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FATE OF THIRAM IN AN OIL PALM NURSERY DURING THE WET SEASON

MAZNAH ZAINOL*; ISMAIL SAHID* and HALIMAH MUHAMAD**

ABSTRACT

Thiram (tetramethylthiuram disulfide) is a fungicide used to control plant pathogenic fungi such as Rhizoctonia *spp,* Phythium *spp. and* Fusarium *spp. which often infest oil palm seedlings from the pre-nursery until the main nursery stage. With increasing applications of thiram in oil palm nurseries, it is necessary to investigate the fate of thiram in the nursery environment. The trial was conducted from July till August 2008,* i.e. *during the wet season, at the Labu Estate Nursery (Sime Darby), Nilai, Negeri Sembilan. The subplots were treated with thiram at the manufacturer's recommended dose and at double recommended dose. Thiram residue was detected in the soil at all depths (from 0-50 cm) for both treatment doses on the day of spraying (0 DAT). The amount of residue was observed to decrease with soil depth. Analyses of water and oil palm leaflets within the trial showed that thiram was found at 0 and 3 days after treatment of the trial plots at the recommended and double the recommended doses. The results showed that adsorption and dissipation of thiram were slowly being influenced by the type of soil and the total amount of rain received during the experiment. Run-off and wash-off were the major causes of the loss of thiram residues from the water in the nursery environment and from the leaflets of the oil palm seedlings.*

Keywords: thiram, nursery, leaching, fate study.

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INTRODUCTION

Pesticides are a group of chemicals used predominantly for crop protection in agriculture and in public health care against vectors that carry diseases such as malaria, filariasis and dengue fever. The use of herbicides is recognised as an economical practice to curb weeds in plantations of industrial crops such as oil palm as they reduce reliance on manpower for manual weeding. Moreover, manual weeding is slower and often delayed, resulting in weed infestation of the plantation (Traore *et al*., 2010). Besides weed and pest problems, the oil palm is also prone to attack by several diseases. The major diseases are vascular wilt, basal stem rot, bud and spear rot, red ring disease and sudden wilt. Therefore, fungicides are used to destroy or inhibit the growth of the pathogenic fungi without injuring the plant, while leaving non-poisonous residues in edible crops.

Previous studies have demonstrated the occurrence of pesticide contamination in rice, tobacco and vegetable agrosystems in Malaysia (Cheah and Lum, 1998; Zuriati *et al*., 2003; Margaret and Chai, 2010). There is, however, limited information on the effects of pesticide use in oil palm agroecosystems because only a few selected pesticides have been studied. Some of the research studies include a study on the run-off and persistence of cypermethrin, deltamethrin and endosulfan in an oil palm plantation in Sungai Buloh Estate (Cheah *et al*., 2001), a study on the mobility of fluroxypyr-MHE in clay soil collected from the Malaysian Agricultural and Horticultural

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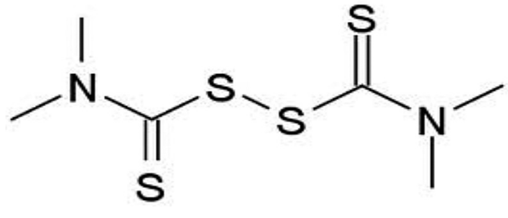
company's oil palm plantation (Halimah *et al*., 2005), and a study on the leaching of chlorpyrifos in the oil palm agroecosystem at Sepang (Halimah *et al*., 2010). The results of the chlorpyrifos study show that when applied at single and double the recommended dosages, chlorpyrifos residue was detected in the soil up to five and seven days after treatment, respectively.

Thiram is the common name for tetramethylthiuram disulfide (chemical formula: $C_6H_{12}N_2S_4$). It is available in a variety of formulations under the trade names of *Thiram* (US), *Thiuram* (Japan), *TMTD* (Russia), *Hexathir, Nomersan, Pomasol, etc*. Thiram belongs to the group of dimethyldithiocarbamate compounds which have melting points ranging from 155˚C-156˚C and a molecular mass of 240.44. The structure of thiram is shown in *Figure 1*. Thiram is used as a fungicide to prevent crop damage in the field and to protect harvested crops from deterioration during storage and transportation (Sharma *et al*., 2003). Ainie *et al*. (2007) reported that thiram was among the most common pesticides used in oil palm plantations in Malaysia from 1999 to 2007. Thiram is mostly used at the nursery stage to prevent seedling blight, and during the second stage of the nursery, thiram is applied when the diseases caused by *Melanconium*, *Glomerella* and *Rhizoctonia* spp. begin to infest the seedlings. Thiram has a low to moderate persistence in the soil and is nearly immobile in clay soils or soils high in organic matter content (Sharma *et al*., 2003). Thomas (2001) reported that thiram is rapidly broken down by hydrolysis and photodegradation, especially under acidic conditions. The major metabolites of thiram in the soil are copper dimethyldithiocarbamate, dimethylamine and carbon disulphide (Extoxnet, 1996).

