Journal of Oil Palm Research Vol. 25 (1) April 2013 p. 149-158

THE FATE OF DIURON IN SOIL IN A MALAYSIAN OIL PALM PLANTATION

HALIMAH MUHAMAD*; MOHD IZWARIE RAMLI; ZURIATI ZAKARIA‡ and ISMAIL SAHID‡‡**

ABSTRACT

A field study on the leaching and persistence of herbicide diuron in an oil palm agro ecosystem was conducted in an oil palm plantation in Sepang, Selangor. Two treatments, namely the recommended and double the recommended dosage of diuron were applied in the field trial. Diuron was sprayed using a knapsack sprayer (18 litres) at the rate of 0.3 kg ha^{-1} (recommended dosage) and 0.6 kg ha^{-1} (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, 5, 7, 14, 21, 30, 60, 90 and 120 days after treatment. Diuron residue was detected in the soil sampled at all depths, for both the dosages applied from day 0 to 60 days after treatment (DAT), with the exception of day 90 where it was only detected at the 0-10 cm depth when the plot was sprayed at double the recommended dosage. The calculated half-life of diuron when applied at both dosages was also determined and results showed that the half-life of diuron in soil when applied at the recommended and double the recommended dosage was in the range of 22.35 - 49.5 days and 18.73 - 57.75 days, respectively.*

Keywords: diuron, soil, half-life, persistence, recovery.

Date received: 19 March 2012; **Sent for revision:** 9 October 2012; **Received in final form:** 15 February 2013; **Accepted:** 18 February 2013.

INTRODUCTION

Malaysia was the largest exporter (2010-2011) of palm oil in the world (MPOB, 2011). In 2011, the cultivated area of oil palm in Malaysia was approximately 5.00 million hectares. Total exports of palm oil products in 2011 were 24.27 million tonnes compared to 23.06 million tonnes in 2010 (MPOB, 2012). Normally in agricultural crops, yield can be affected by weeds that compete for nutrients, water and sunlight (Muhamed *et al*., 2009). Therefore, efforts to control weeds in oil palm plantations constitute a major activity. Herbicides such as diuron have been used in oil palm plantations as an alternative method of weed control (Ainie *et al*., 2007).

Diuron is widely used as a selective pre- and post-emergence herbicide for the control of most broad-leaved weeds and annual grasses (Ainie *et al*., 2007; Mou *et al*., 2008). Diuron is commonly used in oil palm plantations where weeds such as grasses (*Paspalum conjugatum* and *Ottochloa nodosa)*, broad-leaf weeds (*Asystasia intrusa* and *Cleome rutidosperma*), legumes (*Desmodium triflorum* and *Mimosa pudica*) and ferns (*Lygodium flexuous* and *Nephrolepis biserrata*) are found (Wahab, 2001; Ainie *et al*., 2007). Diuron belongs to the phenylurea group of herbicides that kills plants by blocking electron transport at photosystem II, thus inhibiting

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

** School of Chemical Sciences and Food Technology,
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi,
Selangor, Malaysia.

‡ Malaysia-Japanese International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia.

‡‡ School of Enviromental and Natural Resource Sciences,
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi,
Selangor, Malaysia.

photosynthesis. Diuron is absorbed principally through the roots and is a broad spectrum herbicide killing both broad-leaf and grassy weeds.

Diuron is the common name for 3-(3,4-dichlorophenyl)-1,1-dimethyl urea ($C_9H_{10}Cl_2N_2O$). Diuron is relatively stable in the environment, however, it can be hydrolysed under acidic and alkaline conditions or at high temperatures. It has a low solubility in water (42 mg litre^{-1}) at 25°C and a high adsorption rate onto the soil particles (K_{oc} = 418 – 560). This pesticide has a low n-octanol-water partition coefficient (log K_{OW}), of around 2.87 (Kidd and James, 1991; Gooddy *et al*., 2002; Lesueur *et al*., 2008). Therefore, it can be regarded as being highly persistent in the soil and poses a risk to water bodies and sediments through leaching processes. Despite its benefits in increasing agricultural production, diuron can have a negative impact on the environment.

The sorption, behaviour and fate of diuron in the environment has been extensively studied by many researchers (Gooddy *et al*., 2002; Adriana, 2004; Chefetz *et al*., 2004; Giacomazzi and Cochet, 2004; Lanyi and Dinya, 2005; Liyanage *et al*., 2006; Cabrera *et al*., 2007). The studies on the persistence, behaviour and fate of other pesticides in oil palm plantations, such as fluroxypyr (Halimah *et al*., 2005), chlorpyrifos (Halimah *et al*., 2010a), thiram (Maznah *et al*., 2010), fluroxypyr-MHE (Halimah *et al*., 2010b), carbofuran (Farahani *et al*., 2008) and cypermethrin, deltamethrin and endosulfan (Cheah *et al*., 2001) have been carried out. However, no study has been undertaken on the downward movement and persistence of diuron in oil palm plantations of Malaysia. This article presents results on the study to determine the downward movement and half-life of diuron in an oil palm plantation.

MATERIALS AND METHODS

Reagent and Chemicals

Methanol of high pressure liquid chromatography (HPLC) grade, acetonitrile, ethyl acetate and cyclohexane were obtained from Merck, Germany. Water, obtained from a Mili-Q water purification system (Milipore Corp., USA) was used to prepare the mobile phase. Standard diuron was purchased from the Laboratories of Dr Ehrenstorfer, Augsburg, Germany and sodium chloride was purchased from Merck.

