Journal of Oil Palm Research Vol. 22 April 2010 p. 721-728

DOWNWARD MOVEMENT OF CHLORPYRIFOS IN THE SOIL OF AN OIL PALM PLANTATION IN SEPANG, SELANGOR, MALAYSIA

HALIMAH MUHAMAD*; TAN YEW AI*; ISMAIL SAHID and NASHRIYAH MAT⁺**

ABSTRACT

A study on the leaching of chlorpyrifos in an oil palm agro ecosystem was conducted in an oil palm plantation in Sepang, Selangor. The insecticide chlorpyrifos was sprayed using a knapsack sprayer at the recommended and double the recommended dosage. Soil samples were collected at different depths, viz. *0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm at the following intervals: -1 day (before treatment), 0 day (day of treatment, 6 hr later), 1 day, 3, 7, 14, 30 and 60 days after treatment. Recovery of chlorpyrifos from the soil spiked with chlorpyrifos at 4-50 μg kg^{-1} ranged from 88%-99% with the coefficients of variation ranging from 2.0% to 7.5%. Chlorpyrifos residue was detected at 0-10 cm and 10-20 cm depths when applied at the recommended and double the recommended dosages, respectively. The residue was only detected in the soil for up to five and seven days after treatment, respectively, when applied at the recommended and double the recommended dosages.*

Keywords: chlorpyrifos, leaching, oil palm plantation, dosage.

Date received: 7 March 2009; **Sent for revision:** 18 March 2009; **Received in final form:** 16 July 2009; **Accepted:** 9 December 2009.

INTRODUCTION

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 insects on a wide range of crops, including citrus fruits, banana, strawberry and vegetables, as well as for household use (Kidd and James, 1991). The heavy use of chlorpyrifos poses a risk of environmental pollution.

Recently, the environmental fate of pesticides has attracted attention because of the pollution caused. Water bodies can be contaminated by the run off from agricultural fields if pesticide use is not properly managed.

A number of studies has been carried out on chlorpyrifos in the environment (Getzin, 1981a, b; Barra *et al*., 1995; Cid Montanes and Van Hattum, 1995; Gurunathan, 1998), but scarcely any has been undertaken in Malaysia (Cheah *et al*., 1997; 2001; Ismail *et al*., 2002). Therefore, the consequences of using chlorpyrifos under Malaysian conditions remain largely unknown. The objective of this study was to determine the downward movement of chlorpyrifos through the soil profile and its persistence in the soil in an oil palm plantation.

MATERIALS AND METHODS

Reagents

All reagents and solvents used were of analytical grade. Acetonitrile, acetone, dichloromethane and hexane were obtained from Merck, and standard chlorpyrifos of 99.7% purity was purchased from the Laboratories of Dr Ehrenstorfer, Germany. Sodium chloride (GR) and anhydrous sodium sulphate (AR) were also obtained from Merck.

---

* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur, Malaysia.
E-mail: halimah@mpob.gov.my

** School of Environmental and Natural Resource Sciences,
Universiti Kebangsaan Malaysia,
43600 UKM Bangi, Selangor, Malaysia.

⁺ Faculty of Agriculture and Biotechnology,
Universiti Darul Iman Malaysia,
20400 Kuala Terengganu, Malaysia.

Experimental Details

The study was conducted in an oil palm plantation located 6-7 km from the Kuala Lumpur International Airport (KLIA), and owned by the Malaysian Agricultural and Horticultural Sdn Bhd (MAAH). The plantation is at an altitude of 16.3 m, with the geographical coordinates of 2° 44′ N and 101° 42′ E. The number of palms planted per hectare was 142. The experimental site was flat with nine plots drawn out, each measuring approximately 0.33 ha, and containing 6 x 7 = 42 palms. The plots were applied with either the recommended or double the recommended dosage of chlorpyrifos. No chemical was applied in the control plots. Each treatment was replicated thrice in a randomized design and applied at the same time as the rest. The trial was conducted from July 2002 to September 2002.

