

DISSIPATION OF FLUROXYPYR IN A MALAYSIAN AGRICULTURAL SOIL WITH SIMULATION USING THE PERSIST AND VARLEACH MODEL

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ABSTRACT

The study was carried out to compare the dissipation of fluroxypyr in a Malaysian agricultural soil based on field experimentation and simulation using the PERSIST and VARLEACH model. A plot situated in an oil palm plantation near Sepang, Selangor, Malaysia was selected for the field experiment. The plot was treated with fluroxypyr at the recommended dosage (72.5 g ha⁻¹). The soil samples from the field trial were collected and analyses conducted in the laboratory according to the sampling schedule. Simulation of fluroxypyr persistence and leaching was also conducted using computer-run software, PERSIST and VARLEACH. The predicted data obtained using PERSIST for fluroxypyr was found to be higher than the observed data from field measurements. However, the predicted data for fluroxypyr using VARLEACH matched well with the observed data from the field trial.

Keywords: fluroxypyr, soil, dissipation, PERSIST model, VARLEACH model.

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INTRODUCTION

Pesticide is an essential part of commercial agriculture and side by side it is a big environmental threat. Mathematical models are needed to use for making prediction about pesticide use and gauging environmental risk assessment (Ngim *et al.*, 2000; Cheah *et al.*, 2001). Several models have been developed to simulate the movement and persistence of pesticide residues in soil. These include the pesticide root zone model (PRZM) developed by the United States Environmental Protection Agency and its modified version, PELMO

(Ainie *et al.*, 2007), LEACHP, developed at the Cornell University (Farahani *et al.*, 2008; Fuad and Maher, 2010) the more recent version of the CALF model (Buszewski, 2006), then known as VARLEACH (Giacomazzi and Cochet, 2004; Cabrera *et al.*, 2007) and PESTLA, developed in the Netherlands (Boeston, 2000). PERSIST and VARLEACH are specific computer software, which have been used to predict the persistence and leaching of pesticides in soil (Goody *et al.*, 2002; Ismail *et al.*, 2004). Given a valid model, expected behaviour under average and extreme conditions could be predicted with a limited amount of experimental data. Persistence of a compound when applied at different times of the year, for different years or at different geographical areas can be assessed using the PERSIST and VARLEACH models.

The ability of a model to predict the behaviour of a pesticide in soil is potentially of great value both to optimise the performance of soil applied

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compounds as well as to anticipate and minimise the risk of adverse environmental effects. Modeling with regard to field behaviour began around 1970 when available tools and techniques enabled dynamic simulation of pesticide behaviour in the soil/plant system (Chefetz *et al.*, 2004). Considerable progress has been made in the development of simulation models for estimating the movement and degradation of agricultural chemicals (Boeston, 2000; Guardia-rubio *et al.*, 2006.). The role of environmental fate modeling of pesticides has increased steadily, and it now plays a major role in the assessment of the environmental aspects of pesticide behaviour for the process of pesticide registration (Mou *et al.*, 2008; Ismail *et al.*, 2015). Meanwhile, a study comparing the dissipation of chlorpyrifos, chlorothalonil and profenofos was conducted in Cameron Highlands, Pahang, Malaysia to assess the difference between field data and predicted data by simulation using the PERSIST model (Liyange *et al.*, 2006).

A mathematical model described by Ying and Kookana (2001) has been shown to be capable of predicting the persistence of a number of herbicides in soil collected from the field, once the rates of degradation have been established for the same soil in the laboratory. The basis of the model developed by Ismail *et al.* (2004) hinged on the use of data such as temperature and moisture content of the surface soil in the field from weather records, and combining these with laboratory measurements of herbicide degradation rates, for running the program. The original program was written in the simulation language CSMP, 6 for which the daily weather records of soil temperatures at 10 cm depth, the rate of evaporation from an open water surface (E_0 , mm per day) and the rainfall (mm per day) were required. Soil temperature and evaporation measurements were not always available and so the model was therefore modified to use daily measurements of maximum and minimum air temperatures and rainfall records as the input variables. These data records were more readily available from a wide range of sites. Other minor modifications have been incorporated into the original model to simplify its use and the program was rewritten in FORTRAN. Although reports have been published on the persistence and leaching of pesticides in the environment using mathematical models, very limited information on the subject is available for Malaysian environment. Therefore, the present study makes use of the PERSIST and VARLEACH models to investigate the credibility of the two modeling systems for predicting pesticide residues under tropical conditions as found in Malaysia. Fluroxypyr is currently widely used to control weeds in the Malaysian oil palm plantations.