Apparatus

The micro litre pipettes, adjustable between 100 and 1000 µl and pipette tips were obtained from Eppendorf (Hamburg, Germany) and the vortex mixer from Barnstead/Thermolyne Inc. (Dubuque, IA, USA). Oasis® HLB 6cc (200 mg/6 ml) was purchased from Waters Corporation (Milford, MA, USA). The digital refrigerator thermometer was purchased from Libradi Trading Co. Ltd (Connaught Rd, Hong Kong). The vaporiser and nitrogen gas (N-Evap), were obtained from Organomation Associates Inc. (South Berlin, MA, USA) and the ultrasonic bath model 5510 from Branson (Danbury, CT, USA). The beaker (200 ml), round bottom flask (100 ml) and measuring cylinder (100 ml) were used to carry out the experiment.

Preparation of Stock Solution

Acetone (HPLC grade) was used to prepare the standard solution. The stock solution of diuron (100 µg ml^{-1}) was prepared by accurately weighing the exact amount of diuron and dissolving it in the correct volume of acetone. The solution was stored away from light, in a refrigerator. Working standard solutions used for obtaining the calibration curve were prepared by drying aliquots of the stock solution under a gentle nitrogen gas stream and redissolving the residues in an acetonitrile-water mixture (1:1, v/v) to the required concentration, prior to use.

HPLC-ultra Violet System

An Agilent 1100 HPLC system equipped with a quaternary pump (model G1311A), a degasser (model G1322A), an autosampler (model G1313A) and an ultra violet (UV) detector (model G1314A) were used for chromatography. The system was controlled by the Hewlett Packard ChemStation (Agilent Technologies), which also performed data collection from the UV detector and quantitative measurements. The UV detector was set at 254 nm for chromatographic determination. The column used was an Ascentis™ RP-Amide column (25 cm x 4.6 mm, 5 µm) from Supelco (Bellefon, USA). The mobile phase consisted of acetonitrile (solvent A) and water-methanol (2:1, v/v) (solvent B). The ratio of solvent A to solvent B was 4:6 (v/v). The flow rate was 1.0 ml min^{-1} and the volume injected was 100 µl. The column oven was set at 25°C and the analysing time was 15 min.

Experimental Details

The study was conducted at an oil palm plantation located near the Kuala Lumpur International Airport (KLIA) and Sepang International Circuit (SIC). The plantation is owned by the Malaysian Agriculture and Horticultural Association (MAHA). The number of palms planted per hectare was 160. The experimental site was located on flat land consisting of nine sub-

plots, measuring approximately 1.6 ha, with each plot containing 30 (5x6) palms. Eight-year-old palms ±7 m in height were used in the experiment. The plots were divided to two different dosage treatments which were the recommended and double the recommended dosage of diuron. Three sub-plots that were used as the control plots were only treated with 100% water. Each treatment plot was replicated thrice in a randomised block design.

The soil was analysed for its physico-chemical properties using standard laboratory methods (Allison, 1965; Day, 1965). The soil was sandy clay loam with the following physico-chemical properties: moisture (29.5%), total organic carbon (1.1%), clay (27.2%), silt (18.7%), sand (54.2%) and cation exchange capacity (CEC), (4.6 me/100 g). The pH of the soil was 5.4.

Diuron used in the treatments contained 80% a.i. It was sprayed with a conventional knapsack sprayer. The plot applied with diuron at the recommended rate was sprayed at 0.3 kg diuron ha^{-1} while the plot with diuron applied at double the recommended dosage was sprayed at 0.6 kg diuron ha^{-1}. Diuron solution was sprayed at the rate of 450 litres ha^{-1}, around the base of the palms, radius 8 feet. The spraying started on 2 March 2010 (Day 0).

Soil Sampling

The soil samples for the spiking tests were sandy clay loam obtained from the oil palm plantation at KLIA, Sepang. The samples were taken from an area free of diuron application for at least three months. Soil samples were collected using an auger at the following depths: 0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm. Three samples, taken from each depth were combined. The samples were taken at -1 (day before treatment), 0 (day of treatment, after 6 hr) 1, 3, 5, 7, 14, 21, 30, 60, 90 and 120 days after treatment (DAT). All the soil samples were air-dried at room temperature for a week and passed through a 2 mm sieve. The soil samples were stored in plastic bags at -4°C prior to analysis by HPLC-UV.

Method Development of Diuron in Soil

The extraction of diuron from the soil followed the technique suggested by Guardia-Rubio *et al.* (2006) with minor modifications. The 20 g soil samples were accurately weighed and placed in 250 ml conical flasks and spiked with standard solutions of diuron. The mixtures were homogenised using a vortex mixer for 1 min and allowed to stand for 5 min to ensure the homogeneity of the mixture. Then, 5 g of sodium chloride and 40 ml of acetonitrile were added into the conical flask and transferred to the ultrasonic water bath maintained at room temperature, for 20 min. The experiment was conducted in triplicate for samples spiked with diuron at 0.2, 0.6 and 1.0 µg g^{-1}. The extracts were then filtered with filter paper (Whatman, No. 4) at atmospheric pressure. A 10 ml extract was dried completely in nitrogen gas in a water bath set at 40°C. The residue was redissolved by adding 1 ml of a mixture of acetonitrile-water (1:1, v/v) using a vortex mixer and filtered through a 0.45 µm nylon filter to eliminate particulate material. The extract was then transferred to a 2 ml vial for further analysis.

