



## Persistence of cyfluthrin in three Malaysian agricultural soils under laboratory conditions

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### Abstract

The influence of temperature, moisture and organic matter on the persistence of cyfluthrin was determined using three types of Malaysian soils, namely clay, clay loam and sandy clay loam obtained from a tomato farm in Cameron Highlands, Pahang. The persistence of cyfluthrin was observed in the laboratory at two temperature levels of 25 and 35°C and field water capacity of 30 and 80%. Treated soil samples were incubated in a growth chamber for 1, 2, 3, 5, 7, 10, 14, 21 and 28 days. The results from the incubation studies showed that temperature and organic matter content significantly reduced the half-life ( $t_{1/2}$ ) values of cyfluthrin in the three soil types, but moisture content had very little effect. It was observed that cyfluthrin persisted longer at lower temperature and moisture content and higher organic matter content in all the three soil types. The present study demonstrated that under the tropical conditions of Malaysia, cyfluthrin dissipated rapidly in soils compared to its dissipation in soils of temperate regions, evidently due to high temperature.

### Key words

Cyfluthrin, Dissipation, Half-life value, Pesticide, Soil

### Introduction

Pesticides applied to crops for the control of various pests and diseases find their way to soil through spray drift, rain water or by the incorporation into the soil of contaminated crop residues (Gupta and Gajbhiye, 2004). Residues of pesticides in the soil are degraded by biotic and abiotic processes, adsorbed by soil particle surfaces or they migrate from one environmental compartment to another. Movement out of the treated soil could potentially shorten the effective life of a product and result in environmental contamination (Peterson, 2007). Adsorption of pesticides to soils is an important process that influences their migratory behavior in various compartments of the environment (Ismail and Ooi, 2012). The rate and magnitude of rapid transportation seem to be influenced by multiple factors, including not only pesticide properties, but also soil characteristics (structure, organic matter, clay content, iron oxides, etc.), soil hydrological processes and management

(e.g. time of application) (Estevez *et al.*, 2008). The dissipation rate of pesticides in the soil is a useful tool to predict the fate of the pesticides and their leaching behavior in the agroecosystem. Therefore it is vital that the persistence of pesticides be studied under different soil and environmental conditions.

Currently, synthetic pyrethroids are increasingly being used in agricultural production due to their selective insecticidal activity, effectiveness at low doses, non-persistence in the environment, rapid biodegradation and low mammalian toxicity (Muccio *et al.*, 1997; Lopez *et al.*, 2001). Cyfluthrin is a non-systemic, synthetic pyrethroid insecticide, that is widely used to control various types of insects in agricultural farms. Previous studies have shown that cyfluthrin residues do not persist in the soil. This insecticide is degraded biotically and abiotically through hydrolysis and photodegradation processes or adsorbed by particulate matter (Leicht, 1996; Bonwick *et al.*, 1995). In

various soils, cyfluthrin has been observed to degrade rapidly and has shown little leaching potential. Cyfluthrin has been reported to dissipate faster at increased levels of moisture (Gupta and Gajbhiye, 2002) and temperature (Smith *et al.*, 1995).

Information on the degradation and persistence of cyfluthrin in agroecosystems is limited especially under tropical climatic conditions. Therefore, the current study was initiated to investigate the persistence of cyfluthrin in Malaysian agricultural soils under controlled-environmental conditions in order to identify the specific factors that affect the persistence of the pesticide in the soil. The present study aimed at assessing the persistence of cyfluthrin at different temperature and moisture levels in three different types of soil under laboratory conditions.

### Materials and Methods

**Chemicals and soil samples :** An analytical grade mixture of cyfluthrin isomers (purity 98.3%) was obtained from Sigma-Aldrich (Germany), and hexane, acetone, methanol, acetonitrile and ethylacetate (of HPLC grade) from Merck (Germany). The solid phase extraction (SPE) ENV<sup>+</sup> cartridges containing 200 mg of sorbent, were obtained from International Sorbent Technology (IST), MidGlamorgan UK.

Three types of cyfluthrin-free soil samples collected from 0-15 cm depth were taken from three different tomato farms located in Cameron Highlands, Pahang. The soil samples collected were air-dried at room temperature, sieved through a 2 mm mesh and stored at 4°C until time of usage. The soil samples were analyzed and classified at the Soil Testing Laboratory of the School of Environmental and Natural Resource Sciences, UKM. The physico-chemical properties of the three soil types are shown in Table 1. The soil types used in the study were classified as sandy clay loam, clay loam and clay soils. All soil data was recorded on dry weight basis.

