

ISSN 1819-1894

Asian Journal of
Agricultural
Research

Adsorption, Desorption and Mobility of 2,4-D in Two Malaysian Agricultural Soils

¹B.S. Ismail, ¹M. Sameni and ²M. Halimah

¹School of Environmental and Natural Resource Sciences,
Faculty of Science and Technology, Universiti Kebangsaan Malaysia,
43600, UKM, Bangi, Selangor, Malaysia

²Malaysian Palm Oil Board, P.O. Box 10620, 50720, Kuala Lumpur, Malaysia

Abstract: Pesticide adsorption and desorption are important processes that influence the amount of pesticide retained in the soil matrix and its subsequent movement in the soil profile. A study was made on the adsorption-desorption and mobility of the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) in two ricefield soils in the Kerian district, located in the state of Perak, North West Malaysia. Adsorption studies were conducted using the batch equilibrium technique and mobility was studied using a soil column under laboratory conditions. The adsorption and desorption studies fit the Freundlich equation, the adsorption coefficient (K_d) of the clay loam and clay soils were 33.83 and 18.12 L kg⁻¹ and the $1/n_{ads}$ values were found to be lower than unity. The total percentage desorption from the clay loam and clay soils after the fourth desorption process was 18.31 and 28.33%, respectively. Complete leaching of the chemical through the soil column was not observed under the conditions of the present study, as the chemical was not detected in the leachate. The total amount of 2,4-D found in the clay loam and clay soil columns were 66.96 and 72.28% with 5 mm of simulated rainfall per day. The results obtained indicate the importance of organic matter in adsorption-desorption and mobility of 2,4-D in the Malaysian soils studied.

Key words: Adsorption, desorption, mobility, 2,4-dichlorophenoxyacetic acid

INTRODUCTION

Crop protection is an integral part of modern agriculture with pesticide application being a major component. After application, a pesticide finds its way into the soil by spray drift, washing of the plant surfaces by rain, etc. Pesticides in the soil may be taken up by plants, degraded into other chemical forms, or leached downward, possibly, to groundwater. 2,4-D is a commonly used herbicide in the Kerian rice fields which are located in the North West corner of the Perak state. The popularity of 2,4-D for the controlling of broadleaf weeds in the Malaysian rice ecosystem is reflected in the estimated annual expenditure of RM 4 million on the chemical (Cheah *et al.*, 1997).

The pesticide soil sorption coefficient K_d and the soil organic carbon sorption coefficient K_{oc} are basic parameters used by pesticide scientists and regulatory agencies worldwide to describe the environmental fate and behavior of pesticides. Baskaran *et al.*

Corresponding Author: Ismail Bin Sahid, School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, UKM, Bangi, Selangor, Malaysia

(1996) reported that a Horotiu soil had surface and 60 cm depth organic carbon contents of 5.8 and 0.2%, respectively. The $K_{d_{ads}}$ values were 5.65 and 0.39, indicating a much lower adsorption of 2,4-D in the lower soil. The similar trend shows that even the small amount of organic carbon at the greater depth played a very significant role in adsorbing 2,4-D. Cheah *et al.* (1997) studied the Freundlich K and Koc values for two Malaysian soils namely, a sandy loam and an agricultural muck with 1.3 and 30.5% organic carbon, respectively. For the sandy loam, the Freundlich K_{ads} was 0.57 and the K_{des} was 2.57, while the Koc_{ads} and Koc_{des} were 43.9 and 198. These findings indicated that 2,4-D was weakly adsorbed, but strongly held by the soil. In contrast, the K_{ads} and K_{des} values for the agricultural muck were 5.26 and 28.7, while the Koc_{ads} and Koc_{des} were 17.3 and 94.1. Johnson *et al.* (1995) and Barriuso *et al.* (1992) also found higher adsorption on more acidic soils.

Mobility of pesticides generally decreases with increase of soil organic matter content due to the increase of adsorption (Benoit *et al.*, 1999). The movement of pesticides down the soil profile is influenced by the amount of rainfall (Aislabbie and Lloyd, 1995). Studies on pesticide leaching from soils are usually conducted on freshly collected soil, preferably intact cores (Zelles *et al.*, 1991). But this is not always possible, for practical reasons. The soil column or lysimeter studies offer a good way of conducting controlled experiments under laboratory conditions (Bergström *et al.*, 1990; Bergström and Johansson, 1991). The herbicide 2,4-Dichlorophenoxy acetic acid (2,4-D) is commonly used in Malaysian agriculture. The standard application rate of 2,4-D to an agricultural field is 0.28 to 2.3 kg ha⁻¹ (Hiradate *et al.*, 2007). This herbicide is currently being used to control a wide range of broad leaved weeds in crops, such as rice, oil palm, cocoa and rubber (Cheah *et al.*, 1997). Relatively high water solubility and low soil-adsorption coefficient of 2,4-D, suggest that it has high potential to permeate the soil. So, it probably moves to groundwater through percolation (Hall *et al.*, 1993; Wood and Anthony, 1997; Balinova and Mondesky, 1999). The aim of the present study was to investigate the adsorption, desorption and mobility of 2,4-D in two Malaysian agricultural soils under laboratory conditions.