PERSIST is a specific computer software designed by Janitha *et al.* (2006) to predict the persistence of pesticides in the soil. It has been used

successfully to predict pesticide persistence in soils in the United Kingdom and USA with parameters derived from laboratory incubation studies (Lanyi and Dinya, 2005). Studies comparing the observed and predicted residues under tropical conditions such as those found in Malaysia are very limited (Ismail and Kalithasan, 2002). A modeling study using the Hornsby Index, Attenuation Factor and chemical movement in layered soils (CMLS) on 14 pesticides used in cabbage and chrysanthemum farms at the Cameron Highlands, Pahang, Malaysia, demonstrated that only methamidophos had the highest leaching potential (Maznah *et al.*, 2010; Tayeb *et al.*, 2015). A report on the dissipation of permethrin in the Malaysian agricultural soils was documented, where the predicted data derived from the model showed higher values than the observed data (Ismail and Kalithasan, 2002).

The current study comparing the dissipation of fluroxypyr in a field experiment with the predicted values using the PERSIST and VARLEACH simulation would help in better understanding the fate of fluroxypyr in tropical soils such as those found in Malaysia. To the best of our knowledge, no report has been published on the use of a mathematical model on fluroxypyr dissipation in the Malaysian soils. Therefore, the main objective of this study was to investigate the possibility of using the PERSIST and VARLEACH models to predict herbicide residues in soils under tropical conditions as found in Malaysia.

MATERIALS AND METHODS

Field Experiment

Site selection. The study was conducted at the KLIA Oil Palm Plantation of the Malaysian Agricultural Horticultural Sdn Bhd (MAAH). This oil palm estate is situated in the central part of the state of Selangor in Peninsular Malaysia at altitude 70 m to 100 m above sea level. The study plot covered 6 ha, and consisted of nine subplots of 0.66 ha each. The study plot was situated on hilly land of slope 45° with soil predominantly clayey in texture. The physico-chemical properties of the soil were determined. The palm in the study plots were two and the half years old. The area has tropical climate with daily temperatures varying from 25°C to 36°C, average daily humidity usually in excess of 80% and average monthly rainfall between 31-169 mm.

Fluroxypyr 1-methyl heptyl ester (fluroxypyr-MHE) was applied as an aqueous spray using a knapsack sprayer (nozzle 5/64) at spraying volume of 250 litres ha⁻¹. The herbicide was applied at 72.05 g a.i. ha⁻¹ in accordance to the manufacturer's recommended dosage.

Soil sampling. Soil samples were collected from 0-50 cm depth using a soil auger and there were three replicates. The samples were taken at -1 (day before treatment), 0 (day of treatment) and 1, 5, 7, 14, 21, 30, 60 and 90 days after treatment. The soil samples were air-dried, sieved through a 2 mm mesh and stored in black polyethylene bags at -4°C prior to analysis. The soil was classified as clay, containing 52.2% clay, a cation exchange capacity (CEC) of 6.9%, 15% coarse sand, 27% fine sand, 5.8% silt and 1.89% organic matter. The soil moisture content was 10.5% and pH of 4.5.

Recovery study. Soil samples of 50 g were used in the study. The soil samples were spiked with fluroxypyr at five concentrations *viz.* 1, 5, 10, 25 and 50 $\mu\text{g kg}^{-1}$. The pesticide was then extracted from the soil for residual determination.