To the best of the authors' knowledge, no studies have been carried out on the fate of thiram in oil palm nurseries in Malaysia, or anywhere else. Nonetheless, thiram has been used since 1970 and its application in oil palm nurseries in Malaysia is still increasing; therefore, further studies need to be done. The objective of the current study was to determine the presence and the amount of thiram residue in the soil, surrounding water and in oil palm leaflets in an oil palm nursery during the wet season.



Source: Montgomery (2000).

Figure 1. Structure of thiram.

MATERIALS AND METHODS

Experimental Design

The study was conducted at the nursery of Labu Estate (an estate owned by Sime Darby) located in Nilai, Negeri Sembilan. The study area covering 0.5 ha was divided into nine plots to accommodate three treatments, replicated thrice. Each plot was 0.056 ha in size. The three treatments comprised treatments at the manufacturer's recommended dose, at double the recommended dose, and a control without any treatment. Each trial plot carrying 140 polybags of oil palm seedlings was separated from adjacent plots by a buffer zone with two rows of seedlings. The oil palm seedlings used in the study were 6 to 11 months old. The polybags used to raise the seedlings were 38 cm x 46 cm in size and made of black UV stabilised polyethylene.

Fungicides

Thiram (Ancom Thiram 80®) fungicide was applied using a knapsack sprayer (with nozzle No. 5) at a volume of 16 litres per plot. The doses applied were 25.6 g a.i. per plot and 51.2 g a.i. per plot, following the manufacturer's recommended dose and double the recommended dose according to the product label.

Soil Sampling

For each plot, soil samples were taken randomly from the centre of the plot at five points using an auger at the following depths: 0-10, 10-20, 20-30, 30-40 and 40-50 cm (*Figure 2*). Soil samples collected from each replicate at the same depth were combined before analysis. Soil sampling was carried out one day before treatment (-1), immediately after spraying (day 0) and on 1, 3, 5, 7, 14, 21, 30, 60, and 90 DAT (days after treatment). The collected soil samples were air-dried for three to five days in an air-conditioned room at 16ºC, sieved through a 2-mm sieve, and stored at -4ºC prior to analysis to inhibit microbial activity.

Water Sampling

One-litre water samples were collected from each plot at five points (*Figure 2*) on the same days and at the same intervals used for sampling soil described above. The water samples were stored at 4ºC prior to analysis to inhibit microbial activity.

Leaflet Sampling

A total of five leaflets were taken from each seedling at the second frond which is fully opened. The leaflets were taken from three randomly chosen

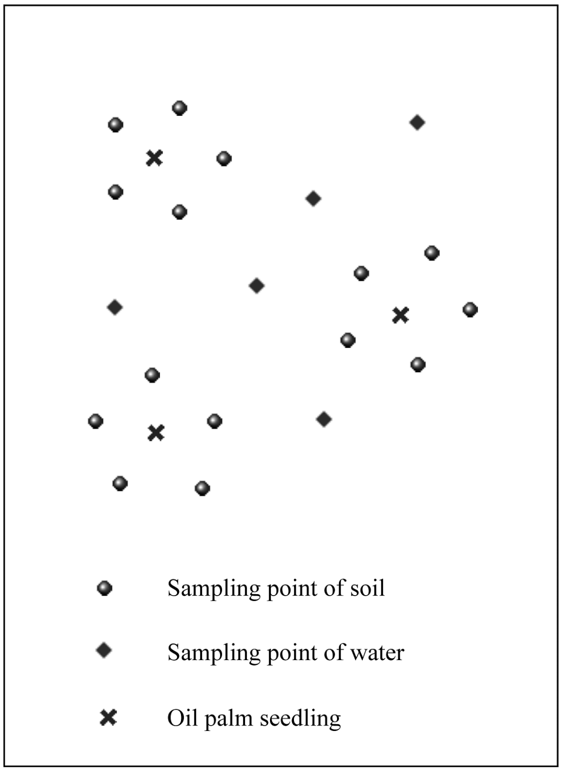


Figure 2. Points from which soil and water were sampled in a plot.

seedlings and bulked together. The leaflets were then ground, weighed in plastic bags and stored at -10ºC prior to analysis. The sampling of leaflets was carried out on the same days and intervals as for soil and water sampling.