MATERIALS AND METHODS

Materials

All reagents and solvents used in this study were of analytical grade. Methanol and hydrochloric acid were obtained from Merck and standard 2,4-D of 99.7% purity was purchased from the Laboratories of Dr. Ehrenstorfer, Germany. The solid phase extraction (SPE) ENV⁺ cartridges containing 200 mg of sorbent were obtained from International Sorbent Technology (IST), MidGlamorgan UK.

Soil Parameter

The two types of soil used in the present experiment was collected from the surface layers of the Kerian ricefields. The experiment was conducted from 24th October 2007 to 4th May 2008. The two different soil types used in the study, were clay loam and clay soil. The soil samples collected were analyzed and the characteristics of each soil type are presented in Table 1. It was found that the clay soil had 22% more clay content than the clay

Table 1: Physico-chemical properties of the clay loam and clay soils

Soil type	pH	Organic carbon	Coarse sand	Fine sand	Silt	Clay	Bulk density (g cm ⁻³)
		----- (%) -----					
Clay loam	5.82	5.94	3.13	31.04	26.76	39.07	1.29
Clay	6.17	2.10	8.20	13.03	28.51	50.26	1.24

loam soil. The clay loam soil had total carbon content more than 64% compared to the clay soil. All soil data reported are expressed on a dry weight basis. The bulk density of the soils was also recorded.

Adsorption and Desorption Studies

The adsorption and desorption studies for the soils were undertaken in accordance with the batch equilibrium method as described by Walker and Exposito (1998). A 2 g sample of each soil type was weighed separately into centrifugal tubes. Then 10 mL 2,4-D at concentrations of 2, 4, 6 and 8 $\mu\text{g mL}^{-1}$ were added. There were three replications for each concentration and a blank containing no 2,4-D was also included. The mixture was shaken for equilibrium using an orbital shaker at 150 rpm. After shaking, the suspensions were centrifuged at 3,500 rpm for 20 min to separate the liquid and solid phases. The concentration of 2,4-D in the clear supernatant was determined using the HPLC.

Desorption studies were performed in a manner similar to that which had been used for the adsorption study as described by Walker and Exposito (1998). After the supernatant obtained by centrifugation (for adsorption) had been removed, 10 mL of 0.01 M CaCl_2 solution was added into the flask. The mixture was then shaken for 15 min and centrifuged at 3,500 rpm for 20 min as described above. A 10 mL aliquot was removed from each vial. The process was repeated four times. The concentration of 2,4-D in the supernatant was determined using the HPLC.

The equilibrium adsorption coefficient (K_{ads}) was calculated from the Freundlich equation as the ratio of adsorbed to aqueous concentration. Difference in the amount of 2,4-D in the initial concentration versus the amount in the supernatant of the samples was considered to be the amount adsorbed. The herbicide sorption isotherm was calculated (Jana and Das, 1997) using the Freundlich equation as follows:

$$\begin{aligned}x/m &= K C_e^{1/n} \\ \ln x/m &= \ln K + 1/n \ln C_e\end{aligned}\quad (1)$$

Where:

K = Adsorption/desorption coefficient

x/m = The adsorbed amount ($\mu\text{g g}^{-1}$)

C_e = Solution concentration (mg L^{-1}) after adsorption equilibrium,

1/n = Constants (slope)

The logarithmic form of the above equation was fitted by the least square method to the set of experimental data. The K_d and n constants were calculated and a linear regression analysis was performed to determine the degree of fit between the observed data and the Freundlich constants.

Mobility Study

To assess the effect of simulated rainfall and soil texture on the mobility of 2,4-D, the method developed by Walker *et al.* (1996) was adopted. The cylinders for the column had an ID of 8.5 cm and were 30 cm long. They were made of transparent polyvinyl chloride (PVC). The cylinders were cut at 5, 10, 15, 20, 25 and 30 cm from the top to produce six smaller tubes, which were re-assembled to create the whole column. The bottom ring of the column was filled with sand and closed with plastic wire mesh. The PVC column was carefully hand-packed with soil from a single soil type ($\approx 1800 \text{ g}$) to a depth of 30 cm and supported vertically by a custom-made wooden rack. The moisture level of the soil was maintained at 50% field capacity.