Extraction of fluroxypyr residue from the soil samples. Soil samples of 5 g were placed into 250 ml conical flasks. Soil samples were spiked with standard fluroxypyr and the contents were mixed thoroughly on a vortex mixer. Each mixture was then allowed to stand for 15 min to enable homogenous distribution. Then 20 ml of acetone: water (95:5, v/v) was added to each conical flask and the mixture was again mixed thoroughly for 30 s on a vortex mixer. Each conical flask was then placed in an ultrasonic bath for 15 min and then the content was transferred into individual test tube and centrifuged at high speed (3500 rpm) at 26°C, for 10 min. The top layer (acetone + water) of each bottle was transferred to a Schott bottle using a glass Pasteur pipette and 200 ml of fluroxypyr-free water were added to each bottle. The bottle was then stoppered and the content mixed by shaking for a few seconds. The bottle was then placed in an ultrasonic bath for 5 min and the pH of the mixture adjusted to 3.0 by the addition of 2N HCl. A SPE cartridge was attached to the manifold, which was pre-washed with 3 ml acetonitrile and 3 ml distilled water. The washings were discarded. The stopper was removed and the SPE tubing was immersed into the mixture. The aspirator was switched on for the water to be sucked through the OASIS® HLB. The flow of the water through the SPE cartridge was controlled by a pressure knob so as to elute the water at 8-10 ml s^{-1} . After the water was completely drawn through the SPE cartridge the bottle was rinsed with 5 ml water. The water from the rinsing was also passed through the SPE cartridge and the cartridge was then vacuum-dried. The fluroxypyr adsorbed in the cartridge was then eluted with 4 ml acetonitrile. The eluate was dried completely in vacuum. The residue was then redissolved in 1 ml acetonitrile before being injected into the high performance liquid chromatography-diode array detector (HPLC-DAD). Quantification

of the analyte was made by comparing it with the fluroxypyr standard solution. There were five replicates and each solution was injected twice.

HPLC analysis. An Agilent HPLC 1100 Series fitted with a DAD was used for the analysis. The column used was a LUNA RP18, 5 μm (250 mm x 4.6 mm I.D.). A guard cartridge RP 18, 5 μm (Phenomenex) with the RP-18 column was used. The wavelength was set at 254 nm. The mobile phase was acetonitrile and acetate buffer (1% acetic acid in water) in the ratio of 60:40 (v/v). The flow rate and injection volume were 0.8 ml min^{-1} and 100 μl , respectively.

Prediction of persistence by the PERSIST model. The simulation of PERSIST on the prediction of persistence was undertaken using a personal computer. Inputs of the data required for the simulations were daily maximum and minimum air temperatures and daily rainfall records. The daily weather data was obtained from the Kuala Lumpur International Airport (KLIA) meteorological station. The weather data was taken from the first day of treatment up to 90 days after the treatment and was used as an input to simulate as close as possible the weather conditions of the field under study. The model also required the input of soil physical properties such as field capacity (at 5 kPa suction) and soil bulk density. Pesticide properties such as half-life in soil moisture at specific temperatures were also required. The half-life value of the pesticide was derived from the field study. The known rate of pesticide application was also required. The geographical location of the plot such as latitude and altitude were prerequisites. The simulation of PERSIST was automatically run on a Microsoft platform. After running the model completely, the prediction would be automatically saved under a file name OUTPUT in the same folder with the program. The output of the simulation came in the standard column format with headings: DAYS (days after application), CONC (residual concentration of pesticide, % of initial), SM (soil moisture content, %), ST (mean soil temperature, °C), PE (calculated potential pan evaporation, mm) and HL (calculated half-life, days).

Prediction of persistence by the VARLEACH model. The same data input used in the PERSIST model was subjected to another simulation model, the VARLEACH model. VARLEACH is a modified version of PERSIST, and it simulates the leaching of the pesticide in the soil profile. For the VARLEACH model, additional inputs were required, namely, the adsorption distribution coefficient constant and water solubility. After a complete run of the VARLEACH program, the prediction would be automatically saved under a file name RESULT. The

file was under the TXT extension, which contained the predicted value of the total pesticide residues in the soil profile at different depths.

Calculation of the Coefficient of Residue Mass for PERSIST and VARLEACH. The degree of agreement between the predicted and the observed values was evaluated using the Coefficient of Residual Mass (CRM) (Vanclouster *et al.*, 2000; Lesueur, 2008). CRM is obtained by dividing the predicted value with the observed value. A value of CRM > 1 indicates that the model over estimated the observed value, while a value of CRM < 1 indicates that the model under estimated the observed value. A perfect agreement between predicted and observed values would be characterised by the value of CRM = 1. If the difference is within 30% of the observed value, the model is considered as practically accurate in predicting residues for the subsequent crops (Lourencetti, 2008).

