Leaching of Chlorpyrifos in Peat Soil of an Oil Palm Plantation in Malaysia

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ABSTRACT

The aim of the paper is to determine the leaching and persistence of chlorpyrifos in a Malaysian peat soil. Leaching of chlorpyrifos in this peat agroecosystem was conducted at an oil palm plantation in Sessang, Sarawak, East Malaysia. The insecticide chlorpyrifos was applied as an aqueous solution into the trench which was approximately 1 meter around the palm base at the rate of 3 L/palm. The insecticide was applied at the manufacturer’s recommended (2.11 gm ai/trunk) and double the recommended dosage (4.22 gm ai/trunk). The control plot was not treated with insecticide. Soil samples were collected at different depths (viz. 0-15, 15-30 and 30-45 cm) at the following intervals; -1 (before treatment), 0, 1, 3, 7, 14, 21, 30 and 60 days after treatment. The recovery of chlorpyrifos as obtained from GC equipped with FPD was determined by analyzing soil samples spiked with chlorpyrifos standard solutions at five different levels viz., 2, 20, 40, 60 and 80 µg/kg. The recovery and relative standard deviation of chlorpyrifos in the spiked soil samples ranged from 93 to 97% and 1.1 to 9.6%; respectively. The results obtained were good and reproducible with high recovery rates and therefore the extraction methods were used for determination of chlorpyrifos in soil samples collected from the field. Chlorpyrifos was detected at all levels of the soil profile (0-45 cm), when applied at the recommended and double the recommended dosages. Chlorpyrifos was detected in the soil up to day 5 after treatment when applied at the recommended dosage. Chlorpyrifos was also detected in the soil at 0-45 cm depth up to day 7 after treatment at double the recommended dosage. Therefore, chlorpyrifos has very low persistence in the soil and therefore may have low impact on the environment.

Key words: Chlorpyrifos, Leaching, Peat soil, Oil palm plantation, Recommended dosage, Double recommended dosage

Introduction

Pesticides are one of the major components of modern farming practices. Pesticides, a component of pest management, are constantly used to safeguard the crop from deleterious effects caused by insects and disease attack. Therefore, pesticides are of economic importance as they help prevent outbreaks that threaten the yield and quality of crops. The fate of pesticides in the soil is greatly influenced by their interaction with the soil components, the environment, and their transport from one environmental compartment to another (Ismail and Kalithasan, 2003; Racke, 1993). The rate of degradation of pesticides in the soil is one of the most important criteria that determine the behaviour of pesticides in the environment (Goring and Hamakers, 1975). Pesticides applied to the field are potential environmental contaminants (Carton et al., 1997).

The environmental fate of pesticides has recently attracted much attention because of its potential to pollute the environment. Lake and river water can undoubtedly be contaminated with the runoff water from adjacent agricultural fields if the use of pesticides is not managed properly.

Heavy usage of pesticides in agricultural activities may cause adverse effects to the environment and consequently human health. The leaching of pesticides into groundwater is a major environmental concern

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because it affects the quality of underground water (Lehmann et al., 1993). The number of different pesticides in ground and surface water has been increasing steadily (Lehmann and Miller, 1989). Therefore, an understanding of adsorption, desorption and mobility of pesticides in the soil warrants immediate attention.

The presence of insecticide residues in the runoff, sediment and leachate, as well as their mobility and persistence in the soil, depends on factors such as the chemical and physical properties of the compound, soil properties, amount of rainfall, soil bed construction and slope (Riley et al., 1994). Most pesticides, for example, persist longer in soils with high organic matter content (Oppong and Sagar, 1992). Soil mobility and degradation are the most important processes that determine the fate of pesticides in the soil.

Chlorpyrifos, a broad-spectrum chemical, is the most intensively used organophosphate insecticide in agriculture (Larson et al., 1997). It is registered for the control of soil insects and some foliar insect on a wide range of crops, including citrus fruits, bananas, strawberries, vegetables, as well as for household use (Kidd and James, 1991). The heavy use of chlorpyrifos poses the risk of environmental pollution.

