Effects of Temperature, Soil Moisture Content and Soil Type on the Degradation of Cypermethrin in Two Types of Malaysian Agricultural Soils

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Abstract: The effects of temperature, soil moisture content and soil type on the degradation of cypermethrin was studied using two agricultural soil types namely peat and silty clay. The cypermethrin residue in the soil was extracted using a mixture of water and acetonitril (ratio 1:2). The final extract was redissolved in hexane prior to GC-ECD analysis. The half-life of cypermethrin decreased from 5.93 to 3.24 weeks when the temperature was increased from 25 to 35°C. Results also showed that the half-life decreased from 6.59 to 2.54 weeks as soil moisture content increased from 40 to 60%. The half-life of cypermethrin in non-autoclaved peat and silty clay soil was lower compared to that in the autoclaved soils. In conclusion, temperature, moisture content and soil type greatly influenced the dissipation of cypermethrin.

Key words: Half-life · Cypermethrin · Persistence · Soils

INTRODUCTION

Information on the degradation of pesticides in soils is vital for the assessment of the fate of the pesticides and their end-products in the environment. Pesticides that are deposited in soil and water may be vulnerable to biotic and abiotic transformations which can affect their persistence in the environment. The potential pathways by which a pesticide might be transported through the soil are volatilisation, surface run-off, leaching and drain-flow. The quantity of pesticide transported depends on the properties of the pesticide, a number of interacting processes within the soil and weather conditions.

Synthetic pyrethroids are a diverse class of more than 1000 powerful, broad-spectrum insecticides used to control insect pests in agriculture, households and stored products [1]. Although their composition is based on the chemical structure and biological activity of pyrethrum, (an extract from plants of the genus Chrysanthemum), the development of synthetic pyrethroids has involved extensive chemical modifications that make the analogues more toxic and less rapidly degraded by light [2]. Synthetic pyrethroids belong to the class of insecticide with advanced toxic properties, meaning they can be applied in very small amounts compared to previously used substances [3]. The history and progress of the development of pyrethroids as insecticides, (from the initial discovery of the insecticidal property of pyrethrum), through the synthesis of analogues of natural pyrethrins, to improvements in the activity and selectivity of the synthetic pyrethroids, has been comprehensively reviewed.

Cypermethrin (RS)-α-cyano-3-phenoxybenzyl (1RS, 3RS, 3SR)-3-(2,2-dichlorovcy)-2,2-dimethylcyclopropanecarboxylate, a synthetic pyrethroid insecticide has been proven to be effective for pest control in cotton, top fruit and vegetables [4-5]. Briggs et al. [6] reported that cypermethrin has a life-span of 30 days. The degradation of cypermethrin in the soil environment was primarily by microbial action with the principal pathway being cleavage of the ester linkage.

Understanding the behavior of pesticide metabolites is an important aspect of assessing the environmental fate of pesticides. Therefore, this study was carried out (i) to determine the effects of various levels of temperature and soil moisture content on degradation rates of cypermethrin under laboratory conditions, using two types of Malaysian agricultural soil.
MATERIALS AND METHODS

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

Two different soil types were selected from different locations. The peat soil samples were obtained from an agricultural plot located near the Kuala Selangor Agriculture Department, Selangor and the silty clay soil samples were collected from vegetable growing areas in Kampung Yu, Selangor. The samples were analyzed and classified at the Soil Testing Laboratory of the Department of Geology, UKM. The physico-chemical properties of each soil type are given in Table 1. All the samples were collected from the 0-10 cm depth, air-dried (30°C, 48 hours) and sieved through a ≤ 2 mm mesh. The samples were placed in labelled black polyethylene bags and stored at -4°C.

The method used to extract cypermethrin from the soil samples was based on the technique suggested by Pang et al. [7] with minor modifications. Each soil sample (20 g) was weighed into a 250 ml conical flask. Distilled water and acetonitrile (150 ml, water:acetonitrile, 1:2) were added, followed by shaking on a reciprocating shaker (Potech Model 719) at 240 rpm for 30 min. The experiment was replicated thrice. The samples were left for 1 hour before being transferred through a separatory funnel. Hexane (20 ml) was added and each sample was shaken for 1 min. NaCl (4%, 50 ml) was then added to the extract and the hexane layer was collected. The hexane layer was filtered through 40 g of Na2SO4 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.

