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Comparison Between Field Experiment and PERSIST Model Simulation: Dissipation of Fenvalerate in a Malaysian Agricultural Soil

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The prediction of the fate of pesticides by mathematical models is now accepted by pesticide legislation, therefore confidence in the models used is very important. The new legislation suggests that models are indispensable tools to be used in the applied environmental sciences to determine pesticide fate. These models have not been evaluated for their suitability in many environments, and for some environments there are no existing models that are capable of describing the fate of pesticides. Several models have been developed to simulate the movement and persistence of pesticide residues in soils. These include the pesticide root zone model (PRZM), LEACHP, VARLEACH, MACRO and PESTLA (Jarvis et al. 2000; Sarmah et al. 2002; Trevisan et al. 2000, 1995).

PERSIST is a specific computer software designed by Allan Walker in 1978 to predict the persistence of pesticides in the soil. It has been used to successfully predict pesticide persistence in soils in the UK and USA using parameters derived from laboratory incubation studies (Walker and Zimdahl 1981). In 1981, Walker and Barnes revised the sofware so that it could predict the persistence of a number of pesticides in soils in the field, once the rates of degradation have been established for the same soil in the laboratory (Walker and Zimdahl 1981). The degradation subroutines in the model PERSIST were then incorporated into the leaching model by Nicholls et al. (1982) and this was further modified by Walker (1978) to permit adsorption/desorption to vary with the residence time of the pesticide in the soil (Trevisan et al. 2000).

Attempts have been made to develop simulation models that predict pesticide persistence in the soil under field conditions, based on laboratory measurements of degradation pathways and rate. However, in some cases, discrepancies between predicted and observed data have been reported (Wagenet and Roa 1990). Laboratory investigations concerning pesticide degradation are usually carried out using homogeneous soil samples (air-dried and sieved), incubated at constant temperature and soil moisture (Accinelli 2003). Under field conditions, pesticide persistence depends on the integrated effect of several factors, and most of them (i.e. soil organic matter, soil microbial biomass and soil moisture) are expected to exhibit spatial and temporal variability (Walker 2003).

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Fenvalerate is a potent insecticide that has been in use since 1976. It is an ester of 2-(4-chlorophenyl)-3-methybutyric acid and alpha-cyano-3-phenoxybenzyl alcohol, but lacks a cycloropropane ring. However, in terms of its insecticidal behaviour, it belongs to the pyrethroid group of insecticides. It is a racemic mixture of four optical isomers with the configurations [2S, alphaS], [2S, alphaR], [2R, alphaR] and [2R, alphaS]. Hill (1981) found that in both soil persistence studies, the RS,SR enantiomeric pair degraded slightly faster than the RR, SS pair. The degradation of fenvalerate has been studied under various conditions (anaerobic/aerobic/laboratory/field) using both radioactive and non-radioactive material. In soil, degradation occurs via ester cleavage, diphenyl ether cleavage, ring hydroxylation, hydration of the group to amide (Eisler 2000), and futher oxidation of the fragments formed to yield carbon dioxide as a major final product. According to the Hornsby Index (1510), the leaching potential of fenvalerate and its degradation products showed that very little downward movement occurs in soils (Wauchope 1992).

Although reports have been published on fenvalerate behaviour in the environment, no studies have been reported on the persistence of fenvalerate under tropical conditions, such as those found in Malaysia. The aim of this study was to investigate the degradation rate and persistence of fenvalerate in a Malaysian soil and to compare the PERSIST prediction against the observed field data.

MATERIALS AND METHODS

The field study was conducted at an experimental plot located near the National University of Malaysia (Universiti Kebangsaan Malaysia, UKM) in Bangi, Selangor. The soil was analyzed for its physico-chemical properties. It contained clay (38.15%), sand (52.25%), silt (9.6%), organic matter (12.67%), pH 5.16, soil moisture 10.5% and CEC 11.56 meq 100^{-1} gm soil. The plot studied contained soil predominantly sandy clay in texture. The Malaysian climate is tropical with daily temperatures ranging from 22.4-33.6°C and an average monthly rainfall of 183.32 mm. The experimental site was rectangular, measuring 3.4 x 1.2 m with a slope of 30^0 at the soil surface.

The seeding of *Brassica chinensis* was done on October 6, 2003. The plot was sprayed with fenvalerate (0.045 a.i g ha^{-1}) at the recommended rate using a knapsack sprayer. The treatment dates were from November 1 until December 6, 2003. On each sampling date, soil samples were randomly taken in triplicate.

Soil cores were divided into four segments: 0-5 cm, 5-10 cm, 10-15 cm and 15-20 cm. The samples were taken at 1, 2, 3, 5, 10, 17, 25, 35 and 50 days after the previous treatment. The soil samples from the specific layers were combined and throughly mixed before being air-dried and sieved through a mesh ($\leq$ 2 mm). The soil sampels were stored in labelled black polyethylene bags at -4°C prior to analysis using the GC.

Soil samples (25 g) were spiked at three concentrations of fenvalerate (10 mL) namely 5, 25 and 50 mg kg^{-1} of analytical grade of fenvalerate. Extraction for the determination of the pesticide residue was then undertaken.

