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Persistence of Fenvalerate in Three Malaysian Agricultural Soils

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Pesticide dissipation is the result of several processes including chemical and biological factors such as pH, soil moisture and microbial population (Ferrel and Vencill 1989). Highly persistent compounds in the soil could lead to accumulation following repeated applications and consequently leach to underground water or exert deleterious effects on soil microbial processes. Therefore, it is important to carry out pesticide persistence studies under different soil environments in order to depict the fate of the compounds in the soil ecosystem.

The Sumicidin® insecticide (fenvalerate) is a broad spectrum synthetic pyrethroid used on a wide variety of crops. The degradation of fenvalerate in the soil environment was primarily by microbial action with the principal pathway being cleavage of the ester linkage (Demoute 1989). Fenvalerate degradation in subsoil materials in subtropical areas was reported (Talekar et al. 1983). Previous investigations on the effects of organic matter (Chapman et al. 1983) and soil moisture (Vinke et al. 2002) on several insecticide activities and their persistence have also been reported. Correlation studies (Zhou et al. 1995) have clearly indicated that the level of organic content in the soil is the factor most negatively correlated to the activity of pyrethroid insecticides.

To the best of the authors' knowledge, no studies have been carried out on the persistence of fenvalerate in tropical soils such as in Malaysia. While much is known about the activity and mode of action of other compounds in the pyrethroid group, published information is scarce concering the mode of dissipation of fenvalerate from the soil, especially in the agroecosystems under tropical conditions. The present was carried out to determine the persistence of fenvalerate at various temperatures and moisture levels in three different soil types.

MATERIALS AND METHODS

The emulsifiable concentrated formulation of commercial grade (Sumicidin®) fenvalerate [(RS) α-cyano-3-phenolxybenzyl (RS) 2-(4-chloro-phenyl)-3-methylbutyrate; 30% of g a.i. L^{-1}] obtained from ACM (Agricultural Chemical (M) Sdn. Bhd.), was used in the study. The analytical grade of fenvalerate (Pestanal®) 99.9% purity, was obtained from Riedel-de Haën.

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Laboratory studies were carried out using three different soil types which were collected from three different locations. The peat soil sample was collected from regular vegetable growing areas in Sepang, Selangor, Malaysia. The sandy clay loam soil from an experimental plot located near the Department of Agriculture, Serdang and the sandy clay soil from an experimental plot, of the Universiti Kebangsaan Malaysia (UKM) in Bangi, Selangor. The soils were analyzed and classified at the Soil Testing Laboratory of the School of Environmental and Natural Resource Sciences, UKM. The physico-chemical properties of each soil are shown in Table 1. All the samples were collected from the 0-10 cm depth, air-dried and sieved through a ($\leq$ 2 mm) mesh. The samples were placed in labelled black polyethylene bags separately, and stored at - 4°C.

Studies on the effect of temperature and moisture on the degradation of fenvalerate in soils were carried out under laboratory conditions. A 525 g air-dried sample (50% moisture of soil) was treated to obtain a final concentration of 100 $\mu g\ g^{-1}$. Control samples were similarly prepared with no pesticide added. After mixing, 25 g samples of the treated soil were kept in each of 21 polyethylene bags. The bags were sealed but they were opened very four days for 20 min to allow for aeration. The bags were divided into two groups and incubated at 30 or 35°C. The final soil moisture level was maintained at about 50% field capacity by watering every 5 days after weighing. One 25 g bag of soil at each temperature level was kept at below 0°C from week 1, 2, 3, 5, 8, 10, and 15. After each week of incubation, samples were thawed and air-dried overnight, after which 25 g of the soil were placed into a flask and treated as described above for the extraction process before determination of the residual level using gas chromatography (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.

In a different set of experiments, the soil samples were divided into two groups with soil moisture levels of 30, or 80% field capacity. All soil samples were incubated at 30°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 thawed and air-dried overnight, after which, 25 g of the soil were placed into a flask and treated as described above for the extraction process before determination of the residual level using GC. The individual half-lives were derived 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. The experimental design was a randomized-block with three replications. Data were subjected to analysis of variance, and means were compared with an LSD test at the 5% level of significance.

A 50 g soil air-dried sample (50% moisture of soil) was spiked at two concentrations of fenvalerate (10 mL) with 25 and 50 $\mu g\ g^{-1}$ of analytical grade of fenvalerate. The soil was then extracted prior to GC analysis. Working standard solutions containing 2-10 $\mu g\ mL^{-1}$ were prepared by appropriate dilution of the standard stock solution.

