogen gas and reconstituted in 1 ml of hexane prior to GC analysis.

Recovery study

The soil sample (50 g) was spiked with 10 ml of analytical grade cypermethrin or deltamethrin at three concentrations i.e. 5, 25 and 50 mg/kg. After mixing, 20 g of the soil was then extracted for the determination of pesticide residue.

Adsorption/desorption

The adsorption and desorption study conducted was similar to those described by other researchers. A 1 g sample of each soil type was put into centrifuged tubes (15 tubes). Then 10 ml at various concentrations i.e. 50, 75, 100, 125 and 150 µg/ml of cypermethrin or deltamethrin were added. The experiment was replicated thrice.

The samples were shaken for 5 hr for both soil types on an orbital shaker (240 rpm). The time of reaction was chosen from preliminary kinetic studies, which showed that adsorption had reached pseudo-equilibrium. After shaking, the suspensions were centrifuged at 3,500 rpm for 15 min. The supernatants (5 ml) were then transferred into a separatory funnel for the extraction process before determination of the residual level using GC. Desorption was determined on the same samples which were used for the adsorption study. After the supernatant obtained by centrifugation for adsorption had been removed, 10 ml of distilled water was added to the centrifuged flask. The mixture was then shaken for 15 min and centrifuged at 3,500 rpm for 15 min as described above. A 5 ml aliquot was removed from each vial. The process was repeated four times. The supernatants were cleaned up before determination of the level of residue by GC. The equilibrium adsorption coefficient (K_{ad}) was calculated from the Freundlich equation as the ratio of adsorbed concentration to aqueous concentration. Differences between the amounts of cypermethrin or deltamethrin in the initial concentration and the amounts in the supernatant of the samples were considered to be the amounts adsorbed. The herbicide sorption isotherm was calculated using the Freundlich equation;

$$x/m = K\,Ce^{1/n}$$

$$\ln x/m = \ln K + 1/n \ln Ce \qquad \text{(I)}$$

where, K = adsorption /desorption coefficient
x/m = The adsorbed amount (μg/g),
Ce = Solution concentration (mg/L) after adsorption equilibrium,
1/n = constants (slope)

The relationship between the organic matter (OM) content and the adsorption percentage was determined according to equation;

$$Koc = \frac{K \times 100}{\%\,OM} \qquad \text{(II)}$$

where, K_{oc} = the Freundlich OM distribution coefficient
% OM = % organic matter

The logarithmic form of the above equation was fitted by the least square method to the set of experimental data. The K_d and n constants were calculated, and a linear regression analysis was performed to determine the degree of fit between observed data and the Freundlich constants.

Mobility study

PVC tubes, 2.5 cm diameter, were cut into 10-cm lengths and reassembled into a tube of 30 cm. Each column was packed with soil from a single soil type to a depth of 30 cm. The process was repeated three times for each soil type. A 250 g (peat and silt clay soils) air-dried sample of soil was mixed with distilled water to maintain a soil moisture level at 50%. Once the soil columns had settled, soils treated with 50 μg/g of cypermethrin or deltamethrin were placed on top of each soil column. The soil surface in each column was covered with one sheet of Whatman No. 3 filter paper. A flask was placed at the bottom of each column to collect the leachate. The experiment was replicated thrice. After 1 hr, the soil columns were watered with 73.1 ml water (equivalent to 150 mm of rainfall), 98.1 ml water (equivalent to 200 mm of rainfall), and 147 ml water (equivalent to 300 mm of rainfall) respectively. The columns were arranged randomly in the greenhouse. After 24 hr, each column was separated into 3 segments (0-10, 10-20 and 20-30 cm), and the leachate was collected. A 20 g soil sample from each segment was placed in a 250 ml conical flask for the extraction process before determination of the residual level using GC.

Statistical Analysis

The experiment design was a randomized complete block with three replications. Data were averaged and subjected to an analysis of variance and the least significant difference test was calculated at P=0.05 to compare residues means.