Soil samples (25 g) were weighed individually into 250 mL conical flasks, and shaken on an orbital shaker (250 rpm) with 10 mL distilled water and 50 mL acetonitrile for 1 hr. The experiment was replicated thrice.The samples were kept for about 1 hr and then transferred into the separatory funnel, when 50 mL hexane were added. Each sample was shaken for about 15 min, then 50 mL of 2% NaCl were added to the extract. The hexane layer was filtered through 40 g of Na_2SO_4 in a glass column. The samples of the supernatant were collected and filtered through an RC membrane (pore size 0.45 μm) to remove particulates. Finally the extracts were evaporated to dryness under a stream of nitrogen gas and reconstituted individually in 1 mL of hexane prior to GC analysis. The method used to extract fenvalerate from the soils was based on the technique suggested by Pang et al. (1995) and Hill (1981) with minor modifications.

Extracted residues were estimated by a Hewlett Packard 6890N Series II Gas Chromatograph equipped with μ-electron capture detector (μ-ECD), manual injector and HP-5 Crosslinked 5% Phenyl Methyl Siloxane column (30.0 m x 0.32 μm id, 0.25 μm film tickness). 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 and maintained for 4 min. The carrier gas was nitrogen (N_2, 99%) with the flow rate of 1 mL min^{-1}. The volume of injection was 1 μL. There were three replicates and each treatment solution was injected twice.

External standards of fenvalerate were used to identify the peaks. The detection limit was set at three times the height of the noise peaks (that appeared where the pesticides peaks should appear if the pesticide concerned existed) in the blank sample.

The modelling of PERSIST was undertaken using a personal computer. Input of data required for the simulation were daily maximum and minimum air temperatures and daily rainfall records. The daily weather data were obtained from the Department of Geography, UKM. The weather data was taken from the day of the first treatment to day 50 and was used as an input to simulate as close as possible the weather conditions of the field under study. The model also required input of soil physical properties such as field capacity (at 5 kPa suction) and soil bulk density. The half-life value was derived from the field study based on the rate of pesticide degradation. The pesticide properties such as half-life in soil moisture at specific temperatures were also required. The output of the simulation came in the standard column format with the headings: DAYS (days after application), CONC (residual concentration of pesticide, % of initial), SM (soil moisture content (%), ST (mean soil temperature), EO (calculated potential pan evaporation, mm) and HL (calculated half life, days).

RESULTS AND DISCUSSION

The recovery rates of fenvalerate from the soil samples were 83.80% and 83.12% when the soils were spiked with either 25 or 50 ppm. The detection limit for fenvalerate was 0.002 ppm. The retention time was 8.187 min for isomer I and 8.390 min for isomer II.

Table 1 shows the residue concentration of fenvalerate in different soil profiles. The result clearly showed that the residue leached easily downward through the soil profile. The residue was detected in the 15-20 cm soil profile even at 1 day after application. The range of concentration in each soil layer, (0-5 cm, 5-10 cm, 10-15 cm and 15-20 cm) during the study period was <0.006-0.0726 μg g^{-1}, <0.01-0.2010 μg g^{-1}, <0.012-0.0755 μg g^{-1} and <0.038-0.1796 μg g^{-1}, respectively. The residue at the top 5 cm could be detected until day 17 after application, however no residue was detected on day 25. In the 15-20 cm soil profile, the residue was only detected until 3 days after application.

In general, fenvalerate degraded rapidly and the concentration decreased with increasing soil depth. Calculated half-life (DT_{50}) of fenvalerate in each segment of soil at 0-5cm, 5-10 cm, 10-15 cm and 15-20 cm was 8.02 days, 9.63 days, 10.0 days and 12.0 days, respectively. Volatilization and runoff may represent a major dissipation pathway for pesticides applied to surface soil or crops, accounting for up to 99% of the application dose in some cases (Bedos et al. 2003). This has been shown by the presence of fenvalerate residues at the 15-20 cm depth 1 day after application. High amount of rainfall plays an important role in the mobility of fenvalerate in the soil. However, the residue remaining for 17 days could be due to strong adsorption of the residue to the soil particles or organic matter in the top 5 cm.

Most of the published studies on the persistence of fenvalerate residues had a range of half-life from 40-80 days depending on the various factors mentioned (Chapman and Harris 1981; Hill 1981; Lee 1985; Ismail and Kalithasan 2002). The results of this study showed shorter half life as compared to the previous studies. Many of the previous studies were carried out under temperate conditions, which are considerably different from tropical conditions. Ismail et al. (2004) reported that the degradation of pesticides in tropical soils was faster that those reported in earlies studies, which may in part be attributable to environmental factors such as higher rainfall in the tropics than under temperate conditions. There is very limited information available on degradation of pyrethroids in tropical agricultural soils (Ismail and Kalithasan 2002; Mazlinda 2002) and besides, the studies were carried out under laboratory conditions, where soil temperature, moisture and other factors may be different from the naturally occuring conditions in the field.