Standard laboratory methods (Allison, 1965; Day, 1965) were used to determine the physico-chemical properties of the soil. All the soil data were expressed on a dry weight basis. The soil was a loam with 30.6% moisture, 6.08% total organic carbon, 17% clay, 31.25% silt, 51.25% fine sand and 0.3% coarse sand, giving a total sand content of 51.55%. The pH of the soil was 4.97.

Chlorpyrifos (Dursban® 75 E) used in the treatments contained 21.2% a.i. It was applied in an aqueous solution to the palms, sprayed 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 chemical product were diluted separately in 9 litres of water. One hundred and fifty millilitres of the diluted product containing 3.8 g a.i. (recommended dosage) and 7.6 g a.i. (double the recommended dosage) were sprayed on each palm at the bole for 2 s and at the crown for 4 s. The date of spraying was 25 June 2003.

Soil Samples

For the mobility study, soil samples were collected at a distance of 200 m from the base of each palm and at different depths of the soil (0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm) as shown in *Figure 1*. For each plot, five samples were taken from each depth and combined. The soil sampling was done using an auger at the following time intervals: -1 day (before treatment), 0 day (6 hr after treatment), 1 day, 3, 7, 14, 30, 60 and 90 days after treatment. The collected soil samples were air-dried in an air conditioned room at 16ºC 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 -4ºC.

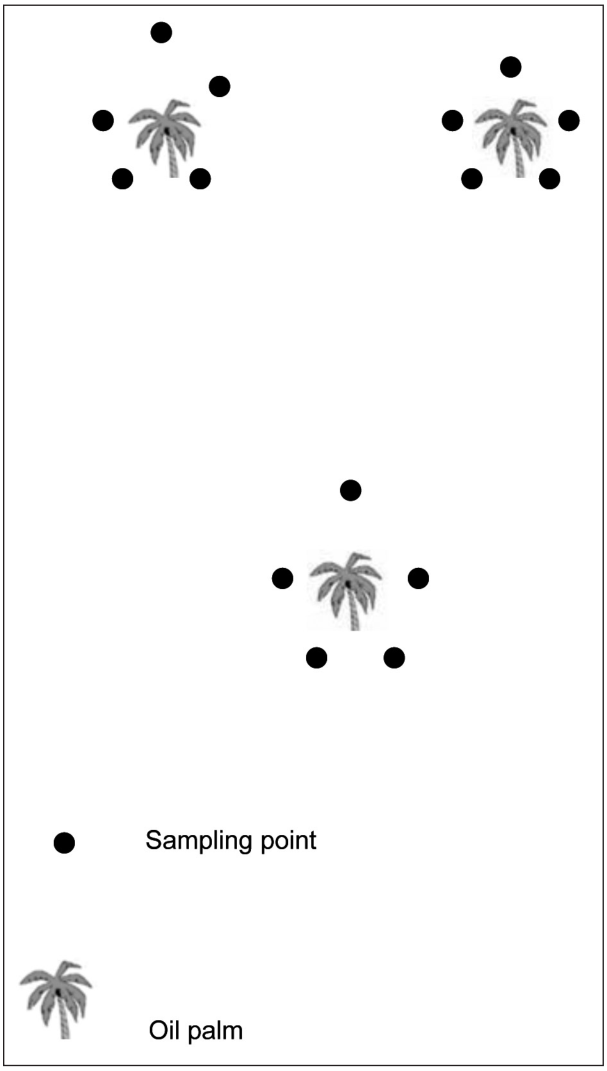

Figure 1. Positions where soil samples were collected.