Once the soil column had settled, a 5 cm thick layer of soil treated with 2,4-D corresponding to 2 kg ha⁻¹ was placed on top of each soil column. The concentration used was the suggested application rate for the field. The soil surface in each column was covered with one sheet of Whatman No. 3 filter paper. The top of the columns were covered with aluminum foil to minimize evaporative losses. Conical flasks (150 mL) with glass funnels were placed at the base of the columns for collection of the leachate. After 1 h of adding the treated soil, 25 mL of distilled water, simulating 5 mm rainfall per day (average rainfall per month during the period of study was 151.8 mm) was poured over the treated soil. This was repeated daily for 10 days. On day 10, the distribution of 2,4-D in each of the 5 cm soil segments was analyzed. Two untreated control columns were maintained simultaneously. For each soil type studied, the experiment was replicated thrice.

Herbicide Extraction Procedure

To extract herbicide residues from the soil, soil samples underwent the following procedure: To 5 g samples (in triplicate) was added 40 mL of methanol acidified to approximately pH 2 with acetic acid (85%) and sonicated for 1 h. Ten milliliter of the extract were pipetted out and transferred into a 10 mL vial. The extract was then filtered (Whatman grade 41) and dried under vacuum and redissolved with 1 mL of methanol prior to analysis using the HPLC (Halimah *et al.*, 2004).

HPLC Estimation of 2,4-D Residues

2,4-D residues were estimated using an Agilent HPLC 1100 Series fitted with a UV detector set at 214 nm. The column used was a C₈-NH₄ (4.6 mm ID×250 mm length 5 μm particle size). The mobile phase of MeOH and buffer (H₂O with + potassium sodium 3.4 g L⁻¹ + hydrochloric acid in pH 2.3), were in the ratio 30:70. The flow rate of the mobile phase and injection volume were 1 mL min⁻¹ and 20 μL, respectively. Under these conditions the retention time of 2,4-D was 4.23 min. The detection limit for this method was 0.04 μg g⁻¹.

RESULTS AND DISCUSSION

The extraction procedure of 2,4-D from the two soil types was found to be efficient as indicated by the recovery rates from fortified samples of soil (0.2, 1.0, 4.0, 8.0 μg mL⁻¹), which were found to be not less than 91.9% while the standard deviation ranged from 0.04 to 0.6.

Adsorption Study

Preliminary studies showed that 2,4-D attained equilibrium at 2 and 4 h by adsorption onto clay loam and clay soils respectively. Table 2 shows the percentage of 2,4-D adsorbed

Table 2: The amount of adsorption (μg g⁻¹) and the percentage adsorption of 2,4-D in clay and clay loam soils (±SD)

Soil	Initial amount (μg mL ⁻¹)	Amount absorbed	
		(μg g ⁻¹) (±SD)	(%)
Clay loam	2	8.20 (±0.17)	82.00
	4	17.44 (±0.10)	87.21
	6	26.25 (±0.08)	87.51
	8	35.30 (±0.20)	88.24
Clay	2	7.13 (±0.06)	71.28
	4	5.44 (±0.11)	77.21
	6	23.93 (±0.10)	79.76
	8	32.46 (±0.23)	81.14

onto the clay loam soil was 82.00, 87.21, 87.51 and 88.24% at concentrations of 2, 4, 6 and 8 $\mu\text{g mL}^{-1}$, respectively, whereas in the clay soil, the percentage adsorbed ranged from 71.28, 77.21, 79.76 and 81.14% at the same respective concentrations. The percentage 2,4-D adsorbed was higher in clay loam than in clay soils.

The fact that more 2,4-D was adsorbed in the clay loam than in the clay soil, may be due to the high soil organic matter content in the clay loam soil. This is attributed to the fact that soil organic matter content plays a major role in the adsorption of organic compounds in the soil and this is supported by previous studies (Ismail *et al.*, 2002). Analysis of variance confirmed that the 2,4-D adsorbed was significantly affected by the different levels of concentration in both the soil types ($p < 0.05$), confirming the results of Vinod *et al.* (2006).