In Malaysia it was registered in 1997 for use on crops such as oil palm, rubber, coconut, chili, cocoa, leguminous crops, pepper and rice. Formulations of chlorpyrifos for use in Malaysian agriculture are available under the trade name Dursban. In Malaysia, chlorpyrifos is extensively used for effective control of the leaf folder and leafhopper that threaten the production of food crops such as rice (Racke, 1993; Arthur, 1995; Chung et al., 1991; Hamnish and David, 1991; Wood and Ng, 1969) as well as in oil palm plantations for the control of the rhinoceros beetle, bagworm, termites, nettle caterpillar and bunch moth (Mohd. Basri and Norman, 2000).

There has been a steady increase in the use of pesticides in developing countries although integrated pest management (IPM) programmes are being promoted and implemented. The increasing use of pesticides poses a growing concern regarding their presence in food and the danger of their residues in the environment. Pesticides used in tropical countries could affect environmental quality (Tanabe et al., 1990). It has been reported that pesticide pollution of ground and surface water is an issue in tropical countries, with heavy rainfall, high humidity and high temperature (Halimah et al., 2010; Ismail et al., 2009; Cheah et al., 2000; Ismail et al., 2002; Khakural et al., 1995). However, there is limited information on the impact of chlorpyrifos in tropical environments such as Malaysia. Although extensive research has been carried out in other countries, the results are not applicable in Malaysia because of differences in climatic and soil conditions. Therefore, the objective of this study is to determine the downward movement of chlorpyrifos through the soil profile and its persistence in the peat soil of an oil palm plantation, near Sessang, Sarawak.

Materials and methods

Experimental Site

The study was conducted at the oil palm plantation of the Malaysian Palm Oil Board (MPOB) located at Sessang, Sarawak. The experimental site was level and nine plots, each measuring approximately 0.75 hectare were used for the study. Analysis showed that the soil contained clay (0%), coarse sand (35.5%), fine sand (4.91%), silt (41.81%) with a total Carbon content of 49.50%, pH 3.48, soil moisture 14.85% and CEC of 59.3 Cmol (+)/kg soil. The soil was classified as peat soil according to its soil characteristics. The palms in the plots were treated with chlorpyrifos at either the recommended or double the recommended dosage. No pesticide was applied to the control plots which were sprayed with water. Each treatment was replicated thrice, the randomized complete block design was used and spraying was carried out simultaneously for all plots. The trial was conducted from 26th July 2006 to 25th October 2006. The monthly rainfall was obtained from the Sessang Meteorological Station during the study period (January till December 2006).

Chlorpyrifos (LORSBAN 40EC; Dow Elanco Ltd)) used in the treatments contained 21.2% a.i. (active ingredient). It was applied as an aqueous solution to the palms by spraying using a conventional knapsack sprayer (nozzle 5/64, fine droplets). To prepare the recommended and double the recommended dosages, 18 and 36 mL of the commercial product were diluted respectively in 9 L of water which is equivalent to 2.11 ai/trunk and 4.22 ai/trunk, respectively. Five L of the diluted product were sprayed on the trunk surface up to the spear and the area around the palm base was drenched.

Sampling of Peat Soil from the Field Trial

The application of the insecticide chlorpyrifos was carried out in all experimental plots (in triplicate). Soil samples were randomly collected from each replicate (plot) using an auger at different depths; 0-15 cm, 15-30 cm and 30-45 cm. Samples were collected at the following intervals: -1 (before treatment), 0 (6 h after treatment), 1, 5, 7, 14, 21, 30, 60 and 90 days after treatment. Soil samples were dried in an air conditioned
room at 16°C and sieved through a 2 mm sieve to remove debris and large particles. The soil samples were then stored at -4°C to inhibit microbial activity before analysis.