Preparation of Chlorpyrifos Stock Solution for Plotting the Standard Curve

Chlorpyrifos (0.05 g) was dissolved in 50 ml hexane to make a stock solution of 1000 μg ml^{-1} concentration. An intermediate stock solution of 100 μg ml^{-1} was prepared by placing 1 ml of the standard stock solution in a 10-ml volumetric flask and making up to the mark with hexane. Working standard solutions containing 0.02 to 1 μg ml^{-1} chlorpyrifos were prepared by appropriate dilution of the intermediate stock solution with hexane. All the working standard solutions were stored in glass bottles with Teflon-lined screw caps and kept at -20ºC before use.

Each of the working standard solutions of chlorpyrifos in hexane was then injected into a gas chromatograph equipped with a halogen-specific detector (GC-XSD) to obtain a calibration curve, constructed by plotting the concentration of chlorpyrifos against the peak area. The linearity of the detector response and reproducibility of the injections were checked by evaluating the curve.

Extraction of Chlorpyrifos from the Soil

Five-gram samples of chlorpyrifos-free soil were placed in 250-ml conical flasks. The samples were spiked with the standard chlorpyrifos solutions in hexane (0.02 to 5.0 μg ml^{-1}), to give equivalent concentrations of 0.001 to 1 μg g^{-1} soil. The contents were then mixed using a vortex mixer, and the mixtures were allowed to homogenize by standing for 20 min. Twenty millilitres of a mixture of hexane: ethyl acetate (95:5) were added to each conical flask and the contents mixed thoroughly again for 30 s on the vortex mixer. Each conical flask was then placed in an ultrasonic bath for 20 min, after which the contents were transferred into a test tube and centrifuged at 3500 rpm at 26ºC for 10 min. The supernatant (10 ml) was then transferred into a graduated micro vial using a Pasteur pipette. The solution was evaporated to dryness using a nitrogen-evaporator and the residue redissolved in 5 ml hexane. This was then mixed in an ultrasonic bath for 3 s prior to injection into the GC-XSD.

A similar procedure was applied to the soil samples from the treated plots before injecting the product into the GC. There were three replications for each concentration.

GC-XSD Conditions

A Hewlett-Packard Model 5890 (US) GC with an OI Analytical Model 5360 XSD was used, together with a non-polar capillary column of 100% dimethylpolysiloxane (DB-1), 30 m length, 0.25 mm i.d. and 0.25 μm film thickness. The carrier gas flow (nitrogen) was 1.0 ml min^{-1}. The injector and detector temperatures were set at 250ºC and 300ºC, respectively. The reactor temperature was 1000ºC with the XSD air flow at 230 ml min^{-1}. The oven was programmed as follows: 40°C for 1 min, ramped at 15ºC min^{-1} to 150ºC, ramped at 25°C min^{-1} to 260ºC, and held for 5 min. The injection volume was 3 ml.

Weather Conditions

Figures 2 to *4* show the daily volume of rainfall, rate of evaporation, and maximum and minimum air temperatures (°C) recorded at the KLIA meteorological station during the study period. The monthly rainfall for July, August and September 2002 was 138.8 mm, 186.0 mm and 190 mm, respectively. The total rain falling from day 0 to day 10 after treatment with chlorpyrifos was 41.1 mm, while from day 11 to day 21 it was 89.6 mm. The maximum air temperature for July, August and September was 34.3ºC, 34.8ºC and 33.8ºC, respectively, while the minimum air temperature was 22.8ºC, 23.2ºC and 22.8ºC, respectively. The average daily evaporation for July, August and September was almost the same at 4.3 mm, 4.4 mm and 3.7 mm, respectively.