The soil partition coefficients $K_{d_{ads}}$ and $K_{d_{des}}$ are measures of the potential for adsorption to soil and for desorption from that soil, respectively. The $K_{d_{ads}}$ and $K_{d_{des}}$ values for the clay and clay loam soils are shown in Table 3. The Freundlich sorption coefficient (K_f) was derived from the interception of the linear form of the Freundlich equation ($\text{Log } [C_s] = \text{Log } K_d + 1/n \text{ Log } [C_{aq}]$) and the Freundlich sorption exponent ($1/n$) from the slope. The extent of sorption and the curvature of the isotherm are described by the K_f and the $1/n$ values, respectively. The $1/n$ values, which are the values for the slope of the line, were obtained using the least square fit (Fig. 1, 2) of the adsorption isotherm and the values are shown in Table 3.

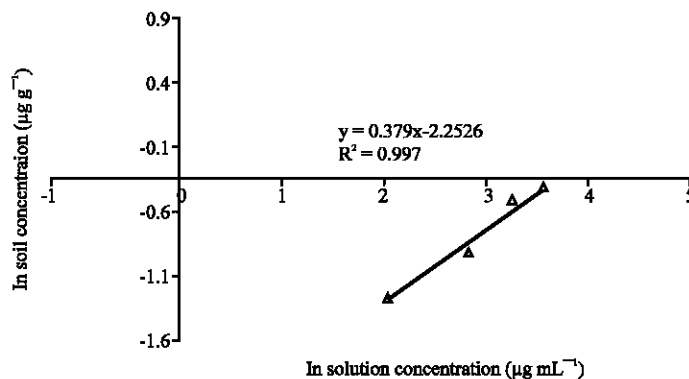


Fig. 1: Freundlich adsorption isotherm of 2,4-D at room temperature in the clay loam soil

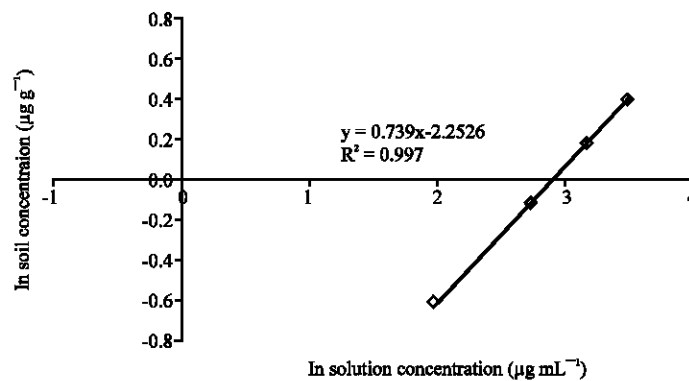


Fig. 2: Freundlich adsorption isotherm of 2,4-D at room temperature in the clay soil

Table 3: Adsorption, desorption and organic carbon distribution coefficients of 2,4-D

Parameter (L kg ⁻¹) ^a	Clay soil	Clay loam soil
K _{ads}	18.12	33.83
K _f	18.33	31.52
1/n _{ads}	0.74	0.85
K _{ocads}	862.85	569.36
r ²	0.99	0.98
K _{des1}	19.1	30
K _{des2}	85.71	119.05
K _{des3}	207.9	NA*
K _{des4}	NA	NA
K _{ocdes}	707.14	403.2

^aExcept for 1/n, *NA-Not available as desorption did not occur

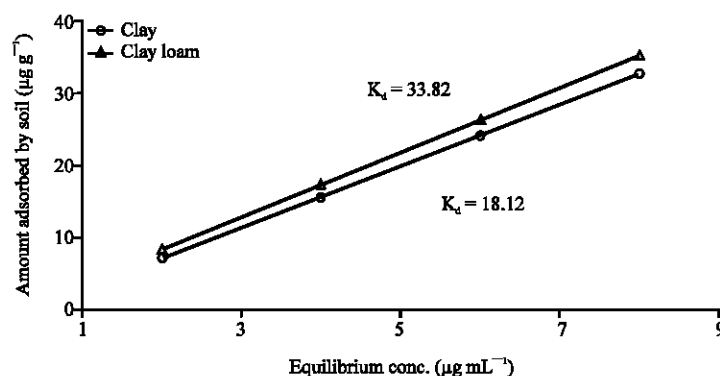


Fig. 3: Adsorption isotherms of 2,4-D in clay and clay loam soil

The Freundlich adsorption distribution coefficients $K_{ads(f)}$ of 31.52 and 18.33 L kg⁻¹ were obtained for the clay loam and clay soils (Table 3), respectively. The corresponding 1/n values observed for the clay loam and clay soils were below unity, indicating that the relative adsorption decreased with increasing solution concentration (Rhodes *et al.*, 1970).