RESULTS AND DISCUSSION

Recovery Study

The recovery and relative standard deviation percentage of fluroxypyr-spiked soil samples at levels of 1, 5, 10, 25 or 50 $\mu\text{g kg}^{-1}$ using OASIS[®] HLB (Table 1) were $107\pm 0.5\%$, $100\pm 4.7\%$, $101\pm 2.5\%$, $100\pm 0.7\%$ and $82\pm 0.9\%$, respectively with relative standard deviation ranging from 0.5% to 4.7%. The linear regression (r) was found to be 0.9989 and the equation derived from the calibration curve was $y = 40039x + 200.15$, where y was the peak height of fluroxypyr butyl ester obtained from gas chromatography (GC) analysis and x was the concentration of fluroxypyr in $\mu\text{g ml}^{-1}$. The detection limit of fluroxypyr was $4 \mu\text{g kg}^{-1}$.

Field Experiment

Chromatograms shown in Figures 1a, 1b and 1c are fluroxypyr in standard solution, untreated and treated soil samples respectively. The retention

time of fluroxypyr was 8.9 min. Table 2 shows the residue concentrations of fluroxypyr in the soil. The fluroxypyr residue was detected at 10-50 cm depth at one day after treatment (DAT) at the recommended dosage. At 1 DAT, the highest concentration ($44 \mu\text{g kg}^{-1}$) was recorded at the depth of 30-40 cm followed by that at the deepest layer (40-50 cm depth), which had a concentration of $35 \mu\text{g kg}^{-1}$. The fluroxypyr concentration decreased with time of sampling. The concentration of fluroxypyr at the top 10 cm of the soil decreased faster than that in the lower profile. No residue was detected at the depth of 0-20 cm at five days after treatment, while on seven days after treatment fluroxypyr residue was only found at the depth of 20-40 cm. However, on Day 14 after treatment, no residue was detected, irrespective of the soil profile. Factors such as volatilisation, runoff, leaching, chemical and biological degradation as well as photolysis could have enhanced the degradation rate especially under tropical climatic conditions such as those found in Malaysia. Moreover, the high temperature, humidity and rainfall throughout the year could have contributed to the rapid loss of the pesticides from the experimental plot. Other factors besides the acceleration of pesticide degradation and dissipation under tropical conditions might also be responsible. One possible factor could be the non-uniform spraying of the pesticides that could have caused uneven pesticide distribution throughout the trial plot.

PERSIST Prediction for Fluroxypyr

The data obtained from the field study of fluroxypyr in the clay soil at the KLIA Oil Palm Plantation, was subjected to the PERSIST simulation model. Table 3 shows the PERSIST predicted values and the observed results of fluroxypyr studied in the clay soil at the KLIA Oil Palm Plantation, Sepang, Selangor, Malaysia. On Day 0 after spraying, there was perfect agreement obtained between the observed and predicted results with CRM = 1. On Day 1 and 5 after spraying, the CRM values for PERSIST were 1.01 and 1.09, which is in almost perfect agreement between the observed and

TABLE 1. RECOVERY OF FLUROXYPYR FROM SPIKED SOIL SAMPLES USING OASIS[®] 200 mg IN CLEAN-UP PROCESS

Concentration of fluroxypyr ($\mu\text{g kg}^{-1}$)	Recovery (%) n=5	Relative standard deviation (%)
1	107	0.5
5	100	4.7
10	101	2.5
25	100	0.7
50	82	0.9