Extraction of Diuron in Soil from Field Trial Plots

The 20 g soil samples from field trial plots were accurately weighed and placed in 250 ml conical flasks. Then, 5 g of sodium chloride and 40 ml of acetonitrile were added into the conical flask and transferred to the ultrasonic water bath maintained at room temperature, for 20 min. The experiment was conducted in triplicate for field trial samples. The extracts were then filtered with filter paper (Whatman, No. 4) at atmospheric pressure. A 10 ml extract was dried completely in nitrogen gas in a water bath set at 40°C. The residue was redissolved by adding 1 ml of a mixture of acetonitrile-water (1:1, v/v) using a vortex mixer and filtered through a 0.45 µm nylon filter to eliminate particulate material. The extract was then transferred to a 2 ml vial for further analysis.

Determination of the Half-life of Diuron in Soil

The concentration of diuron residue obtained from different depths of the soil profile was used to plot the degradation of diuron. The graph logarithm concentration of diuron residue in the soil versus day of sampling was plotted. The half-life of diuron ($t_{1/2}$) in the soil was calculated from the following equation:

$t_{1/2} = 0.693 / K$, where K is degradation coefficient rate.

Weather Conditions

Figure 1 shows the daily rainfall records at the KLIA Meteorological Station during the study period from 1 March until 4 July 2010. The highest monthly rainfall was recorded in March (208 mm) followed by April (172.5 mm), May (155 mm) and June (148.5 mm), respectively. The total rainfall from day 0 (day of treatment) to 120 DAT was 684 mm.

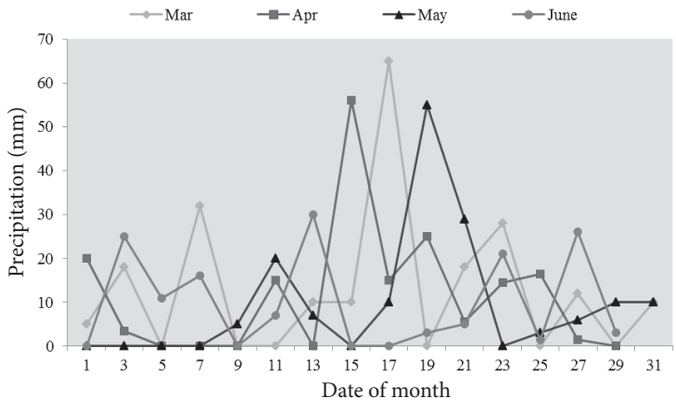

Figure 1. Daily rainfall records from March – June 2010 at Kuala Lumpur International Airport, Sepang.

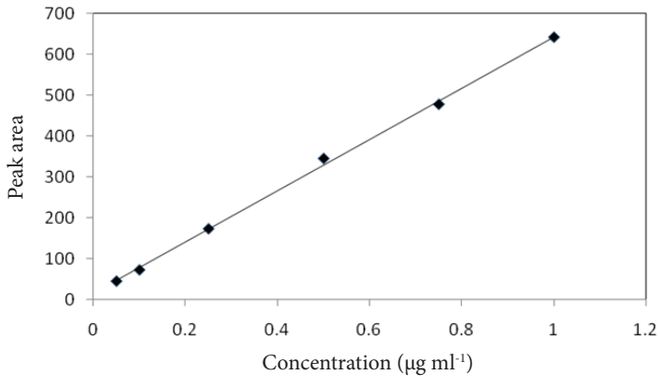

Figure 2. Calibration curve of diuron using high pressure liquid chromatography-ultra violet.

RESULTS AND DISCUSSION

Calibration Curve and Diuron Residue in the Soil Samples

The calibration curve for diuron was constructed using six points and based on the area measurement of working standards ranging from 0.05 to 1.0 µg ml^{-1}. A linear relationship between the peak area versus concentration was observed for diuron by using HPLC-UV analysis. The linear regression coefficient (r^2) was found to be 0.9983 and the equation derived from the calibration curve was y = 626.82x + 16.28, where *y* is the area of the diuron peak obtained from the HPLC analysis and *x* is the concentration of diuron in µg ml^{-1} (*Figure 2*). Since the linear regression obtained was 99.8%, the HPLC and detector were functioning efficiently (Tay, 2012; Fuad and Maher, 2010). It was also reported that the acceptance for linearity for the correlation coefficient is not less than 0.990

TABLE 1. PERCENTAGE RECOVERY OF DIURON FROM THE SOIL SAMPLES

Concentration of diuron µg g^{-1} (n=3)	Recovery (%)	Relative standard deviation (%)
0.2	95.0	2.6
0.6	93.2	1.5
1.0	94.1	4.8

TABLE 2. CONCENTRATION OF DIURON (µg g^{-1}) IN THE SOIL FOR THE TWO DOSAGES APPLIED

Day	Depth (cm)	Concentration of diuron (µg g^{-1}), n=3	
		Recommended dosage	Double recommended dosage
0	0 – 10	0.101 ± 0.013	0.211 ± 0.011
	10 - 20	0.027 ± 0.002	0.034 ± 0.001
	20 - 30	0.019 ± 0.002	0.017 ± 0.005
	30 - 40	0.014 ± 0.002	0.007 ± 0.001
	40 - 50	0.009 ± 0.001	0.010 ± 0.001

TABLE 2. CONCENTRATION OF DIURON (μg g^{-1}) IN THE SOIL FOR THE TWO DOSAGES APPLIED (continued)