The $K_{ads(f)}$ value obtained from the Freundlich equation for the clay (18.33) was slightly higher than the K_{ads} value of 18.12 L kg⁻¹, while the value for $K_{ads(f)}$ for the clay loam soil (31.52) was lower than the K_{ads} value of 33.83. The differences, however, were not significant. A similar observation was made by Cheah *et al.* (1997). In other studies, Chiou *et al.* (1986) reported that herbicide adsorption was only slightly correlated with soil clay, but it was highly correlated with soil organic matter. Brady (1990) stated that the presence of functional groups, such as OH, -CONH₂, -NHR, -NH₂ and -COOH in soil organic matter and humus facilitate herbicide adsorption. Similarly, soil texture has some influence on the sorptive capacity of the soil.

The correlation coefficients for clay and clay loam soil were 0.99 and 0.98, respectively at room temperature. From the study, the K_d of the clay loam soil was higher than that of the clay soil and this could be due to the higher organic matter content in the clay loam soil (Table 3), confirming the results of Hermosin and Cornejo (1991).

It can be seen in Fig. 3 that by increasing the 2,4-D concentration from 2-8 µg mL⁻¹ there was an increase in the K_d values by 46% for the clay loam compared to those of the clay soil. The organic matter content was 5.94 and 2.10% for the clay loam and clay soils respectively. In a previous study, Hermosin and Cornejo (1991), working with 2,4-D found that adsorption was positively correlated to organic matter content.

The K_{oc} values give an idea of the importance of organic carbon in a soil in adsorbing specific chemicals. The K_{oc} values generally are numerically higher than the K_d or K values. For instance Baskaran *et al.* (1996) reported that a Horotiu soil had surface and 24-inch depth organic carbon content of 5.8 and 0.2%, respectively. The $K_{d_{ads}}$ values were 5.65 and 0.39, indicating a much lower adsorption of 2,4-D in the lower soil. However, the $K_{oc_{ads}}$ values were 97 and 195 for the upper and lower depths. The values show that even the small amount of organic carbon at the lower depth played a very significant role in adsorbing 2,4-D.

The relationship between the Organic Matter (OM) content and the adsorption percentage was determined according to the following equation:

$$K_{oc} = \frac{K_d \times 100}{\% OM} \quad (2)$$

Where:

K_{oc} = The Freundlich OM distribution coefficient

K_d = The adsorption coefficient

OM = Organic matter

Table 3 shows the K_{oc} values of 569.36 and 862.85 $L kg^{-1}$ as determined for the clay loam and clay soils respectively. For the clay soil, the Freundlich K_{ads} was 18.12 $L kg^{-1}$ and the K_{des} was 19.10 $L kg^{-1}$, while the $K_{oc_{ads}}$ and $K_{oc_{des}}$ were 862.85 and 909.52 $L kg^{-1}$. These findings indicate that 2,4-D was weakly adsorbed, but slightly held by the soil. Organic carbon played a significant role in adsorption in this soil. In contrast, the K_{ads} and K_{des} values for the clay loam were 33.83 and 38.68 $L kg^{-1}$, while the $K_{oc_{ads}}$ and $K_{oc_{des}}$ were 569.53 and 651.18 $L kg^{-1}$. The 2,4-D was adsorbed firmly by the clay loam soil and retained, though surprisingly the low K_{oc} values of clay loam soil suggested that carbon played less of a role in sorption than with the lower carbon content clay soil. The difference may lie in the different pH values for the soils. The pH for the clay soil was 6.7 (nearly neutral) while the clay loam soil pH was 5.82 (acidic). Johnson *et al.* (1995) found that 2,4-D was adsorbed more strongly at pH 5.0 than at pH 7, although adsorption even in acidic soils was low, possibly due to the low organic carbon content of 0.5 to 1.0%. The $K_{d_{ads}}$ values were 0.06 to 0.19 in pH 7 (neutral soils) and 0.37 to 0.59 in the more acidic pH 5 soils. Barriuso *et al.* (1992) and Cheah *et al.* (1997) also found greater adsorption in the more acidic soils.

Desorption Study

The mobility of a compound in soil can be assessed from desorption studies. The $1/n$ of the Freundlich desorption equilibrium for the two soil types was higher than 1, indicating that the desorption percentages were positively correlated with the total herbicide adsorbed (Fig. 4).

Table 4 shows the weak binding of 2,4-D to soils as indicated by its significant desorption from both soils, with 28.33% of the sorbed 2,4-D being desorbed from the clay soil after four successive desorption processes. A similar desorption pattern was noted for the clay loam soil, with 18.31% of the adsorbed herbicide being desorbed. This suggests that, although there was preferential affinity by 2,4-D for the clay loam soil, the binding was essentially weak. The K_{des} values of 19.10, 85.71 and 207.90 $L kg^{-1}$ were obtained for four successive desorption processes from the clay soil. This is in contrast to the higher values of 38.68 and 119.05 $L kg^{-1}$ obtained for the clay loam soil.