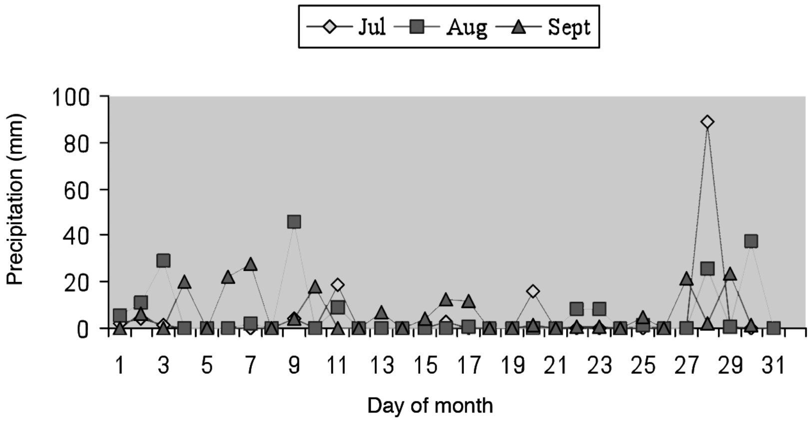

Figure 2. Daily rainfall records from July-September 2002 at KLIA, Sepang.

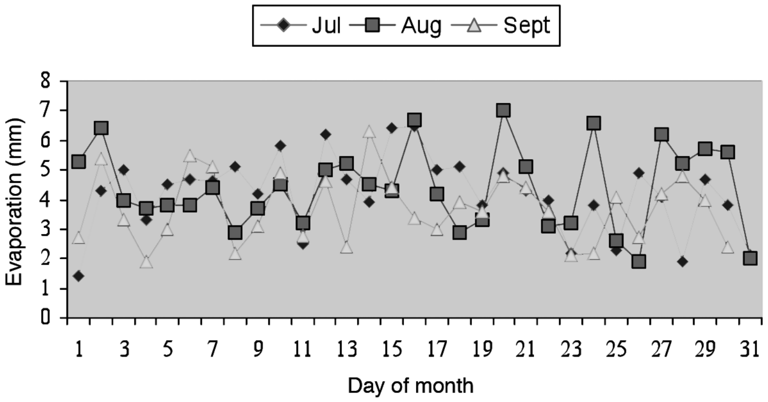

Figure 3. Daily evaporation records from July-September 2002 at KLIA, Sepang.

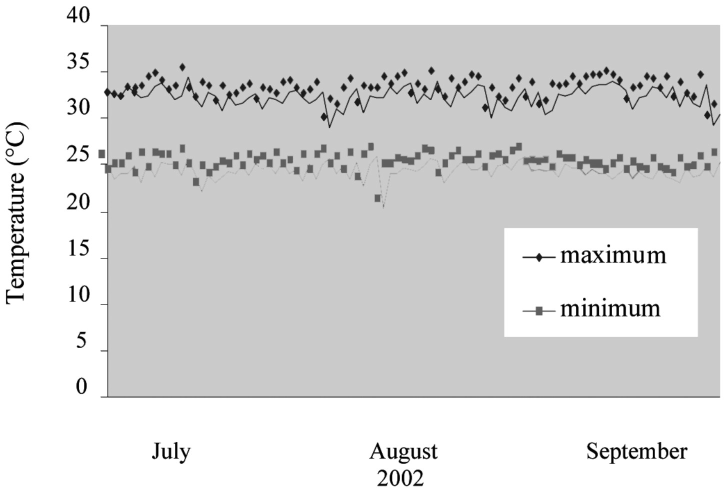

Figure 4. Maximum and minimum air temperatures (°C) from July-September 2002 at KLIA, Sepang.

RESULTS AND DISCUSSION

Figure 5 shows the calibration curve of standard chlorpyrifos against the GC peak area obtained using the XSD detector. The linear regression (R^2) was found to be 0.9993, and the equation derived from the calibration curve was y = 309.99x –1.6367, where *y* is the area of chlorpyrifos and *x* the concentration of chlorpyrifos in μg ml^{-1}.