HPLC Conditions

The HPLC system used for detecting thiram residue consisted of a high pressure pump with a diode array detector (DAD) and the HPChem system for qualitative elaboration. The column used was C_{18}, 25 cm x 4.6 mm id, 5 μm (Ascentis SUPELCO 581325-U). The mobile phase was acetonitrile and water in a ratio of 1:1 at the isocratic mode with a flow rate of 1.0 ml min^{-1}. The UV wavelength was set at 230 nm while the injection volume was 20 μl.

Weather Conditions

Figure 3 shows the monthly rainfall records from January to October 2008 at the Labu Estate Nursery weather station. Monthly rainfall was highest in April, October and July, at 416.5, 256.0 and 236.0 mm, respectively. The field trial was conducted during one of the wet periods from July to August 2008. The amount of rainfall recorded from day 0 to 60 DAT was 330.10 mm, while the total amount of rainfall from January to October 2008 was 1934.10 mm. *Figure 4* shows the daily volume of rainfall recorded at Labu Estate Nursery weather station. The total rain which fell from day 0 to day 3 DAT was 147 mm. The spraying activities were carried out on 15 July 2008 (day 0).

RESULTS AND DISCUSSION

Figure 5 shows the calibration curve of standard thiram against the HPLC peak area obtained using the DAD system. For each treatment, the working standard of thiram was injected in triplicate into HPLC. The results show good linearity with a regression coefficient of $R^2 = 0.999$, and the equation derived from the calibration area data was $y = 152.3x - 36.69$, where y is the area of thiram obtained from the HPLC analysis and x is the concentration of thiram in μg ml^{-1}.

Table 1 shows the concentration of thiram residue in the soil after treatment at the recommended and double the recommended doses, and averaged for the triplicate samples. At double the recommended and at the recommended doses on 0 DAT, the total amount of thiram found in the soil at 0-10

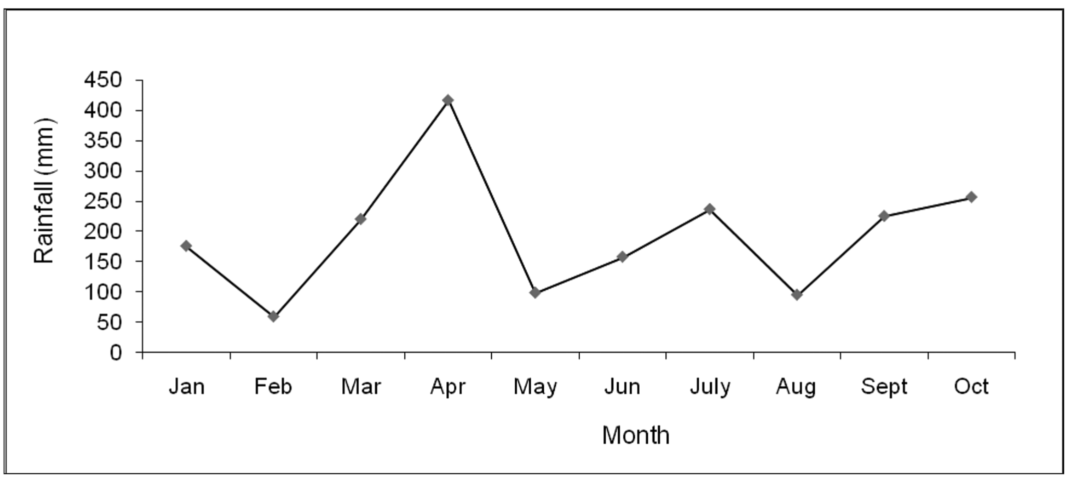


Figure 3. Monthly rainfall records from January to October 2008 at the Labu Estate Oil Palm Nursery in Nilai.