For the mobility study, soil samples were collected at a distance of 200 m from the base of each palm and at different depths (0-15 cm, 15-30 cm, 30-45 cm). For each plot, five samples were taken from each depth and combined. The soil sampling was done using an auger at the following intervals: -1, 0, 1, 3, 7, 14, 30, 60 and 90 days after treatment. The soil samples collected were air-dried in an air-conditioned room at 16°C for one week, and then ground using a mortar and pestle. Prior to the analyses, the air-dried soil samples were sieved through a 4 mm sieve and stored at -4°C.

Reagents and Insecticide

All reagents and solvents used in the study were of analytical grade. Acetone, hexane, petroleum ether, acetonitrile and dichloromethane were obtained from Merck. Standard chlorpyrifos (98.7% purity) was purchased from the Laboratories of Dr. Ehrenstorfer, Germany. Commercial silica cartridges, supelclean LC-SI (1 gm) were purchased from Supelco. Sodium chloride was obtained from Merk.

Apparatus

A Gas Chromatograph (GC: HP 6890 series) fitted with an auto sampler was used. The rotary evaporator, N-Evap Model 1111 for evaporating the solvent, was purchased from Organomation Associates Inc., US. The vortex mixer Type 37600 (used to shake the oil added with the acetonitrile saturated with petroleum ether for extracting chlorpyrifos from the oil) was purchased from Thermolyne Co., USA. A solid phase extraction manifold was purchased from Supelco. Centrifuge tubes (15 mL), vials (20 mL), volumetric flasks (10 mL) and round bottomed flasks 10 and 50 mL were used. The WARING commercial blender was used to cut the leaf.

Conditions for GC-FPD

A Hewlett-Packard Model 6890 GC with a Flame photometric detector (FPD) fitted with a non-polar column coated with 5% phenyl methyl siloxane (HP-5MS), 30 m length, 0.25 mm i.d. and 0.25 mm film thickness was used. Operating conditions for the GC-FPD were as follows: in column flow (Nitrogen) 1.2 mL/min, and inlet pressure 12.20 psi. The injector temperature was 250°C, on splitless mode. The oven temperature was programmed from 40°C for 1 min followed by a gradual increase of 30°C/min to 220°C. After holding for 6 min, the temperature was then increased at 20°C/min from 220 to 280°C and held for 2 min.

Determination of Chlorpyrifos in Peat Soil

The method used for determination of chlorpyrifos in the peat soil samples was according to the method of Halimah et al. (2010) and Halimah (2007). Ten gram soil samples were placed in 250 mL conical flasks. The soil was spiked with standard chlorpyrifos solution in acetone to obtain 2 to 80 mg/kg chlorpyrifos in the soil, and the contents were mixed using a vortex mixer. Fifty mL of hexane were then added to each conical flask and contents were mixed again for 30 sec on the vortex mixer. The conical flask was placed on a shaker for 20 min. Twenty five mL of the extract were then transferred into a 100 mL round bottomed flask using a 20 mL pipette. The solution was evaporated down to about 5 mL using a rotavapour and then transferred into a graduated micro-vial. The extract was further evaporated to 2 mL using a N2 evaporator. The contents were then mixed in a vortex mixer for 3 sec prior to injection into the GC-FPD. The same procedure was adopted for both the untreated and treated from the field trial samples before injection into the GC-FPD, with the exception of the spiked standard solutions.

Results and discussion

Standard Calibration Curve for GC-FPD

To determine the reproducibility of the injection technique and linearity of the FPD response, repeated injections of 0.02 - 0.10 mg/mL standard chlorpyrifos solution were made into the capillary GC column. The calibration curve of the various concentrations of standard chlorpyrifos against the gas chromatographic peak area is as shown in Figure 1. The equation derived from the above data is \[ Y = 2462.6x + 3.7375 \], where \( y \) is the peak area of standard chlorpyrifos solution and \( x \) is the concentration in mg/mL. The \( r^2 \) for the curve is 0.9955 at 99% confidence.
Recovery of Chlorpyrifos from Peat Soil Samples

Table 1 shows the recovery of chlorpyrifos from spiked soil ranging from 93-97% with relative standard deviation of 1.1 to 9.6%. The retention time of chlorpyrifos was around 10.40 min. Figure 2A shows the GC chromatogram of standard chlorpyrifos solution at 0.02 µg/mL. Figures 2B and 2C show the chromatograms of untreated soil samples and spiked soil samples containing 0.02 mg/g chlorpyrifos, respectively. Figure 2D shows the chromatogram of chlorpyrifos in soil from the field at 0 DAT. The limit of quantification for chlorpyrifos in soil was 2 µg/kg.