**Effect of temperature:** The study on the effect of temperature on the degradation of cyfluthrin in soils was carried out under laboratory conditions. A 100 g air-dried sample (50% moisture content) was treated with cyfluthrin to obtain the

fortification level of 1.0 mg g<sup>-1</sup>. Control samples were similarly prepared with no pesticide added. To study the effect of temperature, treated soil samples were tightly sealed in petri dishes and incubated in the dark at 25±1 or 35±1°C. The final soil moisture level was maintained at about 50% field capacity by replenishing the soil with the required amount of water on alternate days after weighing. After 1, 2, 3, 5, 7, 10, 14, 21 and 28 days of incubation, samples were air-dried overnight and 5 g soil samples (in triplicate) were placed into centrifuge tubes and treated as described below, for the extraction process before determination of the residual level using gas chromatography (GC).

**Effect of moisture content:** The effect of moisture content was studied by moisturizing the soil samples to 30 or 80% field capacity, then keeping them in tightly sealed petri dishes and incubating them in the dark at 30±1°C in a growth chamber for 1, 2, 3, 5, 7, 10, 14, 21 and 28 days. A randomized block experimental design was used with three replications for each incubation period. After each incubation period, soil samples were removed and air-dried overnight. Then 5 g soil samples were placed in centrifuge tubes and the extraction process, as described below, was carried out. The residual level was determined by 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 remaining concentration against the time of incubation (Ismail and Maznah, 2005). Data was subjected to analysis of variance, and means were compared using the ANOVA one way at the 5% level of significance.

**Validation method :** The recovery rate of cyfluthrin from the soil samples tested was determined by fortifying the soil samples (50% moisture content) with 0.1 and 1.0 mg g<sup>-1</sup> of analytical grade cyfluthrin and extraction of the pesticide prior to GC analysis. The recovery test was carried out to determine the efficiency of the extraction method. Working standard solutions containing 0.01-1.50 mg ml<sup>-1</sup> were prepared by appropriate dilutions of the standard stock solution of 100 mg ml<sup>-1</sup> with acetone. Materials used for the recovery test were taken from samples previously determined to be free of the pesticide. The usual precautions were taken to avoid contamination.

**Extraction and GC analysis:** Residues of cyfluthrin in the soil samples were extracted using solid-phase extraction. After each incubation period, 5 g soil samples were weighed and placed into 50 ml centrifuge tubes. Then, 20 ml of acetone:distilled water (95:5) were added to the soil samples and shaken for 15 min. The mixture was centrifuged (3500 rpm) for 10 mins and then transferred to 250 ml Schott bottles. Distilled water was added and the contents made up to 200 ml, followed by mixing and shaking for 1 min. The pH of the samples was adjusted to pH 4.0 with 2N HCl and then they

**Table 1 :** Physico-chemical properties of three Malaysian tropical soil types

Parameters	Clay	Clay loam	Sandy clay loam
pH	5.12	6.53	4.89
Organic matter (%)	1.65	0.95	0.55
CEC(meq 100g <sup>-1</sup> )	8.01	14.78	4.66
Sand (%)	37.17	48.8	52.71
Silt (%)	19.8	23.82	25.82
Clay (%)	43.03	27.38	21.47

were placed on an ultrasonic bath for 5 mins. The SPE cartridges were attached to a manifold that was pre-conditioned with 3 ml acetonitrile, 3 ml methanol and 5 ml distilled water without allowing the cartridge to dry out. The stopper was then removed and the SPE tubing immersed into the mixture before the aspirator was switched on. During the aspiration, water was extracted through the ENV<sup>+</sup> cartridge. The aqueous sample was passed through the cartridge at a rate of 4 ml min<sup>-1</sup>. The cartridge was dried under vacuum for 30 mins. The absorbed cyfluthrin was eluted with 6 mL ethylacetate:acetone (1:1, v/v). Finally, the elute was evaporated to dryness under vacuum and redissolved in 1 ml acetone.