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

Physico-chemical properties	Peat soil	Sandy clay soil	Sandy clay loam soil
pH	4.38	5.16	6.61
% Organic matter	82.82	12.67	3.56
% Organic carbon	34.84	0.93	1.02
CEC (meq/100 g)	33.18	11.56	8.64
Sand (%)	2.90	52.25	50.70
Silt (%)	1.20	9.60	26.90
Clay (%)	95.90	38.15	22.40

The extraction method of fenvalerate from soils followed the technique suggested by Pang et al. (1995) and Hill (1981) with minor modifications. Each of the air-dried soil samples, 25 g were weighed then placed into a 250 mL conical flask. Ten-mL distilled water and 50 mL acetonitrile were added to the soil, followed by shaking on an orbital shaker (250 rpm) for 1 hr. The experiment was replicated thrice. The mixture was left for 1 hr and then transferred into the separatory funnel, and 50 mL hexane was added. The sample was shaken again for 15 min, then 50 mL of 2% NaCl was added to the extract. The hexane layer was filtered through 40 g of $NaSO_4$ in a glass column. A sample of the supernatant was collected and filtered through a RC membrane (pore size 0.45 μm) to remove particulates. Finally the extract was evaporated to dryness under a stream of nitrogen gas and then 1 mL of hexane was added prior to GC analysis.

Extracted residues were determined by a Hewlett Packard 6890N Series II Gas Chromatograph equipped with 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, with the oven programmed initially at 205°C for 2 min and then increased to 300°C at the rate of 30°C min^{-1} and maintained for 4 min. The carrier gas was nitrogen (N_2, 99%) with a flow rate of 1 mL min^{-1}. The volume of injection was 1 μL. There were three replicates and each solution was injected twice. Under these conditions the retention time of fenvalerate was 8.187 min (isomer I) and 8.390 min (isomer II).

RESULTS AND DISCUSSION

External standards of the fenvalerate were used to identify the peaks in the three soils studied. The detection limit was set at three times the height of the noise peaks that appeared at the retention times of the pesticide concerned in the blank sample. The detection limit was 0.011, 0.002 and 0.003 μg g^{-1} in peat, sandy clay and sandy clay loam soils, respectively. The percentage recovery of fenvalerate in the three soil types are shown in Table 2, and it can be seen that when the soils were fortified at either 25 or 50 μg g^{-1}, it was more than 80%.

Table 2. Percentage recovery of fenvalerate from the three soil types studied.

Concentration (μg/g)	Peat soil	Sandy clay soil	Sandy clay loam soil
25	84.97 ± 0.681	83.80 ± 0.627	82.00 ± 0.513
50	88.30 ± 0.018	83.12 ± 0.173	84.69 ± 0.188
$LSD_{0.05}$	1.2582	1.2069	1.0359

Table 3. Degradation rate coefficients (k), correlation coefficients (r^2) and half-life (days) of fenvalerate at different temperatures in the three soil types studied.

Soil	Degradation rate coefficients (k)		Correlation coefficients (r^2)		Half-life (weeks)	
	30°C	35°C	30°C	35°C	30°C	35°C
Peat soil	0.1179	0.1690	0.9579	0.9937	5.88	4.10
Sandy clay soil	0.1698	0.2385	0.9671	0.9126	4.08	2.91
Sandy clay loam soil	0.2037	0.2472	0.9327	0.9784	3.40	2.80
$LSD_{0.05}$	0.0151	0.0078	0.0132	0.0099	0.368	0.106

Table 4. Degradation rate coefficients (k), correlation coefficients (r^2) and half-life (days) of fenvalerate at different moisture levels in the three soils types studied.

Soil	Degradation rate coefficients (k)		Correlation coefficients (r^2)		Half-life (weeks)	
	30%	80%	30%	80%	30%	80%
Peat soil	0.0911	0.1864	0.9133	0.9744	7.61	3.72
Sandy clay soil	0.1946	0.2301	0.9506	0.9531	3.56	3.01
Sandy clay loam soil	0.2239	0.3448	0.9663	0.9471	3.10	2.01
$LSD_{0.05}$	0.0484	0.0478	0.0982	0.0295	1.436	0.423

The degradation of fenvalerate under laboratory conditions at 30 or 35°C followed first-order kinetics, with the regression coefficient (r^2) being > 0.9 (Table 3). The degradation coefficient rate (k) of fenvalerate in the three soils ranged from 0.1179 to 0.1690 ($week^{-1}$). The half-life of fenvalerate was inversely correlated to its degradation rate. Temperature had a significant influenced on the degradation rates of fenvalerate in the three soils. It should be noted that the half-life of fenvalerate was longer in peat soil irrespective of the soil temperatures tested. The half-life of fenvalerate at 30°C was 5.88, 4.30 4.08 weeks in peat, sandy clay and sandy clay loam soil, respectively. However at 35°C, the half-life of fenvalerate in the peat soil, sandy clay soil and sandy clay loam soil was 4.10, 2.91 and 2.80, respectively. An increase in temperature of 5°C showed a significant reduction in the half-life of fenvalerate by 17.6, 28.6 and 30.2% in sandy clay loam, sandy clay and peat soil, respectively.