Factors such as volatilization, runoff, leaching, chemical and biological degradation and fotolysis could enhance the degradatation rate especially under tropical climatic conditions. Moreover the high temperature, humidity and rainfall

Table 1. Residue (μg/g) concentration of fenvalerate in soil.

Day after application	Depth of soil (cm)			
	0-5	5-10	10-15	15-20
1	0.0726±0.082	0.2010±0.022	0.0641±0.012	0.1286±0.011
2	0.0689±0.089	0.0996±0.029	0.0587±0.205	0.0337±0.010
3	0.0473±0.050	0.0391±0.097	0.0755±0.322	0.0384±0.027
5	0.0283±0.001	0.0492±0.043	0.0263±0.015	ND
10	0.0114±0.435	0.0136±0.010	0.0127±0.008	ND
17	0.0066±0.762	ND	ND	ND
25	ND	ND	ND	ND

ND: the concentration was below detection limit 0.02 ppm.

Table 2. Comparison of the observed, predicted and CRM values.

Days	Observed	PERSIST	CRM
1	0.2296	0.2476	1.08
2	0.2179	0.2314	1.06
3	0.1496	0.2162	1.45
5	0.0895	0.1905	2.13
10	0.0360	0.1432	3.90
17	0.0210	0.0935	4.45
25	0.0098	0.0432	4.41
35	0.0082	0.0162	1.96
50	0.0041	0.0030	0.73

throughout the year could have contributed to the rapid loss of the pesticides from the experimental plot. Paraiba et al. (2003) reported that the inclusion of soil temperature in the Leaching Potential Index (LPI) proved to be important and essential to estimate the leaching potential of the pesticides studied in tropical conditions.

The degree of agreement between the predicted and the observed values was evaluated using the Coefficient of Residual Mass (CRM) (Vanclooster 1998). The CRM is obtained by dividing the predicted value with the observed value. A value of CRM > 1 indicates that the model over predicted the observed value, while a value of CRM < 1 indicates that the model under predicted the observed value. A prefect agreement between predicted and observed values would be characterized by the value CRM = 1. If the difference is within 30% of the observed value then the model can be considered as practically accurate in predicting residue values for the subsequent crops (Walker and Bond 1978).

The comparison of the observed, predicted and CRM values are shown in Table 2 and Fig. 1. The predicted data gave an acceptable agreement at day 2 with CRM=1.06. The predicted residue values at day 3 until day 35 were more than 30% of the observed value. PERSIST predicted residue fenvalerate (>0.005 μg/g) detected at day 25, but the observed data indicated otherwise. PERSIST gave

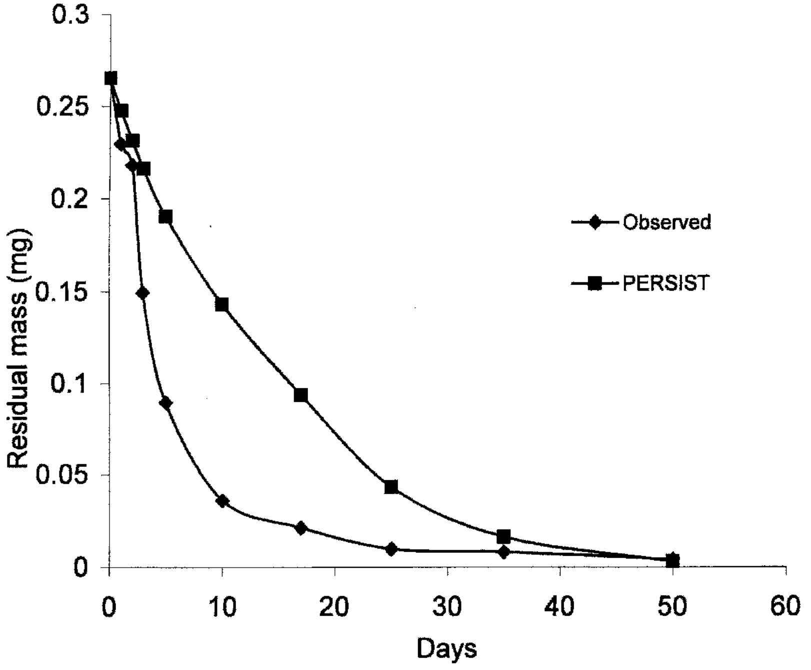

Figure 1. A comparison between observed values of fenvalerate residue with predicted values using PERSIST.

good agreement between the observed and predicted values at day 50, with CRM=0.73.

The predicted values from the simulation model of fenvalerate was higher than the observed values under field conditions. The results are in agreement with a report by Ismail and Kalithasan (2002) where predicted values of permethrin were found to be higher than observed data. Therefore the dissipation of fenvalerate in the field experiment was much faster than that predicted by PERSIST. PERSIST simulation did not take into account other factors such as volatilization that could contribute to rapid dissipation of pesticides (Ngan 2004).

In conclusion, dissipation of fenvalerate under tropical field conditions was faster than that predicted by PERSIST but the simulation model with some modifications can be used to predict dissipation of fenvalerate under tropical conditions. However, the observed data agreed quite well with the predicted values using the PERSIST model.

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