GC Analysis

Extracted residues were estimated by a Altech 4890 Gas Chromatograph equipped with electron capture detector (ECD), manual injector and HP-5 Cross linked 5% Phenyl Methyl Siloxane column (30.0 m x 0.32 μm id, 0.25 μm film thickness). The operating temperatures were: detector 300°C, injector port 280°C, oven programmed initially 205°C for 2 min and then increased to 300°C at the rate of 30°C/min and maintained for 4 min.

The carrier gas was nitrogen (N_2, 99%) with a flow rate of 1 ml/min. The volume of injection was 1 µl. There were three replicates and each solution was injected twice. Under these conditions the retention time of cypermethrin were 11.857 min (isomer I), 12.123 min (isomer II) and 12.371 min (isomer III) and retention time for deltamethrin was 18.175 min.

RESULTS AND DISCUSSION

The percentage recovery of cypermethrin in the two soil types are shown in Table 2. The recovery of cypermethrin was highest at 50 ppm in peat and silt clay soil samples. The highest recovery which was obtained for cypermethrin ranged from 80.73% (peat soil) to 83.15% (silt clay soil) at 50 ppm concentration. Similar results were obtained for deltamethrin, with the highest recovery at 50 ppm concentration recording 92.74% and 91.04% in peat and silt clay soils, respectively. At 5 and 25 ppm concentrations the percentage recovery were lowest ranging from 80.01% – 80.14% and 81.5% – 82.5 % for cypermethrin and 88.68% - 84.59% and 89.36 – 85.52% for deltamethrin in peat and silt clay soils, respectively. Adsorption of cypermethrin to the peat (R^2=0.97) and silt clay (R^2=0.98) soils was found to best fit a Freundlich adsorption isotherm. Freundlich adsorption distribution coefficients (K_{ads}) of 205 and 140 kg^{-1} were obtained for the peat and silt clay soils (Table 3), while the corresponding 1/n values were 0.57 and 0.56, respectively. The 1/n values observed for both soils studied were less than unity, implying that less pesticide was adsorbed with increasing concentrations of the pesticide in the soils [15]. The organic carbon partition coefficients (K_{oc}) values of 256 and 1643 kg^{-1} were obtained for the peat and silt clay soils, respectively. Zhou et al. [16] reports that the K_{oc} values obtained for cypermethrin were not constant, rather they varied with the type and extent of organics coatings [16]. The results showed that cypermethrin sorption was slightly better correlated with clay content than the organic carbon content of the soils. This result was in line with Kumari and Singh [14] where they reported that adsorption of cypermethrin was slightly correlated with clay content as compared with the organic carbon content of the soil because K_{oc} values were by and large higher than K_c values [14]. Adsorption of deltamethrin to the peat (R^2=0.91) and silt clay (R^2=0.94) soils was found to best fit a Freundlich adsorption isotherm. The Freundlich (K_{ads}) adsorptions were found to be similar for both soils. K_{ads} values of 431 and 346 kg^{-1} were obtained for the peat and silt clay soils, respectively (Table 3). Similar results were also obtained for 1/n values with 0.5195 and 0.5492 for the peat and silt clay soils, respectively. K_{oc} values for 539 and 4061 kg^{-1} were noted for peat and silt clay soils. The different adsorption affinity of the two pyrethroids is attributed to differences with respect to their physico-chemical properties. Assuming that the pyrethroids are sorbed by hydrophobic sorption it is expected that the most hydrophobic compound, i.e. the least soluble compound or the compound with the highest K_{ow} will sorb most strongly [17]. K_{ow} values for deltamethrin (6.4) and cypermethrin (6.2) showed that the adsorption of deltamethrin was adsorbed most strongly than cypermethrin onto soil particles. Chaaieri-Oudou and Bruun-Hansen reported that the sorption of four pyrethroids followed the order: Lambda-cyhalothrin> Deltamethrin>Cypermethrin> Fenvalerate [18].

Table 2. Recovery study of cypermethrin and deltamethrin from soil.