The extracted residues of cyfluthrin were analyzed using a Hewlett-Packard model 6890 Series II Gas Chromatograph fitted with a micro electron-capture detector (m-ECD), manual injector for HP-5 Crosslinked 5% Phenyl Methyl Siloxane column (30.0 m x 0.25 mm I.D x 0.25 mm film thickness) (Hewlett-Packard, Waldbrohn, Jerman). The operating temperatures were: detector 310°C, injector port 250°C, with the oven programmed initially at the 100°C isotherm for 1.5 mins and then increased to 290°C at the rate of 20°C min<sup>-1</sup> and maintained for 4 min. The flow rate of the carrier gas (N<sub>2</sub>, 99%) was set at 1 ml min<sup>-1</sup>. The volume of injection was 1 µl in the splitless mode. There were three replicates and each solution was injected twice. Under these GC conditions, total separation of cyfluthrin into the cis and trans isomers was observed, with retention times of 13.089 min (isomer I), 13.220 mins (isomer II) and 13.387 mins (isomer III). The total amount of cyfluthrin was determined by combining the peak areas. The calibration of cyfluthrin ranged from 0.01 to 1.50 µg ml<sup>-1</sup> respectively. Peak areas were linearly related to the concentration of cyfluthrin. The correlations recorded ( $r^2 = 0.9997$ ) were significant ( $p < 0.05$ ).

### Results and Discussion

The gas chromatograph with the microelectron capture detector allowed a highly sensitive method for determination of pyrethroids based on the ratio of the chromatographic signal to the base line noise ( $S/N = 3$ ). The detection limit in clay, clay loam and sandy clay loam soil samples was 0.008, 0.004, 0.005 µg g<sup>-1</sup>, respectively. These limits could potentially be lowered by increasing the volume of injection or by reducing the volume of the solvent used to redissolve the extract residue (Baskaran *et al.*, 1997). The percentage recovery of cyfluthrin from the three soil types are shown in Table 2. The SPE 200 mg ENV<sup>+</sup> cartridges quantitatively adsorbed the non-polar pesticide (cyfluthrin) from the three soil types, and recovery rates (from soil samples fortified at 0.1 and 1.0 µg g<sup>-1</sup>) varied from 83-94%.

The effect of temperature on the dissipation of

cyfluthrin was studied at two temperature regimes, namely 25 and 35°C, under laboratory conditions. The dissipation of cyfluthrin followed first order kinetics (one compartment model), with the regression coefficient ( $r^2$ ) > 0.8. The degradation rate coefficient ( $k$ ) of cyfluthrin in the three soil types ranged from 0.0692 to 0.1025 (Table 3). The calculated half-life values based on the first order kinetics, in clay, clay loam, sandy clay loam at 25°C were 10.01, 9.99 and 8.20 days, respectively. However, the half life of cyfluthrin in clay, clay loam, sandy clay loam at 35°C decreased to 8.98, 7.44 and 6.76 days, respectively. As expected, temperature had a significant effect on the dissipation of cyfluthrin ( $P < 0.05$ ) whereby it persisted longer at the lower temperature tested for all the three soil types. Cyfluthrin degraded rapidly during the first few days of incubation. The dissipation of cyfluthrin increased by 10.29, 25.5, 17.56% in clay, clay loam and sandy clay loam soil, respectively for a temperature increase of 10°C.

The effect of moisture content on degradation of cyfluthrin was studied at two moisture regimes of 30 or 80%

**Table 2 :** Percentage recovery of cyfluthrin from the three soil types studied

Concentration (µg g <sup>-1</sup> )	Clay	Clay loam	Sandy clay loam
0.1	85.94 ± 3.41	83.48 ± 5.38	87.36 ± 4.84
1.0	92.17 ± 2.53	90.68 ± 3.26	94.03 ± 3.74

**Table 3 :** Degradation rate coefficient ( $k$ ), correlation coefficient ( $r^2$ ) and half-life (days) of cyfluthrin at different temperatures in the three soil types studied

Soil	Degradation rate coefficient ( $k$ )		Correlation coefficient ( $r^2$ )		Half-life (days)	
	25°C	35°C	25°C	35°C	25°C	35°C
Clay	0.0692	0.0772	0.8404	0.9668	10.01	8.98
Clay loam	0.0694	0.0932	0.8564	0.9410	9.99	7.44
Sandy clay loam	0.0845	0.1025	0.8930	0.9742	8.20	6.76

**Table 4 :** Degradation rate coefficient ( $k$ ), correlation coefficient ( $r^2$ ) and half-life (days) of cyfluthrin at different moisture levels in the three soil types studied