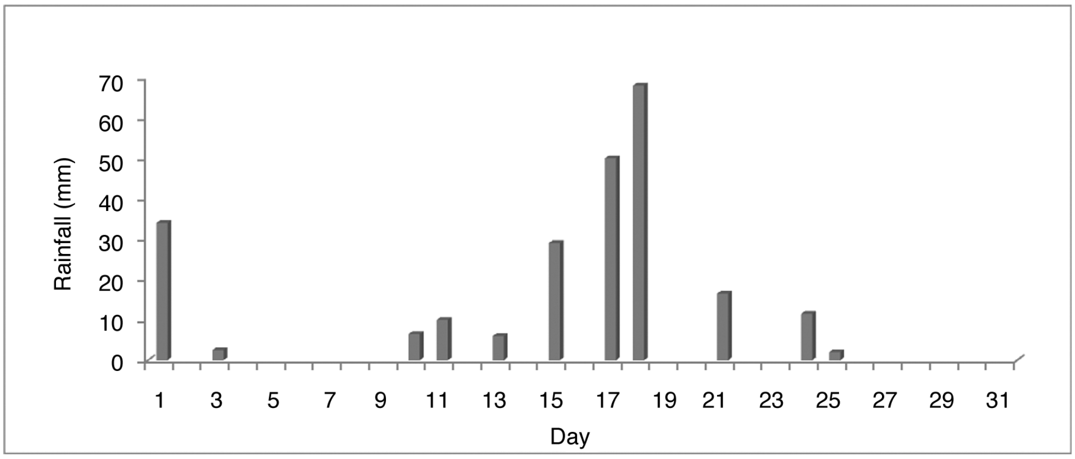


Figure 4. Daily rainfall records in July 2008 at the Labu Estate Oil Palm Nursery in Nilai.

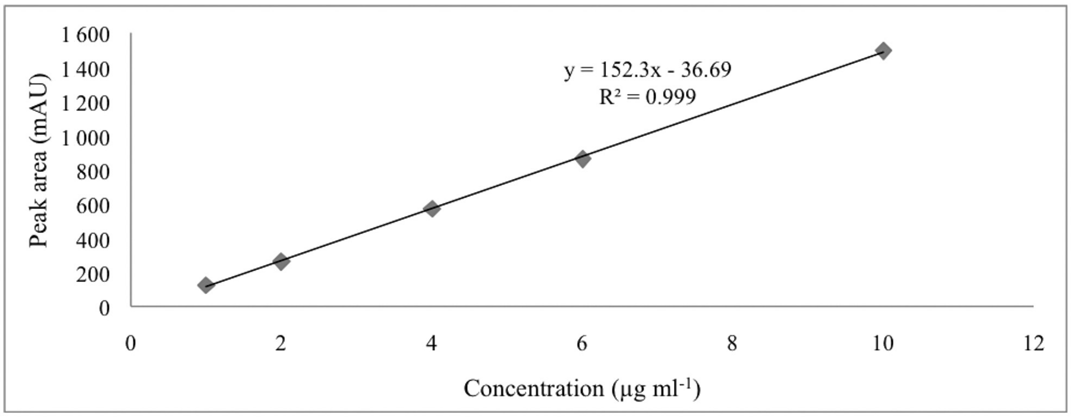


Figure 5. Calibration curve for thiram using HPLC-DAD.

TABLE 1. CONCENTRATIONS OF THIRAM RESIDUE IN THE SOIL PROFILE WHEN APPLIED AT THE MANUFACTURER'S RECOMMENDED DOSE AND AT DOUBLE RECOMMENDED DOSE AT VARIOUS TIME INTERVALS AFTER TREATMENT

DAT*	Depth (cm)	Recommended dose (25.6 g a.i. per plot)	Double the recommended dose (51.2 g a.i. per plot)
		Concentration (μg g^{-1})	
0	0 – 10	79.30 ± 1.21	129.34 ± 1.69
3	10 – 20	64.15 ± 1.54	90.82 ± 5.56
	20 – 30	28.44 ± 1.94	38.73 ±1.76
	30 – 40	12.89 ± 3.97	33.42 ± 1.70
	40 – 50	1.22 ± 0.20	22.08 ± 0.63
	0 – 10	ND**	ND
	10 – 20	ND	ND
	20 – 30	ND	ND
	30 – 40	ND	ND
	40 – 50	ND	ND

Note: *DAT: day after treatment.
**ND: not detected.