Day	Depth (cm)	Concentration of diuron (μg g^{-1}), n=3	
		Recommended dosage	Double recommended dosage
1	0 – 10	0.040 ± 0.002	0.116 ± 0.008
	10 - 20	0.014 ± 0.001	0.029 ± 0.002
	20 - 30	0.014 ± 0.001	0.006 ± 0.001
	30 - 40	0.018 ± 0.006	0.005 ± 0.001
	40 - 50	0.007 ± 0.001	0.003 ± 0.001
3	0 – 10	0.041 ± 0.006	0.176 ± 0.004
	10 - 20	0.011 ± 0.001	0.045 ± 0.003
	20 - 30	0.008 ± 0.001	0.051 ± 0.006
	30 - 40	0.008 ± 0.001	0.034 ± 0.001
	40 - 50	0.007 ± 0.001	0.006 ± 0.001
5	0 – 10	0.059 ± 0.002	0.158 ± 0.004
	10 - 20	0.012 ± 0.001	0.018 ± 0.001
	20 - 30	0.012 ± 0.003	0.008 ± 0.001
	30 - 40	0.009 ± 0.001	0.005 ± 0.001
	40 - 50	0.006 ± 0.001	0.002 ± 0.001
7	0 – 10	0.079 ± 0.004	0.139 ± 0.011
	10 - 20	0.027 ± 0.001	0.020 ± 0.001
	20 - 30	0.024 ± 0.001	0.013 ± 0.001
	30-40	0.011 ± 0.001	0.011 ± 0.002
	40 - 50	0.017 ± 0.001	0.011 ± 0.001
14	0 – 10	0.039 ± 0.002	0.089 ± 0.002
	10 - 20	0.008 ± 0.001	0.036 ± 0.007
	20 - 30	0.005 ± 0.001	0.021 ± 0.004
	30 - 40	0.008 ± 0.001	0.015 ± 0.001
	40 - 50	0.010 ± 0.004	0.010 ± 0.001
21	0 – 10	0.033 ± 0.002	0.071 ± 0.001
	10 - 20	0.014 ± 0.001	0.013 ± 0.001
	20 - 30	0.003 ± 0.001	0.011 ± 0.001
	30 - 40	0.011 ± 0.002	0.011 ± 0.001
	40 - 50	0.013 ± 0.001	0.005 ± 0.000
30	0 – 10	0.021 ± 0.003	0.028 ± 0.001
	10 - 20	0.007 ± 0.001	0.008 ± 0.001
	20 - 30	0.004 ± 0.001	0.006 ± 0.001
	30 - 40	0.002 ± 0.001	0.004 ± 0.001
	40 - 50	0.003 ± 0.001	0.001 ± 0.001
60	0 – 10	0.013 ± 0.003	0.039 ± 0.004
	10 - 20	0.004 ± 0.001	0.011 ± 0.001
	20 - 30	0.003 ± 0.001	0.007 ± 0.001
	30 - 40	0.006 ± 0.001	0.005 ± 0.001
	40 - 50	0.004 ± 0.001	0.001 ± 0.001
90	0 – 10	ND	0.004 ± 0.001
	10 - 20	ND	ND
	20 - 30	ND	ND
	30 - 40	ND	ND
	40 - 50	ND	ND
120	0 – 10	ND	ND
	10 - 20	ND	ND
	20 - 30	ND	ND
	30 - 40	ND	ND
	40 - 50	ND	ND

Note: ND: not detected.

(99%) with relative standard deviation (RSD) not greater than 5.0% at all standard concentration (International Conference on Harmonization, 2005). The percentage recoveries and RSD for diuron residues in the soil are shown in *Table 1*. The recoveries of diuron from the soil fortified with 0.2, 0.6 and 1.0 μg g^{-1} of standard diuron solution were in the range of 93.2%- 95.0%. Meanwhile, the RSD ranged from 1.5% to 4.8%. Therefore, the method used for determination of diuron in soil samples from field trial is good and satisfactory. The limit of detection for the method was 0.002 μg g^{-1} (S/N = 3).

Table 2 shows the concentration of diuron residue in soil collected from field trial. Diuron residue was found at all depths of the soil profile (0-50 cm) when it was applied at the recommended and double the recommended dosage. The results showed that the residue was inversely proportional to increased soil depth. The ranges of diuron concentration at the recommended dosage at each soil depth were as follows: 0.013 – 0.101 μg g^{-1} (0-10 cm), 0.004- 0.027 μg g^{-1} (10-20 cm), 0.003 – 0.024 μg g^{-1} (20-30 cm), 0.002 – 0.018 μg g^{-1} (30-40 cm) and 0.003-0.017 μg g^{-1} (40-50 cm), respectively. The RSD were in the range of 0%-0.013%. The concentration of diuron residue when applied at double the recommended dosage were in the range of 0.004 – 0.211 μg g^{-1} (0-10 cm), 0.008 – 0.045 μg g^{-1} (10-20 cm), 0.004 – 0.051 μg g^{-1} (20-30 cm), 0.004 – 0.034 μg g^{-1} (30-40 cm) and 0.001 – 0.011 μg g^{-1} (40-50 cm), respectively. The RSD were in the range of 0.001%-0.011%.

The highest concentration of diuron residue was detected on the day of treatment (Day 0) for both of dosages applied. As expected, it was found that the diuron residue detected for application at the recommended dosage plot was low when compared to that detected in plots applied at double the recommended dosage plot. The diuron residue was also detected at all depths (0-50 cm) up to 60 DAT for both the dosages. However, at 90 DAT the residue was detected at the 0-10 cm depth only when diuron was sprayed at double recommended dosage.