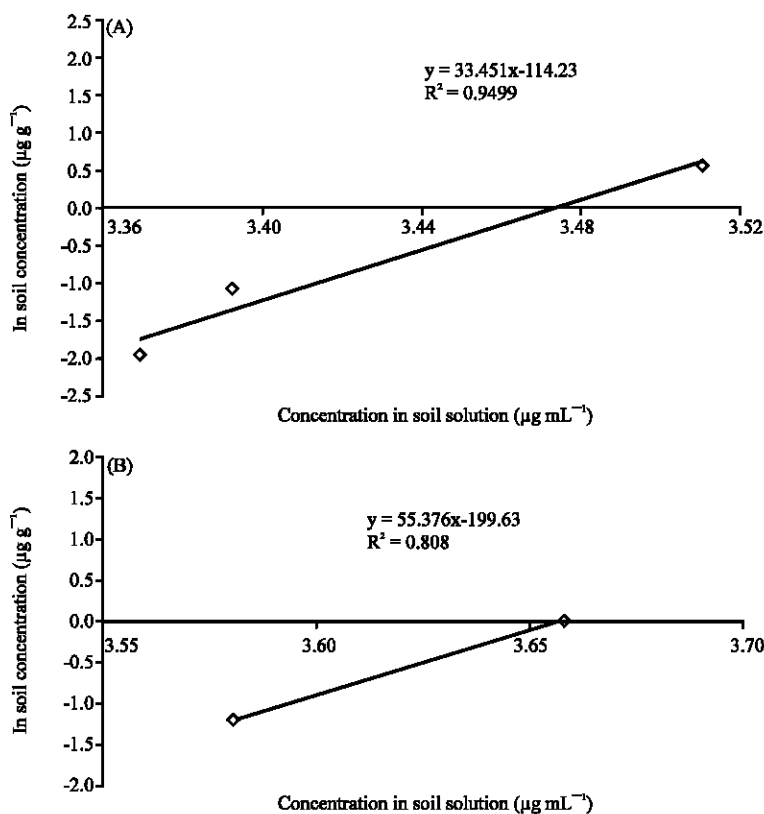


Fig. 4: Desorption of 2,4-D in (A) clay soil and (B) clay loam soil

Table 4: Desorption of 2,4-D in clay loam and clay soils

Desorption process	Clay loam		Clay	
	Desorbed (%)	Amount desorbed (µg)	Desorbed (%)	Amount desorbed (µg)
1	14.28 (±0.37)	12.92 (±0.34)	20.47 (±1.24)	17.22 (±1.04)
2	4.03 (±0.094)	3.02 (±0.07)	5.51 (±0.10)	3.47 (±0.06)
3	0.00 (±0.00)	0.00 (±0.00)	2.36 (±0.10)	1.40 (±0.06)
4	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)	0.00 (±0.00)
Total desorption	18.31	15.94	28.33	22.09

Standard deviation (±), Mean and standard deviation from 3 replicates, adsorption at equilibrium 84.141 and 90.453 µg for clay and clay loam, respectively

Mobility Study

Leaching of herbicides through the soil column is important to determine their efficacy as well as their potential for causing crop damage and environmental pollution (Mersie and Foy, 1986). 2,4-D is highly soluble in water and if sorption in soil is relatively low, it is expected to exhibit considerable mobility in the soils. Leaching of 2,4-D to 30 cm has been reported (Johnson *et al.*, 1995). In the present study, the clay and clay loam soil samples were subjected to a total of 151.8 mm per month simulated rainfall over a 10 day period following the application of 2,4-D at the field application rate.

Figure 5 shows the 2,4-D residue detected in the layers of both types of soil. It was observed that 2,4-D in the clay loam soil column amounted to 66.96% up to 15 cm depth. However, the total amount of 2,4-D found in the clay soil was 72.28% up to 20 cm depth, with