cm was 129.34 μg g^{-1} and 79.30 μg g^{-1}, respectively. Throughout the soil profile studied, at double the recommended dose, the amount of thiram deposited in the soil ranged from 22.08 to 129.34 μg g^{-1} with standard deviations ranging from 0.63 to 1.69. At the recommended dose, the amount of thiram deposited varied from 1.22 to 79.30 μg g^{-1} with standard deviations ranging from 0.20 to 1.21. Most of the thiram was deposited on the top layer of the soil (0-10 cm) and the concentration decreased as the depth increased for both treatments. This field study indicates that thiram leached down to a depth of 50 cm when applied at the recommended and double the recommended doses. Three days after treatment, thiram was not detected at all depths of the soil profile (0-50 cm), for both treatment doses.

Results of ANOVA, at 95% confidence level, show that there was a significant difference between the two treatment doses for samples from each depth of the soil profile on the day of treatment (day 0). Analyses of thiram in soil at control plot were also carried out, however no residue was detected.

Pesticide persistence in the soil is influenced by a wide range of factors, including soil constituents, weather conditions and the physico-chemical properties of the compound (Accinelli *et al.*, 2003). Several factors, such as adsorption of the pesticide onto soil particles, water solubility of the pesticide, volume of the leachate, pH and soil texture, can influence the leaching of the pesticide through the soil profile (Kidd and James, 1991). However, adsorption of a pesticide to the soil plays a major role, and adsorption is stronger in soils with a higher organic carbon content and in soils with low pH (acidic) (Ismail *et al.*, 2009). It should be noted that the soil in the current study was a sandy clay loam with the following characteristics: 50.75% sand, 28.32% silt, 20.93% clay, 4.16% OM, CEC of 13.35 meq./100 g and pH of 5.52. Hence, thiram residue in the soil profile was only detected on day 0 (immediately after spraying), which means that thiram was not well adsorbed onto the soil. Valverde-Garcia *et al*. (1988) concluded that the adsorption of thiram in Almeria soils depended primarily on the organic matter content, followed by the clay content of the soil. The greater mobility of pesticides in sandy clay loam was due to their lower adsorption, thereby contributing to a faster downward movement through the soil profile. Therefore, the thiram residue could be found at each studied depth of the soil profile, decreasing with soil depth.

Rainfall during this study was considered heavy after the spraying activities. On the days of the first, second and third sampling, the total rainfall received was 29, 50 and 68 mm, respectively, leading to movement of the thiram through the soil profile. Previous results by Oppong and Sagar (1992) indicate that the movement of triasulfuron down the soil profile was 22.5 cm when exposed to 52.8 mm rainfall as compared with an exposure to 36 mm rainfall where the triasulfuron was detected only at the 0-7.5 cm depth. Lee *et al*. (2000) reported that due to intense rainfall and timing, a high concentration of pendimethalin was found in the run-off samples. Kloppel *et al*. (1994) and Van Wesenbeeck *et al*. (2001) suggested that pesticide run-off was greatest when rain fell immediately after the pesticide application. Run-off in relation to high rainfall would result in high application losses of the pesticides (Southwick *et al.*, 2003). Immediately after a heavy rainstorm, pesticide residues dissolved in the soil solution are rapidly transported through the macropores in the soil profile, leaching to the bottom (Bergstrom, 1995).

The study was undertaken during a wet season when rain fell almost every day. Rainfall affects pesticides in the following ways: it breaks their bond with the soil, dissolves them in water, or loosens and transports the pesticide-laden soil particles through erosion (Anon., 1999). As expected, thiram residue could only be found on day 0 (6 hr after spraying) in both the treatment plots, while after three days, there were no more residues left in the soil. Halimah *et al*. (2009) demonstrated that the residue of fluroxypyr was found in the soil only on 1 DAT during the wet season, whereas during the dry season, fluroxypyr was detected on 1 and 5 DAT. Ismail *et al*. (2004) reported on the effect of rainfall on the mobility of chlorpyrifos in a vegetable farm in Cameron Highlands. The rate and route of water infiltration into the soil to a large extent determine the pesticide concentration and loss in the surface run-off. Gouy *et al*. (1999) reported that the total amount of isoproturon and atrazine founds in the run-off, and transferred mostly in solution, was correlated to the K_d values. Atrazine which is highly soluble in water (33 mg litre^{-1}) was well distributed in solution in the run-off compared with that in the sediment during the experiment. Thiram with a high solubility in water (30 mg litre^{-1}) would be expected to behave in the same manner as atrazine.