In the present study, the concentration of diuron residue detected was higher than values recorded in previous studies conducted by other researchers. Buszewski *et al.* (2006) reported that the concentration of diuron detected in the sandy soil studied was 0.018 μg g^{-1}. A mobility study of diuron conducted by Alva and Singh (1990) showed that diuron rapidly leached through the soil. The concentration of diuron residue was 0.08 μg g^{-1} at the depth of 25 cm compared to 0.45 μg g^{-1} at the depth of 120 cm. However, in the current study the results showed that the concentration of diuron decreased with increasing soil depth. This result is similar to that reported by Tworkoski *et al.* (2000), where the concentration of diuron was not

detected at the depth of 70 cm. This could be due to the similarity of physical characteristic of soil.

The factors that influence the persistence of diuron in the soil are the environment stability, water solubility (K_{ow}), adsorption rate on the soil particles (soil organic-carbon adsorption coefficient, K_{oc}), pH, organic matter and rainfall (Kidd and James, 1991; Gooddy *et al.,* 2002; Turner and Gillbanks, 2003; Muhamad *et al.,* 2004; Ismail and Maznah, 2005; Halimah *et al.,* 2010a). The K_{OC} values are useful to predict the mobility of organic soil contaminants. The higher K_{OC} values correspond to less mobile organic chemicals while lower K_{OC} values correspond to more mobile organic chemicals (USEPA, 2001). Diuron is stable in the environment with low water solubility (K_{ow} = 42 mg litre^{-1} at 25°C) and high adsorption rate on the soil particles (K_{oc} = 418 – 560) (Gooddy *et al*., 2002). In addition, diuron is not a volatile compound based on the low value of Henry's constant which is 5.10 x 10^{-10} atm m^3 mol^{-1}.

The persistence of diuron was reported to be directly proportional to the organic matter content of the soil (Alva and Singh, 1990; Adriana, 2004). The mobility of the diuron in the soil was highest when the percentage of organic matter was low. Another factor that favours the leaching process is high soil permeability to water, especially in coarse soils. The organic matter content of the soil in the study area was low (3.8%). Therefore, the mobility of the diuron residue in this study was higher due to the higher content of organic matter. The diuron residue was detected at the depth of 50 cm on the day of treatment (Day 0) and up to 60 DAT. A similar result was reported by Janitha *et al.* (2006), who indicated that low diuron residue was detected in 43 types of soil such as Agalawatta, Akurana, Boralu *etc*. with low organic matter content in Sri Lanka.

In addition, the pH of the soil also affects the persistence of diuron in soil. According to Hager and Refsell (2008), the higher soil pH can decreased the adsorption of herbicides in soils. Chemical breakdown and microbial breakdown are often slower in soils of higher pH. In the present study, the pH of the soil in the study area was low (pH 5.4). Hence, the adsorption of diuron slightly increased and therefore diuron persisted when applied at both dosages.

Soil moisture also affects the persistence and rate of degradation of pesticides in the soil. According to Ismail and Maznah (2005), the rate of pesticide degradation increased with increasing soil moisture. Water molecules in the soil compete with pesticides for adsorption onto the colloids in the soil. This phenomenon will cause an increase in the concentration of pesticides in the soil. In the current study, the detectable residue of diuron was high and persistent because of the low soil moisture content which was 29.5%.

The persistence and adsorption of pesticides in the soil are also dependent on the soil grain size, for the CEC value. The CEC values are directly proportional to the persistence and adsorption onto the soil, but inversely proportional to the pesticides leaching into the soil (Maznah, 2005). However, in the present study, the results showed that the low CEC values at 4.63 g me/100 g caused increased persistence of diuron in the soil. This study also showed that diuron leached fast and was detected at a depth of 50 cm on the day of spraying (Day 0).

Rainfall also affects the persistence and mobility of diuron in the environment. Diuron residue on the soil surface can flow into reservoirs, lakes and rivers and can also be leached underground (Vouvoulis *et al*., 2002; Guardia-Rubio *et al.,* 2006; Lourencetti *et al.,* 2008). In the current study, the highest rainfall was recorded from March until June. On the day of treatment (Day 0, 2 March 2010), 15 mm of rainfall was recorded in the morning, and 3 mm in the evening. This shows that the treatment was carried out during the rainy season. That could be the reason why diuron residue was detected at the depth of 0-50 cm 6 hr after application.

The biotic and abiotic factors such as hydrolysis, photolysis and microbial activity in the soil could enhance the degradation rate of pesticides especially under the Malaysian climatic conditions (Ismail *et al.,* 2004). Volatilisation, runoff and leaching processes could affect the degradation rate as well. Microbial degradation is the primary means of diuron dissipation in the soil, while photodegradation is not considered a primary dissipation route (Hess and Warren, 2002). Due to the persistence and mobility of diuron, its half-life in each segment of the soil profile was calculated as mentioned earlier. *Table 3* shows that the half-life of diuron in the field plots for application rates at the recommended and double the recommended dosage ranging from 22.35-49.5 days and 18.73-57.75 days, respectively. The half-life of diuron in each segment of the soil for plots sprayed at the recommended dosage was 24.8 days (0-10 cm), 27.7 days (10-20 cm), 22.4 days (20-30 cm), 38.5 days (30-40 cm) and 49.5 days (40-50 cm), respectively. Meanwhile, for plots sprayed at double the recommended dosage the half-lives were 18.7 days (0-10 cm), 31.5 days (10-20 cm), 46.2 days (20-30 cm), 57.8 days (30-40 cm) and 21.7 days (40-50 cm).