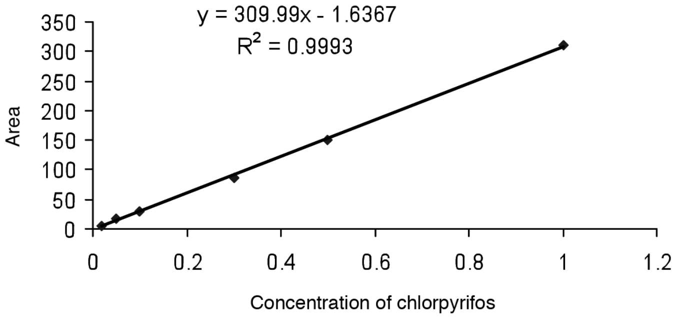

Figure 5. Calibration curve for chlorpyrifos using GC-XSD.

TABLE 1. RECOVERY OF CHLORPYRIFOS FROM THE SPIKED SOIL

Amount spiked (μg g^{-1})	Mean recovery (%) N=5	Relative standard deviation (%)
0.001	91	7.5
0.05	96	3.9
0.1	92	5.9
0.2	88	2.5
1.0	99	2.0

Table 1 shows that the method used for extracting chlorpyrifos gave reproducible results. The recovery of chlorpyrifos from the spiked soil samples ranged from 88%-99% with standard deviations of 2.0% to 7.5%. The minimum detection limit of chlorpyrifos was 0.001 μg g^{-1} and was calculated as five times the chromatographic noise level of the standard solution. The results showed that the method used to extract chlorpyrifos from the soil is reproducible and acceptable.

Table 2 shows the chlorpyrifos residue in soil samples at the recommended and double the recommended dosages, averaged over triplicate samples. When applied at the recommended dosage, the residue (57.7 μg kg^{-1}) detected at 0-10 cm depth on day 0 (sample taken 6 hr after application) decreased with time. The concentrations in the top 10 cm of the soil were 43.2, 16.5 and 5.1 ug kg^{-1} at 1 day, 3 and 5 days after treatment, respectively. There was no leaching below 10 cm depth. No residue was detected at all in the soil (at all depths) from day 7 onwards.

When applied at double the recommended dosage, residues were detected as deep as 20 cm with 80.2 μg kg^{-1} and 43.1 μg kg^{-1} in the 0-10 cm and 10-20 cm profiles, respectively, when sampled approximately 6 hr later. The concentration also decreased more with time in the top soil profile than in the lower. The concentration decreased by 74.7% and 50.9% at 0-10 cm and 10-20 cm depth within three days. Chlorpyrifos residue could be detected at 0-20 cm depth until five days after treatment (*Table 2*). On day 7, residue was only detected at 10-20 cm soil depth, but no residue was detected at 0-10 cm depth (*Table 2*). As in the treatments with the recommended dosage, no residue was detected at all after day 7 (*Table 2*).

Previous studies have demonstrated that several factors, such as adsorption of the pesticide by the soil particles, water solubility of the pesticide, volume of leachate, pH and soil texture, can influence the leaching of the pesticide through the soil (Kidd and James, 1991; Crisanto *et al.*, 2000; Halimah *et al.*, 2004). However, adsorption is the most important factor (Nicholls 1988). The adsorption processes are affected by soil composition, such as organic matter (OM) content. A higher OM content increases adsorption, hence reducing downward movement of the pesticide. It is worthwhile to note that the soil in this study was a loam (higher OM than a sandy soil). Therefore, it is not surprising that at the recommended dosage the residue was not detected below 10 cm depth. These results differ from those reported by Ismail *et al.* (2004), where the mobility of chlorpyrifos was studied in a sandy loam in the Cameron Highlands. They reported that chlorpyrifos residue was detected at a depth of 0-50 cm one day after application. The mobility of the pesticide was greater in the sandy loam because of its lower adsorption, thereby contributing to faster downward movement. The results of the present study are in agreement with those of other researchers (Walker *et al.*, 1989; Walker and Exposito, 1998), who also proved that OM had an influence on the adsorption of pesticides in the soil. It is well documented that the leaching potential of pesticides in the soil is influenced by the soil's physico-chemical properties, such as its organic matter content and the solubility of the compound applied. Halimah *et al.* (2004) and Ismail *et al.* (2004) reported a positive correlation between the adsorption of pesticide and OM content.