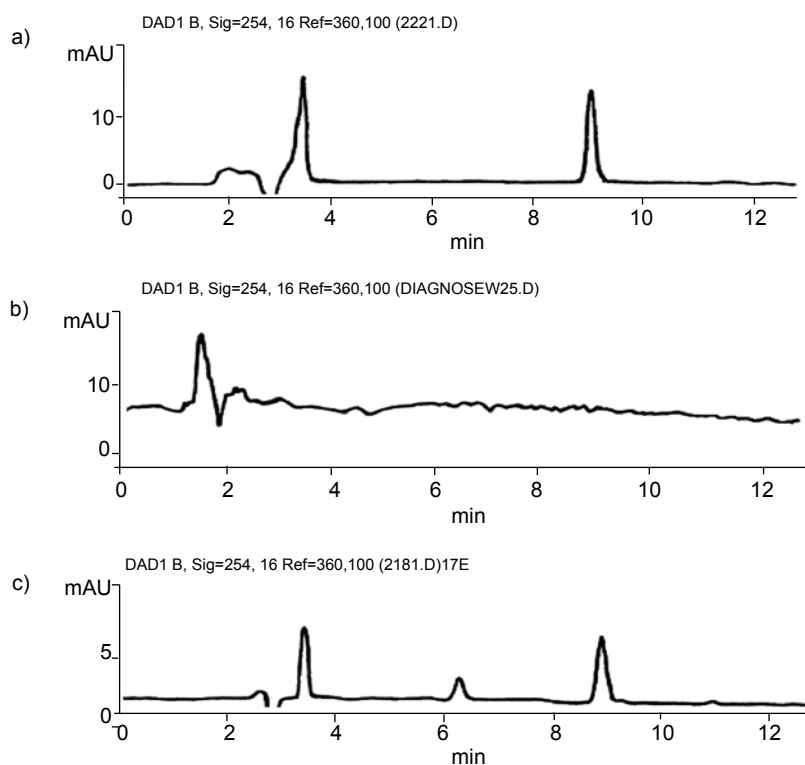


Figure 1. High performance liquid chromatography-diode array detector (HPLC-DAD) chromatograms of (a) untreated sample of soil, (b) standard fluroxypyr solution, $0.02 \mu\text{g ml}^{-1}$ and (c) spiked soil sample containing $0.05 \mu\text{g g}^{-1}$ of fluroxypyr.

TABLE 2. CONCENTRATION OF FLUROXYPYR RESIDUE IN SOIL SAMPLES TREATED AT THE MANUFACTURER’S RECOMMENDED DOSAGE

DAT	Depth (cm)	Concentration of fluroxypyr ($\mu\text{g kg}^{-1}$)
1	0-10	ND
	10-20	15 ± 1.1
	20-30	28 ± 2.1
	30-40	44 ± 1.4
	40-50	35 ± 2.1
5	0-10	ND
	10-20	ND
	20-30	42 ± 0.7
	30-40	29 ± 0.7
	40-50	25 ± 1.3
7	0-10	ND
	10-20	ND
	20-30	25 ± 0.7
	30-40	11 ± 0.7
	40-50	ND
14	0-10	ND
	10-20	ND
	20-30	ND
	30-40	ND
	40-50	ND

Note: DAT - day after treatment.
 ND - not detected = $< 1 \mu\text{g kg}^{-1}$.

predicted results. Results from the field observation indicated that fluroxypyr residue was not detected from Day 7 onwards, while the prediction from PERSIST showed that there would be fluroxypyr residue up to Day 7 after spraying (Figure 2).

The Day 1 and 5 after spraying; the percentage difference between observed and predicted values were 1.13% and 9.85%, respectively (Table 3). However, these values were less than the allowable 30%, so the prediction of PERSIST for fluroxypyr does conform very well with the observed values. Thus, the PERSIST model is acceptable for predicting fluroxypyr residue in soil.

VARLEACH Prediction for Fluroxypyr Residue

Predicted results for VARLEACH obtained from the computer program and results observed from the field trial are shown in Figure 3. The field trial values were lower than the predicted values except on the day of spraying (Day 0). Furthermore, the dissipation of fluroxypyr in the field trial was much faster than that predicted by VARLEACH. Fluroxypyr was detected in the soil on Day 0, 1 and 5 after spraying. Meanwhile, in the VARLEACH simulation, fluroxypyr was predicted to dissipate completely from Day 30 onwards. The dissipation time of fluroxypyr was longer in the VARLEACH prediction. This might be due to other factors such

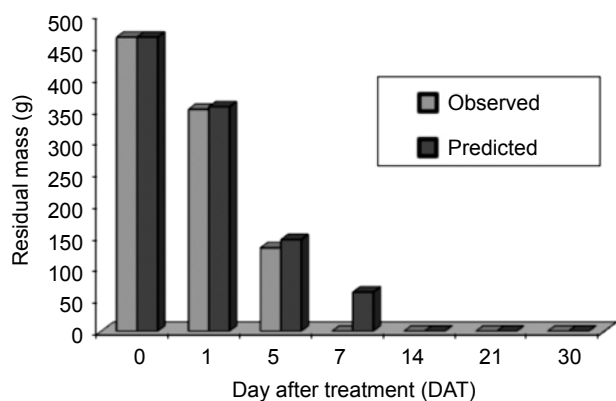


Figure 2. Measured and predicted dissipation of fluroxypyr in the soil (PERSIST simulation).