Most studies on the persistence of diuron residues in soil reported that the half-life of diuron ranged from 90 – 365 days, depending on the application rate and various other factors mentioned, such as environment stability, water solubility, adsorption rate on the soil particles, pH, organic matter and rainfall (Kidd and James, 1991; Adriana, 2004; Anon., 2005). Adriana (2004) reported that the half-life of diuron in plots treated

with diuron for 12 years, was 37 days. Our results differed because the current study was conducted under tropical conditions where there are considerable differences from temperate conditions such as soil pH, type of soil and seasons (summer, spring, winter and autumn). According to Ismail *et al.* (2004), the degradation rates of pesticides in tropical soils are much faster than those under temperate conditions.

Half-life for Diuron in Soil

Half-life of diuron in the soil was determined by drawing a graph of ln diuron concentration versus sampling day. The graph was plotted using diuron concentration at soil depths of 0-10, 10-20, 20-30, 30-40 and 40-50 cm for the trial plots treated with the recommended and double recommended dosage. *Figure 3* shows the graph logarithm concentrations of diuron residue in the soil versus day of sampling at the recommended dosage. Meanwhile, *Figure 4* is the graph logarithm concentrations of diuron residue in the soil versus day of sampling at the double recommended dosage. The results showed that the half-life of diuron in the soil for both dosages vary according to the depth of soil profile. This study has found concordance with the results of other studies (Beigel *et al.*, 1999; Fomsguard, 1994; Plimmer, 1992) where the reaction of pesticides in the environment is complex because they are affected by various factors such as pesticide chemical structures, reactions of microbes, water and oxygen content in soil, initial concentration and spray method and the type of soil pesticides. Van der Werf (1996) also suggested the loss of pesticides after spraying through decomposition process, sprays where pesticides evaporated into the air, leaching into the soil and being absorbed by soil microorganisms or adsorbed on soil particles.

TABLE 3. THE HALF-LIFE OF DIURON SPRAYED AT THE RECOMMENDED AND DOUBLE THE RECOMMENDED DOSAGE FOR EACH SOIL DEPTH

Depth of soil (cm)	y = mx+c	r^2	K (degradation coefficient rate)	$t_{1/2}$
Recommended dosage				
0-10	y = -0.028x - 2.7734	0.750	0.028	24.75
10-20	y = -0.025x - 4.0507	0.630	0.025	27.72
20-30	y = -0.031x - 4.3639	0.574	0.031	22.35
30-40	y = -0.018x - 4.4890	0.323	0.018	38.50
40-50	y = -0.014x - 4.6703	0.272	0.014	49.05
Double the recommended dosage				
0-10	y = -0.037x - 1.7918	0.889	0.037	18.73
10-20	y = -0.022x – 3.5418	0.512	0.022	31.50
20-30	y = -0.015x - 4.1858	0.171	0.015	46.20
30-40	y = -0.012x - 4.5819	0.120	0.012	57.75
40-50	y = -0.032x - 5.0413	0.438	0.032	21.66

The recommended dosage for the half-life of diuron at 40-50 cm depth was 49.5 days which is the longest half-life recorded in this study, when compared with the other soil depth profile (*Table 3*). Meanwhile, the shortest half-life of diuron was at a depth of 20-30 cm of the soil profile at 22.4 days

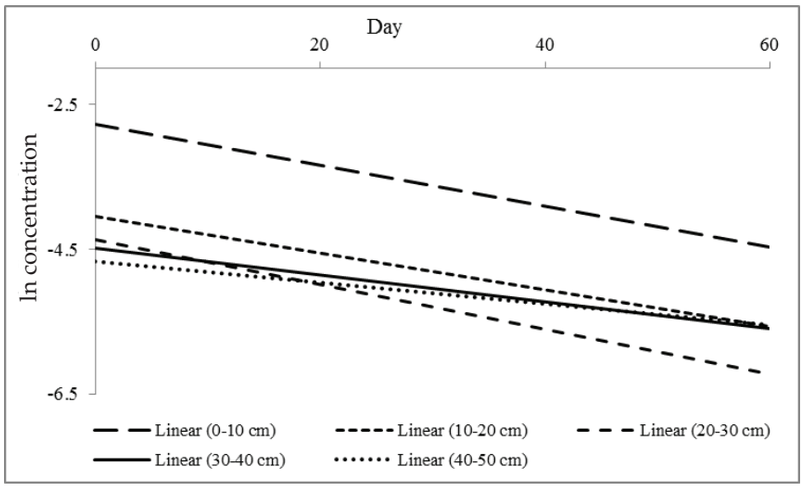

Figure 3. The graph logarithm concentrations of diuron residue in the soil vs. *day of sampling at recommended dosage.*

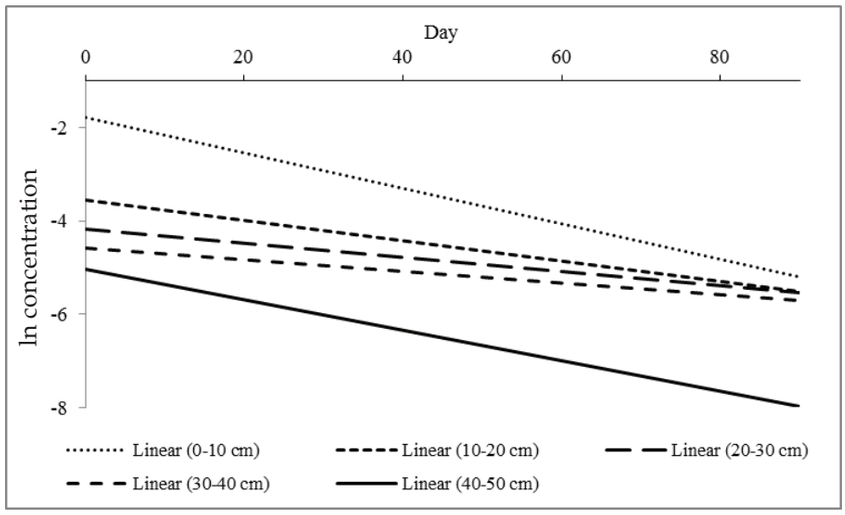

Figure 4. The graph logarithm concentrations of diuron residue in the soil vs. *day of sampling at double recommended dosage.*

(*Table 3*). From this study, the loss of diuron was also due to a number of factors: evaporation in the air during spraying, leaching of diuron in the soil, degradation by microorganism and the intensity of rainfall.