Table 2 shows thiram residue was found in the water samples collected from both the treated plots. Thiram residue in the water was only detected on 0 and 1 DAT. In the plot applied with thiram at the recommended dose, the residue was detected at 7.30 ± 0.25 μg litre^{-1} and 5.65 ± 0.22 μg litre^{-1} on 0 day and 1 DAT, respectively. The amount of residue was higher in the plot applied with double the recommended dose, being 8.41 ± 0.23 μg litre^{-1} and 8.56 ± 0.10 μg litre^{-1} on 0 and 1 DAT, respectively. On 3 DAT, no residue was found in the water samples from both the treatment plots. Results from ANOVA indicate that the concentration of thiram in plots treated with a single dose showed a significant difference (P=0.05) between day 0 and day 1, but in plots treated with the double dose, no significant difference was observed. Thiram residue was not detected in water at control plot at any interval.

TABLE 2. CONCENTRATION OF THIRAM RESIDUE IN WATER SAMPLES FROM EACH TREATMENT PLOT

DAT*	Recommended dose (25.6 g a.i. per plot)	Double the recommended dose (51.2 g a.i. per plot)
	Concentration (μg litre^{-1})	
0	7.30 ± 0.25	8.41 ± 0.23
1	5.65 ± 0.22	8.56 ± 0.10
3	ND**	ND

Note: *DAT: days after treatment.
**ND: not detected.

TABLE 3. CONCENTRATION OF THIRAM RESIDUE IN THE OIL PALM LEAFLET SAMPLES FROM EACH TREATMENT PLOT

DAT*	Recommended dose (25.6 g a.i. per plot)	Double the recommended dose (51.2 g a.i. per plot)
	Concentration (μg g^{-1})	
0	0.58 ± 0.02	1.28 ± 0.02
1	0.23 ± 0.01	0.28 ± 0.00
3	ND**	ND

Note: *DAT: days after treatment.
**ND: not detected.

Table 3 shows thiram residues obtained from leaflet samples in the treatment plots. At 6 hr after spraying, thiram residue in leaflets from the plot receiving double the recommended dose was found to be higher compared with that of the leaflets sampled from the plot treated with the recommended dose, being 1.28 ± 0.02 μg g^{-1} and 0.58 ± 0.02 μg g^{-1}, respectively. At 1 DAT, the concentration of thiram in the leaflets was lower for both treatments: at 0.23 ± 0.01 μg g^{-1} and 0.28 ± 0.00 μg g^{-1} for the recommended and double the recommended doses, respectively. Similar to the observations on the water samples, thiram was also undetectable in the leaflet samples at 3 DAT. From the results of ANOVA, the calculated F value was higher than the F critical value at the 95% confidence level. These results show that there was a significant difference in thiram concentration for both treatments between day 0 and day 1. With the high amount of rainfall, the residue washed-off from the leaflets might have led to the immediate dissipation of thiram. Thiram residue was not detected in leaflets at any interval for control plot.

Occasionally during spraying activities, the release of pesticides into the environment can be harmful because the entire amount of the applied chemicals does not reach the target site. The pesticide could be absorbed by plant leaves, could contaminate water, and could drift downwind outside the target application site. Thiram residue was found only on 0 and 1 DAT in the leaflet and water samples. The data show that a higher residue was detected in the water compared with that in the leaflets of the oil palm seedlings. The solubility of thiram in water could have contributed to its higher concentration in the water.

In the field, the interactions of the processes and pathways related to pesticide movement in soil are complex. The combined influence of soil structure, pesticide properties, environmental and climatic effects could affect pesticide persistence in ecosystems. From the soil, the pesticide could move into other segments of the environment. Pesticide residues are absorbed by plants, through which they could enter the food chain, where they could later become concentrated in animal fat or edible products (Ainie *et al.*, 2007). Therefore, the amount of pesticides applied should be just adequate to control the target organisms and yet have minimal effects on the environment and food chain.

CONCLUSION

The study revealed that weather conditions such as rainfall have significant influence on the dissipation of thiram in the soil, surrounding water and leaflets of the oil palm seedlings. The loss of thiram into the environment was also affected by the physico-chemical properties of thiram. However, further studies to ascertain whether preferential flow is one of the causes of the loss of thiram in sandy clay loam soil need to be carried out in order to get a clearer picture of the fate of applied thiram.

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