Concentration (ppm)	Peat soil	Silt clay soil
Cypermethrin		
5	80.01±0.63	81.50±0.95
25	80.14±1.11	82.50±0.88
50	80.73±1.47	83.15±0.70
$LSD_{0.05}$	3.94	3.01
Deltamethrin		
5	88.60±0.04	89.36±0.01
25	84.59±1.02	85.52±0.08
50	92.74±0.04	91.04±0.02
$LSD_{0.05}$	6.60	2.58

The significant desorption of cypermethrin and deltamethrin from peat and silt clay soils suggests strong binding of cypermethrin and deltamethrin onto soil particles of less than 1%. Approximately 0.351 and 0.756% of the adsorbed cypermethrin were desorbed from peat and silt clay soils after four successive desorption processes. Deltamethrin was desorbed approximately 0.243 and 0.362% from peat and silt clay soils after four successive desorption processes. Zhou et al. [16] reported that the sorption experiments showed that about 95% of tefluthrin (pyrethroid group) was sorbed onto soil particles and only a small percentage (<3%) was left [16].

Table 3. Adsorption, desorption and organic carbon distribution coefficients of cypermethrin and deltamethrin in the soil studied.

Parameter	**Peat soil**	**Silt clay soil**
Cypermethrin		
K_{ads} (1/kg)	205	140
1/n	0.5671	0.5563
K_{oc} (1/kg)	256	1643
r^2	0.9678	0.9785
Deltamethrin		
K_{ads} (1/kg)	431	346
1/n	0.5195	0.5492
K_{oc} (1/kg)	539	4061
r^2	0.9123	0.9397

Table 4. The effects of total amount rainfall on the mobility cypermethrin in soil column studied.

Peat soil		
Amount rainfall (mm)	% Movement in soil	% Residue in leachate
150	29.7	0
200	45.2	2.66
300	52.5	8.12
$LSD_{0.05}$	3.95	0.38
Silt clay soil		
150	12.3	0
200	18	0
300	30	0.88
$LSD_{0.05}$	0.73	0.17

Table 5. The effects of total amount rainfall on the mobility deltamethrin in soil column studied.

Peat soil		
Amount rainfall (mm)	% Movement in soil	% Residue in leachate
150	24.7	0
200	22.8	0
300	27.4	1.46
$LSD_{0.05}$	5.81	0.20
Silt clay soil		
150	6.98	0
200	18.7	0
300	22.1	0
$LSD_{0.05}$	0.19	0

The results of the column leaching study are presented in Table 4. The insecticide was consistently more mobile in peat soil than in silt clay soil and the movement of the insecticide depended on the total amount of rainfall. Cypermethrin residues were detected in the leachates of peat soil columns at 200 mm and 300 mm simulated rainfall, whereas, in the silt clay column, residue was only detected in the leachate at 300 mm simulated rainfall. Similar observation was obtained for deltamethrin whereby in the peat soil column, residue was only detected in the leachate at 300 mm simulated rainfall, while no residue was detected in all the silt clay columns studied.
The movement of cypermethrin and deltamethrin was more effective in peat soil. Approximately 52% of applied cypermethrin moved downwards into the peat soil and about 30% was detected in the silt clay column study. Approximately 27% of applied deltamethrin was found in the peat soil compared to 22% in the silt clay column study. Soil organic matter content is generally inversely correlated with pesticide mobility in the soil but the mobility of DCVA and PBAs (pyrethroid degradation products) showed differently [19, 20, 21]. A more effective macro pore flow was also suggested to be the main reason why more pesticides leached in silt soil treated with a small water input [22]. Chatupote and Panapitukul [23] reported that the movement of permethrin and cypermethrin was slower compared to carbofuran, metolachlore and carbendazim in the soils studied [23]. Selim and Zhu reported that cumulative leaching of deltamethrin was small and ranged from only 3 to 8% of that applied [24].

CONCLUSION

The adsorption-desorption studies demonstrate that cypermethrin and deltamethrin possesses a stronger affinity to the silt clay soil than peat soil while mobility evaluation of the two insecticides showed cypermethrin to be highly mobile as compared to the less mobile deltamethrin. While the risk of contamination arising from the use of cypermethrin and deltamethrin appears to be low due to high mobility, the validity of this observation depended on the soil characteristics, properties of insecticides and environmental conditions.

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