CONCLUSION

Diuron is moderately to highly persistent in the soil and this is influenced by the physico-chemical properties of the soil environment stability, water solubility and adsorption rate onto the soil particles. In the present study, diuron was highly persistent in the sandy clay loam soil at the two dosages applied. Diuron residue was detected at 60 DAT when applied at the recommended dosage, while for application at double the recommended dosage diuron was detected up to 90 DAT at 0-10 cm depth. Therefore, it is not surprising that diuron was detected on the soil surface on Day 90. Diuron residues were detected at 0-50 cm depth from 0 until 60 DAT. The half-life was calculated and found to be in the range of 22.35 – 49.5 days (recommended dosage) and 18.73 – 57.75 days (double the recommended dosage). The calculated half-life of diuron in the present study was shorter compared to those obtained in other studies and this is attributed to low organic matter content.

ACKNOWLEDGEMENT

The authors would like to thank MPOB for financially supporting this work and the Director-General of MPOB for permission to publish this article. Appreciation is expressed to the Malaysian Agriculture and Horticulture Sdn Bhd and its staff for their help in completing field research. The authors are also indebted Ms Rosilawati and Ms Rosliza for the technical support.

REFERENCES

ADRIANA, M (2004). *Enviromental Fate of Diuron*. California Enviromental Protection Agency, Department of Pesticide Regulation, Enviromental Monitoring Branch.

AINIE, K; TAN, Y A; NORMAN, K and YEOH, C B (2007). Pesticide application in the oil palm plantation. *Oil Palm Bulletin No. 54*: 52-67.

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

ALVA, A K and SINGH, M (1990). Sorption of bromacil, diuron, norfluron and simazine at various horizons in two soils. *Bull. Environ. Contam. Tocixol., 45*: 365-374.

ANON. (2005). Diuron Factsheet. http://www.pan-uk.org/pestnews/Actives/Diuron.htm, accessed on 12 May 2010.

BEIGEL, C; CHARNAY, M-P and BARRIUSO, E (1999). Degradation of formulated and unformulated triticonazole fungicide in soil: effect of application rate. *Soil Biology and Biochemistry, 31*: 525-534.

BUSZEWSKI, B; RUTKOWSKI, T; ZEBROWSKI, W and MICHEL, M (2006). Isolation and determination of urea herbicides in soil by hyphenated chromatographic techniques. *Liquid Chromatography and Related Technologies, 29*: 1933-1949.

CABRERA, A; COX, L; VELARDE, P; KOSKINEN, W C and CORNEJO, J (2007). Fate of diuron and terbuthylazine in soils amended with two-phase olive oil mill waste. *Agriculture and Food Chemistry, 55*: 4828-4834.

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*. p. 105-113.

CHEFETZ, B; BILKIS, Y I and POLUBESOVA, T (2004). Sorption-desorption behavior of triazine and phenylurea herbicides in Kishon river sediments. *Water Research, 38*: 4383-4394.

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

FARAHANI, G H N; ISMAIL, B S; ZURIATI, Z; AINIE, K and DZOLKIFLI, O (2008). Study on the downward movement of carbofuran in two Malaysian soils. *Bull. Environ. Contam. Toxicol., 81*: 294-298.

FOMSGAARD, I S (1994). Degradation of pesticides in subsurface soils, unsaturated zone – a review of methods and results. *International Journal of Environmental Analytical Chemistry, 58*: 231-245.

FUAD, A and MAHER, K (2010). Analysis of azithromycin and its related compounds by RP-HPLC with UV detection. *J. Chromatographic Science, 48*: 86-90.

GIACOMAZZI, S and COCHET, N (2004). Enviromental impact of diuron transformation: a review. *Chemosphere, 56*: 1021-1032.

GOODDY, D C; CHILTON, P J and HARRISON, I (2002). A field study to assess the degradation and transport of diuron and its metabolites in a calcareous soil. *The Science of the Total Enviromental, 297*: 67-83.

GUARDIA-RUBIO, M; BANEGAS-FONT, V; MOLINA-DIAZ, A and AYORA-CANADA, M J (2006). Determination of triazine herbicides and diuron in mud from olive washing devices and soils using gas chromatography with selective detectors. *Analytical Letters, 39*: 835-850.

HAGER, A G and REFSELL, D (2008). Chapter 13: Herbicide persistence and how to test for residues in soils. *Illinois Agricultural Pest Management Handbook: Serving Agriculture and the Environment* (Bissonnette, S and Overmier, M eds.). USA: University of Illinois.

HALIMAH, M; TAN, Y A and ISMAIL, B S (2005). The fate of fluroxypyr in the soil in an oil palm agroecosystem. *Weed Biology and Management, 5(4)*: 184-189.

HALIMAH, M; TAN, Y A; ISMAIL, S and NASHRIYAH, M (2010a). Downward movement of chlorpyrifos in the soil of an oil palm plantation in Sepang, Selangor, Malaysia. *J. Oil Palm Res. Vol. 22*: 721-728.