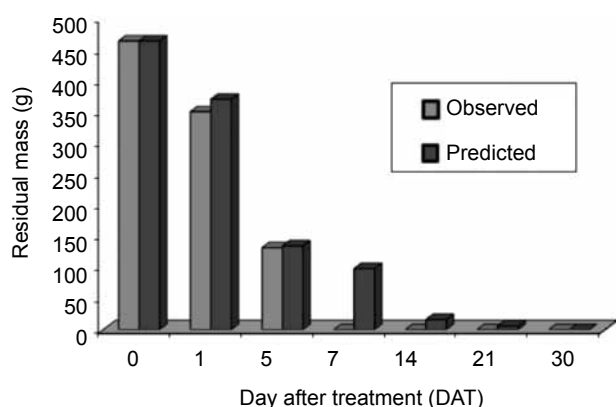


Figure 3. Observed and predicted dissipation of fluroxypyr in the soil (VARLEACH simulation).

as volatilisation and microbial activity that may have contributed to rapid dissipation of fluroxypyr in the field trial. Similar findings on dissipation have been reported by Ismail and Kalithasan (2002), where the predicted data derived from the model showed higher values than the observed data. Tay (2012) also reported comparable results in which the VARLEACH model predicted the movement of propyzamide, linuron and isoxaben with considerable agreement to the field observation.

Predicted results for VARLEACH obtained from the computer program and data derived from the field trial are shown in Table 4. On Day 0 after treatment there was a perfect agreement between predicted and observed values since the value of CRM was equal to 1 and no differences were observed between model simulation and field trial results. The CRM values for VARLEACH on Day 1 and 5 after spraying were very close to 1 that is 1.05 and 1.02, respectively, indicating that the simulation model gave only a very slight overestimation. Therefore, there was good agreement between data derived from the simulation model and that of the observed field results.

The differences between the simulation model and field trial data were very low, namely 0%, 5.7% and 2.3% on Day 0, 1 and 5, respectively, after spraying (Figure 3). Therefore, we can conclude that the VARLEACH model values and field trial results for fluroxypyr compounds were in very good agreement.

TABLE 3. DEGREE OF AGREEMENT AND ACCURACY OF PERSIST MODELING FOR FLUROXYPYR RESIDUES IN SOIL

Day	CRM for PERSIST	% Difference between observed and PERSIST
0	1	0
1	1.01	1.13
5	1.09	9.85
7	-	-
14	-	-

Note: CRM – Coefficient of Residual Mass.

TABLE 4. DEGREE OF AGREEMENT AND ACCURACY OF VARLEACH MODELING FOR FLUROXYPYR RESIDUES IN SOIL

Day	CRM for VARLEACH	% Difference between observed and VARLEACH
0	1	0
1	1.05	5.7
5	1.02	2.3
7	-	-
14	-	-

Note: CRM – Coefficient of Residual Mass.

CONCLUSION

PERSIST prediction for fluroxypyr residues in soils planted with oil palm was found to be accurate and conformed to the observed results. The model PERSIST predicted that fluroxypyr would remain longer in soil but the observed data indicated that the residue persisted in soil was for a shorter period compared to the predicted value. However, the dissipation rate of fluroxypyr predicted via modelling showed similar pattern to the observed data. It was evident that the VARLEACH model gave accurate predictions for fluroxypyr residues, in agreement with the observed results. The VARLEACH predictions and the observed data were in good agreement. There was a slight variability in the accuracy of the VARLEACH prediction for fluroxypyr. However, the predicted VARLEACH and observed values were well fitted to each other even though the VARLEACH values were overestimated. Therefore these models are useful in evaluating the persistence and mobility of fluroxypyr in the soil.

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