The soil samples (50 g) were spiked with the analytical grade of cypermethrin (10 ml) at three concentrations of 5, 25 and 50 mg/kg. After thorough mixing, from 20 g of soil, hexane extraction was carried out to determine the level of pesticide residue.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Peat soil</th>
<th>Silty clay soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.16</td>
<td>5.49</td>
</tr>
<tr>
<td>% Organic matter</td>
<td>79.96</td>
<td>8.52</td>
</tr>
<tr>
<td>CEC (meq/100 g)</td>
<td>33.82</td>
<td>202.6</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>3.00</td>
<td>2.85</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>-</td>
<td>46.10</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>-</td>
<td>51.05</td>
</tr>
<tr>
<td>% Water content</td>
<td>42.00</td>
<td>29.10</td>
</tr>
</tbody>
</table>

Studies on the effect of temperature on the degradation of cypermethrin in soils was carried out under laboratory conditions (30°C). A 3600 g air-dried sample of soil (peat/silty clay) was treated to obtain a final concentration of 50 mg of cypermethrin/kg soil. Control samples were similarly prepared with no pesticide added. After thorough mixing, 50 g samples of the treated soil were kept separately in 72 polyethylene bags. The bags were divided into four groups and incubated at 1) 25°C with light, 2) 25°C without light, 3) 35°C with light and 4) 35°C without light. The initial water content was 42% and 29.1% for peat and silty clay soils, respectively (Table 1). The soil moisture was adjusted to 40% and 60% field capacity for each soil type. In order to maintain the soil moisture content at 40 and 60% field capacity, the soil in each bag was weighed every 5 days and the weight loss was compensated by adding the appropriate amount of water. One 50 g bag of soil for each temperature level was kept at below 0°C from week 1, 2, 3, 4, 8 and 16. The whole experiment was a randomized-block design (benches being the block) with three replicates. After each week of incubation, samples were removed and air-dried overnight and each soil sample was placed into a flask and treated as described above for the extraction process before the determination of the residual level of the pesticide using GC. The half-lives were derived individually from the slope of the line of best fit, calculated by linear regression analysis of the logarithm of the concentration remaining, against the time of incubation.

A 2700 g air-dried sample of soil (peat and silty clay) was treated to obtain a final concentration of 50 mg of cypermethrin/kg soil. The soil samples were divided into three groups with soil moisture levels of 40%, 60% and at the initial soil moisture content. After mixing, samples of the treated soil were kept individually in 54 polyethylene bags. All the soil samples were incubated at 25/35°C. The bags were weighed weekly and, when necessary, water was added to restore the initial moisture level. After each week of incubation, the soil samples were air-dried overnight, after which, 20 g of the soil was placed into a flask and treated as described above for the extraction process, before determination of the residual level using GC.
A 1800 g air-dried sample of soil (peat/silty clay) was divided into two groups for autoclaving. The soil sample was autoclaved at a pressure of 15 psi and 121°C for 1 hour. Then, 900 g of the soil was treated with cypermethrin to obtain a final concentration of 50 mg cypermethrin/kg soil and kept separately in 36 polyethylene bags. The bags were weighed weekly and, when necessary, water was added to restore the initial moisture level. After each week of incubation, the soil samples were air-dried overnight, after which, 20 g of the soil was placed into a flask and treated as described above for the extraction process, before determination of the residual level using GC. The whole experimental design was a randomized-block with three replicates. All data was subjected to analysis of variance and means were compared (LSD) at the 5% level of significance.

Extracted residues were detected using the Alttech (Agilent) 4890 Gas Chromatograph equipped with the electron capture detector (ECD), manual injector and HP-5 Crosslinked 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. The oven was programmed initially at 205°C for 2 min and then the temperature was increased to 300°C at the rate of 30°C/min and maintained for 4 min. The carrier gas was nitrogen (N2, 99%) with the 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 times for cypermethrin were as follows: 11.857 min (isomer I), 12.123 min (isomer II) and 12.371 min (isomer III).

RESULTS AND DISCUSSION

The percentage recovery of cypermethrin from the two soil types are shown in Table 2. The recovery of cypermethrin was highest at 50 ppm in the silty clay soil samples. The highest recovery obtained for cypermethrin ranged from 74.73% (peat soil) to 83.15% (silty clay soil) at 50 ppm concentration. At 5 and 25 ppm concentration the percentage recovery was lower, ranging from 18-39% and 45-56%, respectively.