HALIMAH, M; NASHRIYAH, M; ISMAIL, S and TAN, Y A (2010b). Determination of fluroxypyr-MHE in clay soil during dry and wet season. *J. Agrobiotechnology, 1*: 59-68.

HESS, D and WARREN, F (2002). *The Herbicide Handbook of the Weed Science Society of America*. 8th edition. p. 159-161.

INTERNATIONAL CONFERENCE ON HARMONIZATION (ICH) (2005). Validation of analytical procedures-PA/PH/OMCL (05) 47 DEF, elaborated by OMCL Network /EDQM of the Council of Europe.

ISMAIL, B S; NGAN, C K; CHEAH, U B and WAN ABDULLAH, W Y (2004). Leaching potential of pesticides in a vegetable farm in the Cameron Highlands, Malaysia. *Bull. Environ. Contam. Toxicol., 12*: 836-843.

ISMAIL, B S and MAZNAH, Z (2005). Comparison between field experiment and PERSIST model simulation: dissipation of fenvalerate in a Malaysian agriculture soil. *Bull. Environ. Contam. Toxicol., 74*: 1143-1150.

JANITHA, A L; RANSILU, C W; PIYAL ARAVINNA, A G; LESTER, S and RAI, S K (2006). Sorption of cabofuran and diuron pesticides in 43 tropical soils of Sri Lanka. *Agricultural and Food Chemistry, 54*: 1784-1791.

KIDD, H and JAMES, D R (1991). *The Agrochemicals Handbook*. Third edition. Royal Society of Chemistry, Cambridge, UK.

LANYI, K and DINYA, Z (2005). Photodegradation study for assessing the enviromental fate of some triazine-, urea- and thiolcarbamate-type herbicides. *Microchemical, 80*: 79-87.

LESUEUR, C; GARTNER, M; MENTLER, A and FUERHACKER, M (2008). Comparison of four extraction methods for the analysis of 24 pesticides in soil samples with gas chromatography-mass spectrometry and liquid chromatography-ion trap-mass spectrometry. *Talanta, 75*: 284-293.

LIYANAGE, J A; WATAWALA, R C; ARAVINNA, A G P; SMITH, L and KOOKANA, R S (2006). Sorption of cabofuran and diuron pesticides in 43 tropical soils of Sri Lanka. *Agricultural and Food Chemistry, 54*: 1784–1791.

LOURENCETTI, C; DE-MARCHI, M R R and RIBEIRO, M L (2008). Determination of sugar cane herbicides in soil and soil treated with sugar cane vinasse by solid-phase extraction and HPLC-UV. *Talanta, 77 (2)*: 701-709.

MAZNAH, Z (2005). *Kajian Nasib Fenvalerate dalam Tanah Pertanian Terpilih*. M. Sc. thesis. School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia.

MAZNAH, Z; ISMAIL, S and HALIMAH, M (2010). Fate of thiram in oil palm nursery ecosystem during wet season. *Proc. of the 2010 National Seminar: Palm Oil Milling, Refining, Enviroment and Quality (POMREQ).* p. 396.

MOU, R X; CHEN, M X and ZHI, J L (2008). Simultaneous determination of 15 phenylurea herbicides in rice and corn using HPLC with flourescene detection combined with UV decomposition and post-column derivatisation. *Chromatography, B 875.* p. 437-443.

MPOB (2012). *Overview of the Malaysian Oil Palm Industry 2011*.

MPOB (2011). *Malaysian Oil Palm Statictics 2011.* MPOB, Bangi. p. 185.

MUHAMAD, H; AI, T Y and CHIAN, S S (2004). Optimisation of the sweep co-distillation clean-up method for the determination of organoclorine pesticide residues in palm oil. *J. Oil Palm Res. Vol. 16 No. 2*: 30-36.

MUHAMED, R A L; MOHD AHDLY, A and TEY, C C (2009). Efficacy of generic herbicides of glyphosate, glufosunate ammonium and metsulfuron methyl for weed control in oil palm. *Proc. of the Agriculture, Biotechnology and Sustainability Conference.* Vol II. p. 425-438.

PLIMMER, J R (1992). Dissipation of pesticides in the environment. *Fate of Pesticides and Chemicals in the Environment* (Schnoor, J L ed.). John Wiley & Sons, Inc. USA. p. 79-90.

TAY, B Y P (2012). Analysis of isopropyl para-toluenesulphonate in palm-based esters by gas chromatography with flame ionisation detection and confirmed with mass spectrometry. *International Journal of Cosmetic Science*: 1-7.

TURNER, P D and GILLBANKS, R A (2003). Chapter 7: Weeds and their control. *Oil Palm Cultivation and Management.* The Incorporated Society of Planters, Kuala Lumpur. p. 321-396.

TWORKOSKI, T J; WELKER, W and VASS, G D (2000). Soil residues following repeat applications of diuron, simazine and terbacil. *Weed Technol., 14*: 191-196.

US EPA (2001). *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites*. Peer review draft, OSWER 9355, Table C-1, accessed on 4-24 March 2001.

VAN DER WELF, H M G (1996). Assessing the impact of pesticides on the environment. *Agriculture, Ecosystems and Environment, 60*: 81-96.

VOUVOULIS, N; SCRIMSHAW, M D and LESTER, J N (2002). Partitioning of selected antifouling biocides in the aquatic enviroment. *Mar. Environ. Res, 53*: 1-16.

WAHAB, H A (2001). Forages in oil palm and rubber plantations in Malaysia. http://www.fao.org/ag/AGP/AGPC/doc/Proceedings/manado/chap4.htm, accessed in June 2010.