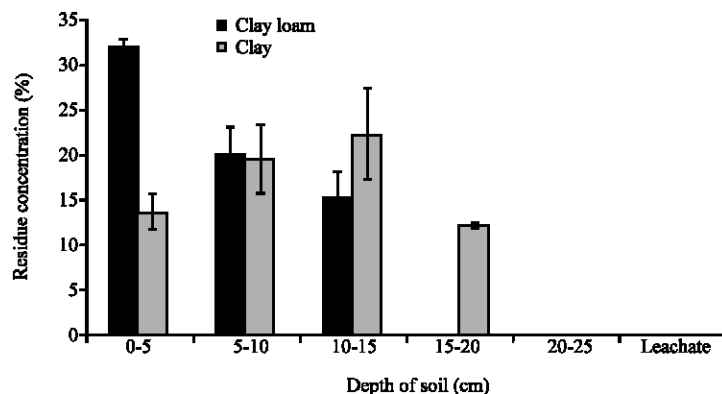


Fig. 5: Leaching of 2,4-D in clay and clay loam soil

50 mm of simulated rainfall. Soils high in organic matter often have high microbiological activity, which favors pesticide degradation. However, the total percentage recovery of applied 2,4-D from the soil decreased with time. Microbial breakdown of 2,4-D has been known to occur in the soil and the lifespan of 2,4-D in the soil is short as it is easily biodegradable.

Castro and Yoshida (1971) have reported that the organochlorine insecticides were found to degrade faster in soils with high organic matter content. In acidic rice soils of Kerala, India, Sethunathan (1973) observed that parathion degraded faster in the soils that had higher organic matter content. Organic matter has been found to be the most prominent soil factor that affects sorption of pesticides in the soil. The downward mobility of the residue in a column may have been enhanced by the looser texture of the repacked soil of both soil types as compared to their natural state in the field. Other researchers (Bergström and Jarvis, 1993; Sharma and Awasthi, 1997), showed that the loose structure of the soil increased downward flow of the compound.

It appears that the structure of the soil and the total organic matter content influences the mobility of 2,4-D in the soil column. Figure 5 shows that the mobility of 2,4-D significantly decreased with the amount of organic matter and had a significant negative correlation with the soil K_d value. In the clay soil, with the K_d value of 18.12, 2,4-D seemed to have moved downward to 20 cm. Whilst, in the clay loam soil (K_d value, 33.83), 2,4-D moved only to the depth of 15 cm.

The study showed that 2,4-D moved less in the soil profile in the clay loam than in the clay soil. Gerstl and Yaron (1983) reported that soil structure influences the distribution of applied chemicals, resulting in deeper penetration than might otherwise be expected. Boyd and Sun (1990) showed that highly sorptive anthropogenic organic phases in soils and sediments significantly increased the immobilization of organic contaminants thereby strongly influencing their environmental fate and behavior.

CONCLUSIONS

Environmental contamination by any pesticide is particularly harmful as it poses a major health risk to human and endangers wildlife. 2,4-D is no exception. Controlled laboratory batch equilibrium and mobility studies were designed to measure the adsorptive and mobile properties of 2,4-D in two representative Malaysian agricultural soils. 2,4-D exhibited variable

adsorption and desorption rates in the soils depending on individual soil parameters. In both soil types, adsorption was moderate to low, but the adsorbed materials tended to stay bound to the soil particles once adsorbed. Adsorption is stronger in soils with higher organic carbon content and soils with low pH (acidic). The study showed that the structure of the soil and the total organic matter content also affected the mobility of 2,4-D in the soil column.