Dissipation of the pesticide was also accelerated in soil with high moisture contents. The degradation rate coefficient (k) was found to be higher at 80% than at 30% soil moisture (Table 4). The degradation rate of fenvalerate at different soil moisture levels followed a first-order linear relationship with correlation coefficient $r^2 > 0.90$. The half-life of fenvalerate at 30% soil moisture was 7.61, 3.56 and 3.10 weeks in peat, sandy clay and sandy clay loam soils, respectively. However at 80% soil moisture the half-life of fenvalerate in the sandy clay and sandy clay loam soil had reduced to 3.01 and 2.01 weeks, respectively. The half-life of fenvalerate decreased from 7.61 to 3.72 weeks (a decrease of 51.1%) in peat soil when the soil moisture increased from 30 to 80%, and this was considerably greater than that of the others two soils.

The persistence of pesticides in the soil is greatly influenced by soil temperature, moisture and soil characteristics (Chapman et al. 1983). Increased degradation rates of many pesticide at increased temperatures have been confirmed in numerous field studies (Dictor et al. 2003, Ferrell and Vencil 2003). The results of this study clearly showed that the half-life of fenvalerate decreased as the temperature increased from 30 to 35°C. Greater reduction of approximately 30.2% was observed in peat soil. There is evidence that pesticide degradation rates increase with higher temperatures which, in most instances, probably reflect increased microbial activity, especially in organic soils. The organic content of peat soil is considerably high as compared to the other two soils studied (Table 1). Positive correlations between temperature and degradation rates have been reported in previous studies (Chapman and Harris 1981). Higher temperatures are also favourable for microbial growth (Lehmann et al. 1992) and probably reflect increased biological and non-biological activity of pesticide dissipation (Ismail and Rahman 1994). Lee (1985) suggested that the degradation processes of fenvalerate were predominantly caused by microbial activity. Microbial activities play an important role in the degradation of synthetic pyrethroids (Khan et al. 1988). However, in this study , the degradation products of fenvalerate were not determined. Faster degradation of pesticides at higher temperatures could also partly be attributed to volatility and photodecomposition of the molecules (Oppong and Sagar 1994).

A similar observation has be reported by Chapman and Harris (1981) where the concentration of fenvalerate was reduced from 46 to 38 ppm as the soil moisture content increased from 0.5% to 5%. On the other hand, insecticides from the pyrethroid group also showed the same trend whereby, the half-life of permethrin (pyrethroid) was reduced from 23 to 19 days when the soil moisture content increased from 10.3% to 15.4% (Skidmore 1994). The result of this study showed that the half-life of fenvalerate is shorter at 80% moisture level. Greater reduction in the half-life of fenvalerate (51.1%) was observed in peat soil. Decrease in the half-life at higher soil moisture levels may be the result of weak adsorption of the pesticide molecules to the soil particles. At higher soil moisture levels, water molecules compete with the pesticide for adsorption sites on the soil colloids and increased pesticide concentration in the soil solution make them more readily available to soil microbes (Fomsgaard 1994). This probably explains the shorter half-life of fenvalerate in soils at 80% moisture. As mentioned earlier, microbial decomposition is the major avenue for dissipation of most pesticides including fenvalerate from soils, with chemical degradation accounting for less than 2% of the observed losses under field condition (Demoute 1989). Reports on studies with a wide range of compounds have been published (Ismail and Hanijah 1999) showing the expected effect of increased degradation rates with increasing soil moisture up to field capacity. On the other hand, the microbial degradability of fenvalerate is definitely decelerated and a relevant persistence is revealed by the extended lag phase of 48 days under anaerobic conditions (Vinke et al. 2002).

The half-life and degradation of fenvalerate was greatly influenced by soil characteristic especially OM content of the soil. It was observed that the half-life of fenvalerate was the longest in peat soil. As shown in Table 1, peat soil contained the highest percentage OM as compared with the other two soils. Soil OM has been shown (Oppong and Sagar 1992) to have the highest cation exchange capacity of all the soil constituents. Strong adsorption onto soil OM may protect the pesticide molecules from microbial degradation and other processes such as leaching and volatilization. This may explain the longer half-life of fenvalerate in peat soil than in the two other soils. The results of this study showed that the dissipation of fenvalerate is greater as the temperature and moisture content increased. The results have shown that the half-life of fenvalerate in peat soil was reduced by 30.2 and 51.1% as the temperature and moisture increased, respectively. It has been reported that bacterial and fungal populations of the soils are usually not significantly altered by the application of pesticides (Ismail and Yap 1994). Therefore, it is possible that fenvalerate applied at the recommended rate would not exert an adverse effect on the soil environment as its half-life might be much shorter under field conditions.

The study revealed that temperature and soil moisture have significant influence on the degradation of fenvalerate in the soil. However, the rate of dissipation is also affected by the physico-chemical properties of the soil especially the organic matter content. Generally, the half-life of fenvalerate in tropical soils showed slightly faster degradation than in temperate regions where the climatic conditions and soil characteristics are very different. In tropical areas where temperature and

total rainfall are relatively high, the accumulation of toxic residues in the soil may not be a serious problem. However, long-term studies under field conditions need to be carried out to get a clearer picture on the fate of this pesticide.

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