![Fig. 1: Calibration curve of standard chlorpyrifos solution against the peak area (GC-FPD)](image)

![Fig. 2: GC-FPD Chromatograms of A) Chlorpyrifos standard solution @ 0.02 µg/mL, B) Blank sample of soil and C) Spiked soil samples containing 0.02 µg/g of chlorpyrifos D) Soil samples from the field trial at 0 DAT](image)
Table 1: Recovery of chlorpyrifos from spiked soil samples

<table>
<thead>
<tr>
<th>Amount added µg/kg</th>
<th>Mean recovery (%) N=5</th>
<th>Relative standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>97</td>
<td>6.1</td>
</tr>
<tr>
<td>20</td>
<td>93</td>
<td>1.1</td>
</tr>
<tr>
<td>40</td>
<td>93</td>
<td>9.6</td>
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<tr>
<td>60</td>
<td>94</td>
<td>3.3</td>
</tr>
<tr>
<td>80</td>
<td>95</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The Level of Chlorpyrifos Residue in the Soil

Figure 3 shows the chlorpyrifos residue in soil samples with treatment at the recommended dosage. Residues of chlorpyrifos were detected in the soil samples collected at intervals of 0, 1, 3 and 5 days after treatment at the recommended dosage. Amounts of chlorpyrifos residue detected in the soil, ranged from 0.005 - 0.306 mg/g for sampling intervals of 0 and 5 days after treatment. Chlorpyrifos residue was detected at the depth of 0-45 cm on day 0 (the sample was taken 6 hours after application) and up to day 5 after treatment. The highest concentration (0.0306 mg/g) was found at the depth of 15-30 cm on day 0. The rapid downward movement of chlorpyrifos may be due to the high rainfall during the study period. It should be noted that the monthly rainfall recorded for July, August, September and October 2006 were 96.40, 132.0, 336.80 and 212.0 mm, respectively. The total amount of chlorpyrifos at the depth of 0-45 cm was reduced by 52% from 0 Day after treatment (DAT) to 1 DAT and by 17.41% from 1 DAT to 3 DAT for the recommended dosage. Meanwhile, at 3 DAT to 5 DAT, the total amount of chlorpyrifos was further reduced by 42.8%. It was also observed that chlorpyrifos was not detected at all depths tested on 7 DAT onwards (0-45 cm).

Fig. 3: The concentration of chlorpyrifos residue in the soil profile when applied at the recommended and double the manufacturer’s recommended dosage

Figure 3 also shows chlorpyrifos residue in the soil when applied at double the recommended dosage. A similar pattern was observed in the downward movement of chlorpyrifos for both the recommended and double the recommended dosages, where it was observed that the applied insecticide moved downwards through the soil profile from 0-45 cm depth.

On 1 DAT, the amount of chlorpyrifos ranged from 0.0936 to 0.1540 mg/g at all soil depths when the plot was sprayed at double the recommended dosage. It was also found that on the first day after treatment, chlorpyrifos was deposited mostly at the depths of 30-45 cm. However, this compound did not persist long in the environment and it was not detected on 14 DAT.
Conclusion

In conclusion, chlorpyrifos was observed to have easily leached into the lower layers of the soil profile (0-45 cm depth), probably due to heavy rainfall during the study period. The persistence of chlorpyrifos in the soil occurred for a shorter period when applied at the recommended dosage compared to persistence at double recommended dosage. However, the chlorpyrifos residue in the soil was not detected at 14 DAT when applied at double the recommended dosage. The results clearly showed that the half-life is shorter in tropical areas and may not cause detrimental effects on the environment. However, this primary conclusion needs to be proved with further research and experiments.

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References