REFERENCES

- Aislabbie, J. and G.J. Lloyd, 1995. A review of bacterial degradation of pesticides. *Aust. J. Soil Res.*, 33: 925-942.
- Balinova, A.M. and M. Mondesky, 1999. Pesticide contamination of ground and surface water in Bulgarian Danube plain. *J. Environ. Sci. Health Part B*, 34: 33-46.
- Barriuso, E.C., C. Feller, R. Calvet and C. Cerri, 1992. Sorption of atrazine, terbutryn and 2,4-d herbicides in two brazilian oxisols. *Geoderma*, 53: 155-167.
- Baskaran, S., N.S. Bolan, A. Rahman and R.W. Tillman, 1996. Pesticide sorption by allophanic and non-allophanic soils of New Zealand. *N.Z. J. Agric. Res.*, 39: 297-310.
- Benoit, P., E. Barriuso and G. Soulas, 1999. Degradation of 2,4-d, 2,4-dichlorophenol and 4-chlorophenol in soil after sorption on humified and nonhumified organic matter. *J. Environ. Qual.*, 28: 1127-1135.
- Bergström, L.F., A.S. McGibbon, S.R. Day and M. Snel, 1990. Leaching potential and decomposition of fluroxypyr in Swedish soils under field conditions. *Pestic. Sci.*, 29: 405-417.
- Bergström, L. and R. Johansson, 1991. Leaching of nitrate from monolith lysimeters of different types of agricultural soils. *J. Environ. Qual.*, 20: 801-807.
- Bergström, L.F. and N.J. Jarvis, 1993. Leaching of dichlorprop, bentazon and 36Cl in undisturbed field lysimeters of different agricultural soils. *Weed Sci.*, 41: 251-261.
- Boyd, S.A. and S. Sun, 1990. Residual petroleum and polychlorobiphenyl oils as sorptive phases for organic contaminants in soils. *Environ. Sci. Technol.*, 24: 142-144.
- Brady, N.C., 1990. *Soil and Chemical Pollution, Nature and Properties of Soils*. 10th Edn., MacMillan Publishing Co., New York, ISBN: 0-02-313361-9, pp: 517-546.
- Castro, T.F. and T. Yoshida, 1971. Degradation of organochlorine insecticides in flooded soils in the Philippines. *J. Agric. Food Chem.*, 19: 1168-1170.
- Cheah, U.B., R.C. Kirkwood and K.Y. Lum, 1997. Adsorption-desorption and mobility of four commonly used pesticides in Malaysia. *Agric. Soil. Pestic. Sci.*, 50: 53-63.
- Chiou, C.T., R.L. Malcolm, T.I. Brinton and D.E. Kile, 1986. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol.*, 20: 502-508.
- Gerstl, Z. and B. Yaron, 1983. Behavior of bromacil and napropamide in soils: II. distribution after application from a point source. *Soil Sci. Soc. Am. J.*, 47: 478-483.
- Halimah, M., Y.A. Tan and B.S. Ismail, 2004. Method development for determination of fluroxypyr in soil. *J. Environ. Sci. Health B*, 39: 765-777.
- Hall, J.C., T.D. Vandeynze, J. Struger and C.H. Chan, 1993. Enzyme-immunoassay-based survey of precipitation and surface water for the presence of atrazine, metolachlor and 2,4-D. *J. Environ. Sci. Health Part B*, 28: 577-598.
- Hermosin, M.C. and J. Cornejo, 1991. Soil adsorption of 2,4-D as affected by the clay mineralogy. *Toxicol. Environ. Chem.*, 31: 69-77.
- Hiradate, S., A. Furubayashi, N. Uchida and Y. Fujii, 2007. Adsorption of 2,4-dichlorophenoxyacetic acid by an andosol. *J. Environ. Qual.*, 36: 101-109.

- Ismail, B.S., A.O.S. Enoma, U.B. Cheah, K.Y. Lum and M. Zulkifli, 2002. Adsorption, desorption and mobility of two insecticides in Malaysian agricultural soil. *J. Environ. Sci. Health Part B*, 37: 355-364.
- Jana, T.K. and B. Das, 1997. Sorption of carbaryl (1-Naphthyl N-Methyl Carbamate) by soil. *Bull. Environ. Contam. Toxicol.*, 59: 65-71.
- Johnson, W.G., T.L. Lavy and E.E. Gbur, 1995. Sorption, mobility and degradation of Triclopyr and 2,4-D on four soils. *Weed Sci.*, 43: 678-684.
- Mersie, W. and C.L. Foy, 1986. Adsorption, desorption and mobility of chlorosulfuron in soils. *J. Agric. Food Chem.*, 34: 89-92.
- Rhodes R.C., I.J. Belasco and H.L. Pease, 1970. Determination of mobility and adsorption of agrichemicals on soils. *J. Agric. Food Chem.*, 18: 524-528.
- Sethunathan, N., 1973. Organic matter and parathion degradation in flooded soil. *Soil Biol. Biochem.*, 5: 602-604.
- Sharma, D. and M.D. Awasthi, 1997. Adsorption and movement of metalaxyl in soils under unsaturated flow conditions. *Plant Soil*, 195: 293-298.
- Vinod, K., G. Imran, A. Suhas and K.S. Vipin, 2006. Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes. *J. Colloid Interface Sci.*, 299: 556-563.
- Walker, A., L. Cox, M.C. Hermosin and J. Cornejo, 1996. Measurement and simulation of the movement of thiazafuron, clopyralid and metamitron in soil column. *Weed Res.*, 36: 419-429.
- Walker, A. and M.J. Exposito, 1998. Adsorption of isoproturon, diuron and metsulfuron methyl in two soils at high soil-solution ratio. *Weed Res.*, 38: 229-238.
- Wood, J.A. and D.H.J. Anthony, 1997. Herbicide contamination of prairie springs at ultratrace levels of detection. *J. Environ. Qual.*, 26: 1308-1318.
- Zelles, L., P. Adrian, Q.Y. Bai, K. Stepper, M.V. Adrian, K. Fischer, A. Maier and A. Ziegler, 1991. Microbial activity measured in soils stored under different temperature and humidity conditions. *Soil Biol. Biochem.*, 23: 955-962.