As expected, at double the recommended dosage, more chlorpyrifos leached deeper into the soil than at the recommended dosage. The more chlorpyrifos applied, the more of it would be available to leach downwards. Kotoula-Syka *et al.* (1993) reported that more leaching occurred at higher concentrations of the insecticide applied.

The weather, especially rain, also plays an important role in the mobility of chlorpyrifos. Rainfall was low during the study, and it was therefore not surprising that most of the residue remained in the top 10 cm depth. Ismail *et al.* (2004) demonstrated the effect of rainfall on the mobility

TABLE 2. CONCENTRATION OF CHLORPYRIFOS RESIDUE IN THE SOIL PROFILE APPLIED AT THE RECOMMENDED AND DOUBLE THE RECOMMENDED DOSAGES

DAT[a]	Depth (cm)	Concentration of chlorpyrifos ($\mu g\ kg^{-1}$)	
		Recommended dosage (N = 3)	Double recommended dosage (N = 3)
0	0-10	57.7 ± 3.7	80.2 ± 7.4
	10-20	ND	41.3 ± 3.0
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND
1	0-10	43.2 ± 3.6	20.3 ± 2.1
	10-20	ND	68.4 ± 4.0
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND
3	0-10	16.5 ± 2.5	14.2 ± 4.5
	10-20	ND	20.3 ± 5.4
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND
5	0-10	5.1 ± 1.1	3.4 ± 2.3
	10-20	ND	8.1 ± 3.2
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND
7	0-10	ND	ND
	10-20	ND	6.7 ± 1.0
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND
14	0-10	ND	ND
	10-20	ND	ND
	20-30	ND	ND
	30-40	ND	ND
	40-50	ND	ND

Note: ND: not detected, *i.e.* < 1 $\mu g\ kg^{-1}$; [a]day after treatment.

of chlorpyrifos with residues detected at 50 cm depth, just one day after application. The rainfall during their study was considerably higher than in this study.

The residue degraded quickly in the loam soil as no residue was detected on day 7 and day 14 for both dosages. The dissipation rate was faster in the top 10 cm layer. The soil microbial population is higher in top soil (Ismail *et al.*, 2004), so degradation can be expected to be faster there. Therefore, no residue was detectable in the top 10 cm whereas it could still be detected in the 10-20 cm depth after a similar length of time had passed.

The current results differ from those of Ismail *et al.* (2004). The difference may in part be attributable to the different environmental factors of the studies, such as higher rainfall, geographical features (such as the rugged terrain and slopes often greater than 40^o) found in Cameron Highlands, as well as the lower soil OM content. Under the above conditions, chlorpyrifos is easily washed into the streams and can leach away quickly, thus reducing its concentration in the soil. Oppong and Sagar (1992) also found that most pesticides persist longer in soils with high OM content. Therefore, it is not surprising that chlorpyrifos was detected for a slightly longer time in this study than in the study by Ismail *et al.* (2004).

Residues could be detected down to depths of 10 cm and 20 cm at the recommended and double the recommended dosages, respectively. Chlorpyrifos was not very persistent in the soil, as the residues could only be detected up to day 5 and day 7 after application at the recommended and double the recommended dosages, respectively.

REFERENCES

ALLISON, L E (1965). Organic carbon. *Methods of Soil Analyses, Part 2* (Black, C A ed.). American Society of Agronomy, Wisconsin. p. 1367.

BARRA, R; VIGHI, M and DI GUARDO, A (1995). Prediction of surface water input of chloridazon and chlorpyrifos from an agricultural watershed in Chile. *Chemosphere*, *30(3)*: 485-500.

CHEAH, U B; KIRKWOOD, R C and LUM, K Y (1997). Adsorption-desorption and mobility of four commonly used pesticides in Malaysian agricultural soils. *Pesticide Sci.*, *50*: 53-63.