Soil	Degradation rate coefficient ( $k$ )		Correlation coefficient ( $r^2$ )		Half-life (days)	
	30%	80%	30%	80%	30%	80%
Clay	0.0633	0.0727	0.8616	0.8776	10.95	9.53
Clay loam	0.0651	0.0750	0.8168	0.9493	10.65	9.24
Sandy clay loam	0.0815	0.0900	0.8991	0.9920	8.5	7.7

field capacity under laboratory conditions. The degradation rate coefficient ( $k$ ) of cyfluthrin in the three soil types was higher at 80% than at 30% soil moisture content (Table 4). The degradation of cyfluthrin at different moisture regimes followed first order linear relationship, with the regression coefficient ( $r^2$ ) > 0.8. The present study revealed that the half life of cyfluthrin in clay, clay loam, sandy clay loam at 30% soil moisture content was 10.95, 10.65 and 8.5 days, respectively. However, the half life of cyfluthrin in clay, clay loam, sandy clay loam at 80% soil moisture content decreased to 9.53, 9.24 and 7.70 days, respectively. The ANOVA results showed that the half life of cyfluthrin on sandy clay loam, clay loam and clay soils was not significantly affected ( $P > 0.05$ ) by the moisture content.

The degradation of the pesticide was accelerated by high temperature, moisture content and diversity of soil microbes (Ngan *et al.*, 2005). Several studies have revealed that the degradation rate of pesticides in the soil was greatly influenced by temperature (Ismail and Maznah, 2005; Wu and Nofziger, 1999). The results of the present study showed that the half life of cyfluthrin decreased as the temperature increased from 25 to 35°C for the three soil types. Printz *et al.* (1995) observed that the dissipation of the pesticide, as well as formation of bound residues and the metabolite demethyl-MBT was enhanced at higher temperatures. Increasing temperatures may promote higher microbial activity in the soil (Gevao *et al.*, 2000), as microbial degradation is the main cause of dissipation of insecticide residues in the soil (Amal *et al.*, 2003). A previous study on dissipation of cyfluthrin in the soil by Smith *et al.* (1995) in Louisiana, USA showed that the  $DT_{50}$  of cyfluthrin was in the range of 27 to 39 days. The shorter half life of cyfluthrin observed in the present study compared to that in Louisiana which has temperate climate could be due to the tropical climate.

The present study shows that the half life of cyfluthrin is shorter at 80% moisture content. The degradation of cyfluthrin increased by 9.41, 13.24, 12.97% in sandy clay loam, clay loam and clay soil, respectively for an increase of 50% in soil moisture content. However, the soil moisture content had very little effect on the degradation of cyfluthrin in the three soil types (Table 4). This may be due to low solubility of cyfluthrin ( $0.002 \mu\text{g ml}^{-1}$ ) and strong adsorption of pesticide molecules to the soil particles. The half life of cyfluthrin at different moisture regimes was quite similar, indicating that the difference in moisture level was not important in this study. Similar results have been obtained by Smith *et al.* (1995), where the dissipation of cyfluthrin in amended soil was found to follow the first-order kinetics and the half life in soil with 26.5 and 20.2% moisture was reported to be 27 and 29 days, respectively. The longer persistence and hence slower dissipation under

low moisture content conditions could be attributed to low microbial activity in dry soil. Similar results have also been reported for thifluzamide (Gupta and Gajbhiye, 2004) and  $\beta$ -cyfluthrin (Gupta and Gajbhiye, 2002) in alluvial soil, and fenvalerate in peat, sandy clay and sandy clay loam soils (Ismail and Maznah, 2005).

The dissipation and half life of cyfluthrin was highly affected by organic matter content in the soil. It was seen that the longest half life of cyfluthrin was observed in the clay soil (Table 3 and Table 4). The clay soil studied contained the highest percentage of OM compared to the other two soil types (Table 1). Strong adsorption onto soil organic matter may protect the pesticide molecules from microbial degradation and other processes such as leaching and volatilization (Ismail and Maznah, 2005). Similar results have been reported for fenvalerate (Ismail and Maznah, 2005) and metolachlor (Ismail and Quirinus, 2000). Smith *et al.* (1995) showed that the persistence of cyfluthrin in the soil was affected by organic matter. However, the half life of cyfluthrin decreased from 39 (unamended soil) to 27 days in the amended soil samples with added organic matter (derived from the addition and thorough mixing with cotton plant residue composed of stalks, petioles and leaves).

In conclusion, this study revealed that the degradation of cyfluthrin in the soil was significantly influenced by temperature and organic matter content but appeared unaffected by soil moisture content. The hot and humid conditions is likely to cause more rapid breakdown of cyfluthrin compared to temperate environments. However, long term studies need to be carried out to obtain more data on the fate of cyfluthrin in the tropical soil environment.

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