Calculated degradation of half-life showed that temperature had significant influence on the degradation rates of cypermethrin in the soils studied (Table 3). The apparent half-life of cypermethrin decreased from 5.46 to 3.25 weeks and 4.25 to 2.98 weeks in the peat soil and silty clay soil when the temperature was increased from 25 to 35°C (dark). In the presence of light, the half-life of cypermethrin in peat soil and silty clay soil decreased from 4.87 to 2.72 weeks and 4.08 to 2.92 weeks, respectively. The results showed that by increasing the temperature by 10°C (25-35°C) the half-life of cypermethrin was reduced by 40.3% (dark) and 44.1% (light).

The degradation rate of cypermethrin in the soils studied increased significantly with increasing soil moisture levels (Table 4). The observed half-life of cypermethrin decreased in peat soil from 5.74 to 2.88 weeks, while in silty clay soil, it decreased from 5.05 to 2.54 weeks as the soil moisture content was increased from 40 to 60%. From the results obtained, the degradation rate of cypermethrin was higher in silty clay soil compared to peat soil. However, at the initial soil moisture it was observed that the half-life of cypermethrin was longer in silty clay soil than in peat soil.
In non-autoclaved and autoclaved peat soil, the half-life of cypermethrin was slightly shorter than that in the silty clay soil (Table 5). The half-life was 5.97 and 3.04 weeks in the silty clay and peat soil respectively. The half-life of cypermethrin in the autoclaved soil samples of both soil types was longer than that in non-autoclaved soil samples. In general, the half-life of cypermethrin in the autoclaved soil of both peat and silty clay was not very different.

Degradation of cypermethrin in the two soil types under laboratory conditions is well described by first order kinetics, with the regression coefficient ($r^2$) being $>0.9$. Results showed that almost 50% of the cypermethrin was lost one week after application. Hill [8] reported that the rate of degradation of pyrethroids in the soil is generally fast, with loss of 50% of the applied material within a few weeks; cypermethrin is degraded very rapidly. The results showed that the range of degradation of the half-life was from 2 to 7 weeks depending on the soil moisture content and temperature. The half-life of cypermethrin was comparatively shorter in the peat soil than in the silty clay soil and ranged from 2 to 6 weeks in the soils studied.

In general, the breakdown of the pesticide was slower at 20°C than at 35°C. Increased degradation rates of many pesticides at higher temperatures is a well established fact [9-10]. There is evidence that pesticide degradation rates increased at higher temperatures which, in most instances, probably reflected increased biological activity. The results clearly showed that cypermethrin was very strongly adsorbed to peat soil, where the high organic matter content could have contributed to the adsorption of the insecticide. The effect of organic matter content on the adsorption of pesticide molecules have been reported by Oppong and Sagar [11].

Soil moisture content seems to be an important factor in the degradation of cypermethrin in the soil [10-13]. Decrease in the half-life at higher soil moisture levels may be the result of weak adsorption of the pesticide molecules by the soil particles. At higher soil moisture levels, water molecules compete with the pesticide for adsorption sites on the soil colloids and cause an increase in the pesticide concentration of the soil solution, making it more readily available to soil microbes. Smith et al. [14] reported that degradation of cyfluthrin (pyrethroid group) increased significantly with increasing soil moisture levels.

The degradation of cypermethrin was slightly more rapid in non-sterilized than in the sterilized soil. These results show a considerable involvement of microbial activity in the soil, indicated by the gradual disappearance of the residue in non-autoclaved soil, in line with other previous reports [15-16]. Microorganisms play an important role not only in the degradation of the parent compound but also in the subsequent metabolism of the breakdown products [17-19]. Khan et al. [20] reported that bacterial species utilize pesticides as a source of carbon and energy. The results of the current study is in agreement with those of Khan et al. [20] for deltamethrin and Tu [21] for five pyrethroids.

CONCLUSION

From the study it could be concluded that the degradation of cypermethrin in the two soil types studied developed according to the first order kinetic equation. Temperature and soil moisture content affected the degradation rates of cypermethrin in the soil. Microorganisms in the soil played an important role in the degradation of cypermethrin in the two soil types studied. Dissipation of cypermethrin was found to be slower in soils with high organic matter content.

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REFERENCES