CHEAH, U B; MA, C K; DZOLKHIFLI, O; AINIE, K and CHUNG, G F (2001). Persistence of cypermethrin, deltamethrin and endosulfan in an oil palm agroecosystem. *Proc. of the 2001 PIPOC International Palm Oil Congress*. 20-22 August 2001, Hotel Istana, Kuala Lumpur, Malaysia. p. 105-113.

CID MONTANES, J F and VAN HATTUM, B (1995). Bioconcentration of chlorpyrifos by the freshwater isopod *Assellus aquaticus* (L) in outdoor experimental ditches. *Environmental Pollution*, *88*: 137-146.

CRISANTO, T; SANCHEZ-MARTIN, M J and SANCHEZ-CAMAZANO, M (2000). Mobility of pesticides in soils influence of soil properties and pesticide structure. *Toxicol. Environ. Chem.*, *47*: 97-104.

DAY, P R (1965). Particle fractionation and particle size analysis. *Methods of Soil Analyses, Part 1* (Black, C A ed.). American Society of Agronomy, Wisconsin. p. 545.

GETZIN, L W (1981a). Degradation of chlorpyrifos in soil: influence of autoclaving, soil moisture, and temperature. *J. Econ. Entomol.*, *74*: 158-162.

GETZIN, L W (1981b). Dissipation of chlorpyrifos from dry soil surfaces. *J. Econ . Entomol.*, *74*: 707-713.

GURUNATHAN, S (1998). Accumulation of chlorpyrifos on residual surface and toys accessible to children. *Environ. Hlth. Perspec.*, *106*: 9-16.

HALIMAH, M N; NASHRIYAH, M; TAN, Y A and ISMAIL, B S (2004). Adsorption and desorption study of ^{14}C-chlorpyrifos in two Malaysian agricultural soils. *J. Nuclear and Related Technologies*, *1(1)*: 31-40.

ISMAIL, B S; ENOMA, A O; CHEAH, U B; LUM, K Y and ZULKIFLI, M (2002). Adsorption, desorption and mobility of two insecticides in Malaysian agriculture soil. *J. Environ. Sci. Health*, *B3*, *4*: 355-364.

ISMAIL, B S; NGAN, C K; CHEAH, U B and ABDULLAH, W Y (2004). Leaching potential of pesticides in a vegetable farm in the Cameron Highlands, Malaysia. *Bull. Environ. Contam. Toxicol.*, *72(4)*: 836-843.

KIDD, H and JAMES, D R (1991). *The Agrochemicals Handbook*, *A 0791/Aug 91*. Third edition. Unwin Brothers Limited Old Working, Surney.

KOTOULA-SYKA, E; ELEFTHEROHONINOS, I G; GAGIANA, A A and SCIFAS, A G (1993). Persistence and pre-emergence application of chlorsulfuron, metsulfuron, triasulfuron and tribenuron in three soils in Greece. *Weed Sci.*, *41*: 246-250.

LARSON, S J; CAPEL, P D and MAJEWSKI, M S (1997). *Pesticides in Surface Waters: Distribution, Trend and Governing Factors*. Ann Arbor Press, Chelsea.

NICHOLLS, P H (1988). Factors influencing entry of pesticides into soil water. *Pestic. Sci.*, *22*: 123-137.

OPPONG, F K and SAGAR, G R (1992). Degradation of triasulfuron in soil under laboratory conditions. *Weed Res.*, *32*: 157-165.

WALKER, A and EXPOSITO, M J (1998). Adsorption of isoproturon, diuron and metsulfuron methyl in two soils at high soil-solution ratio. *Weed Res.*, *38*: 229-238.

WALKER, A; COTTERILL, E G and WELCH, S J (1989). Adsorption and degradation of chlorsulfuron and metsulfuron-methyl and triasulfuron in soils from different depths. *Weed Sci.*, *29*: 281-287.