Research reports

Adsorption, desorption and mobility of metsulfuron-methyl in Malaysian soils under oil palm plantation

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Summary
Metsulfuron-methyl adsorption, desorption and mobility in Malaysian soils under oil palm plantation, viz. Serdang Series, Sungai Buloh Series, Holyrood Series, Rengam Series, Lating Series and peat soil, were studied under laboratory conditions. The greatest adsorption of metsulfuron-methyl was observed in the peat soil. The highest K_a was in the soil with higher organic matter (OM). Adsorption was positively correlated with the OM contents (r = 0.9997). The K_d value of peat soil was higher than the other soils studied. On the other hand, desorption of metsulfuron-methyl was lowest in the peat soil. Based on K_{oc} values, metsulfuron-methyl is considered mobile in soil columns whereby the residue is detected in the leachate.

Introduction
Metsulfuron-methyl is a herbicide developed for pre- and post-emergence control of a number of broad leaved and grassy weeds. It is widely used in Malaysia for the control of weeds in oil palm and rubber plantations as well as in vegetable growing areas.

Since this herbicide has high herbicidal activity, its behaviour in soils is very important because of its potential damage to crops and pollution of the environment. The herbicide has become popular because of their low application rates (10–40 g ha^{-1}), low mammalian toxicity, and unprecedented herbicidal activity. Information on the activities of metsulfuron-methyl in Malaysian agricultural soils is limited. Only a few studies on the persistence and bioactivity of metsulfuron-methyl in agricultural soils have been reported (Mersie and Foy 1986, Ismail and Kalithasan 1997, Rahman *et al*. 1997). The earlier studies used bioassay methods, which are unable to provide details of the actual amount of residues in soils. The disadvantage of the bioassay method is that the strongly bound residues may not be able to be detected by the bioassay plants. However, bioassay procedures for specific herbicides may be less difficult to develop than chemical assay procedures. In chemical analysis the extractants may remove tightly bound herbicide fractions from the soil complex.

Cranmer *et al*. (1999) have reported that the coefficient correlation of metsulfuron-methyl in Colorado soils was correlated to several soil parameters, with the correlations with pH (-0773) and percent soil OM (0.666) the strongest, although low. Adsorption of sulfonylurea herbicides to soil is negatively correlated to pH, but moisture, OM and temperature also affect sorption in important ways (Mersie and Foy 1985, Walker *et al.* 1989). Adsorption to clay has only a minor effect on leaching. Although there have been many reports on adsorption/desorption of sulfonylurea herbicide (Mersie and Foy 1985, Walker *et al.* 1989, Cranmer *et al*. 1999), little information is as yet available on adsorption/desorption and leaching of metsulfuron-methyl in tropical agricultural soils (Ismail and Quirinus 1997). Cheah *et al*. (1997) reported on the adsorption/desorption of other groups of herbicides such as glyphosate, paraquat and 2,4-D. Therefore, this study on adsorption/desorption and mobility of metsulfuron-methyl in Malaysian agricultural soils is an important contribution towards understanding the fate of this herbicide under tropical conditions.

The objective of this study is to determine the adsorption, desorption and mobility of metsulfuron-methyl using chemical analyses for six Malaysian agricultural soils, namely Serdang Series, Sungai Buloh Series, Rengam Series, Lating Series, Holyrood Series and peat soil.

Materials and methods
Soils

Soils samples, viz. Sungai Buloh Series, Serdang Series, Holyrood Series and Rengam Series were collected from the Sungai Buloh areas, Selangor, while the peat and Lating Series soils were collected from the MARDI Station Jalan Kebun, Kelang and the MPOB Oil Palm Plantation, Bangi, Selangor, respectively. The soils were collected from the 0–10 cm depth, air dried (at room temperature 27°C for 72 h) and screened through a 2 mm sieve prior to use. The physico-chemical properties of the soils were analysed and presented in Table 1.

Herbicide

The commercial grade of metsulfuron-methyl (Ally®, 20% a.i, DuPont) used in this study was obtained from the agrochemical retail. [phenyl-U-^{14}C] metsulfuron-methyl, specific activity 32.2 mCi mg^{-1}, supplied by DuPont, USA, was used to spike the commercial product.

Adsorption study

Two grams of soil samples were weighed into 50 mL conical flasks, to which 10 mL

Table 1. Physico-chemical properties of six Malaysian agricultural soils.

Physico-chemical properties	Soil (Series)					
	Holyrood	Sungai Buloh	Rengam	Serdang	Lating	Peat
Soil texture	Sand	Sand	Sandy loam	Sandy loam	Loamy clay	Organic
% sand	95.90	91.23	85.88	71.25	42.43	13.15
% silt	3.05	6.34	7.16	8.22	20.58	5.50
% clay	1.05	2.43	6.96	20.53	36.99	4.21
% organic matter	3.26	4.69	7.91	3.59	6.09	75.00
CEC (meq/100g) *	2.02	3.28	8.56	1.96	52.33	4.33
pH (H_2O)	3.69	3.95	3.62	4.17	4.23	3.63

* CEC is Cation exchange capacity.

of 0.1 , 0.5, 1, 2 or 5 mg L^{-1} spiked with 0.0586 mCi ^{14}C labelled metsulfuron-methyl were then added. The samples were shaken at 160 rpm (25°C) using an orbital shaker for 24 h, a period that preliminary studies showed was sufficient to attain equilibrium. Subsequently, the samples were centrifuged at 3000 rpm for 15 min. A 1 mL aliquot was removed from each tube, placed in 10 mL of scintillation fluid (NBCS104, Amersham), and counted with a liquid scintillation counter (LSC). The resulting radioactivity in solution was compared to 1 mL aliquot of the concentration standards. Differences between the amounts of ^{14}C found in standard solutions and the supernatant of samples were considered to be the amounts absorbed.

The herbicide sorption isotherm was calculated using the Freundlich adsorption distribution coefficients (K_a):

$$S = K_a C^{1/n}$$

where S = adsorbed concentration (mg kg^{-1}), C = the equilibrium solution concentration (mg L^{-1}) after adsorption equilibrium, 1/n = Freundlich equilibrium constant.

The relationship between the organic content and the adsorption percentage was determined by:

$$K_{oc} = (K_a / \% OM) \times 100$$

where K_{oc} = Freundlich OM distribution coefficients.

Desorption study

Desorption was determined on the same samples used for adsorption. After the supernatant obtained by centrifugation for adsorption was removed, 10 mL of 0.01 M $CaCl_2$ was added to the same centrifuged cell. The mixture was then shaken and centrifuged as described above. A 1 mL aliquot was removed and counted at the end of a 24 h equilibration period. The soil (300 mg) was air-dried (at 25°C, 48 h) and combusted using the biological oxidizer and the carbon dioxide released was collected and radioassayed using LSC.

Mobility study

Ninety PVC tubes, 2.5 cm diameter and 25 cm long, were cut at 10, 20 and 25 cm from the top to produce three smaller tubes, which were reassembled to recreate the whole column. Each column was packed carefully with each soil type individually. About 100 mL distilled water was passed through each column in order to compact and stabilize the soils. A flask was placed at the bottom of each column to collect the leachate. The column was arranged in the greenhouse under natural conditions.

Forty eight hours later, 2 mL of either 0.1, 0.5, 1, 2 or 5 mg L^{-1} of metsulfuron-methyl (spiked with 0.1172 mCi labelled metsulfuron-methyl) was treated onto the soil column. Then, 98.1 mL distilled water (equivalent to 200 mm rainfall) was passed through the column. It should be noted that an average of annual rainfall in Malaysia ranging from 2000 to 2300 mm**.** The flow rate was adjusted to 0.05 mL min^{-1}. The leachate was collected after 48 h. A 1 mL aliquot of each column was radioassayed as before.

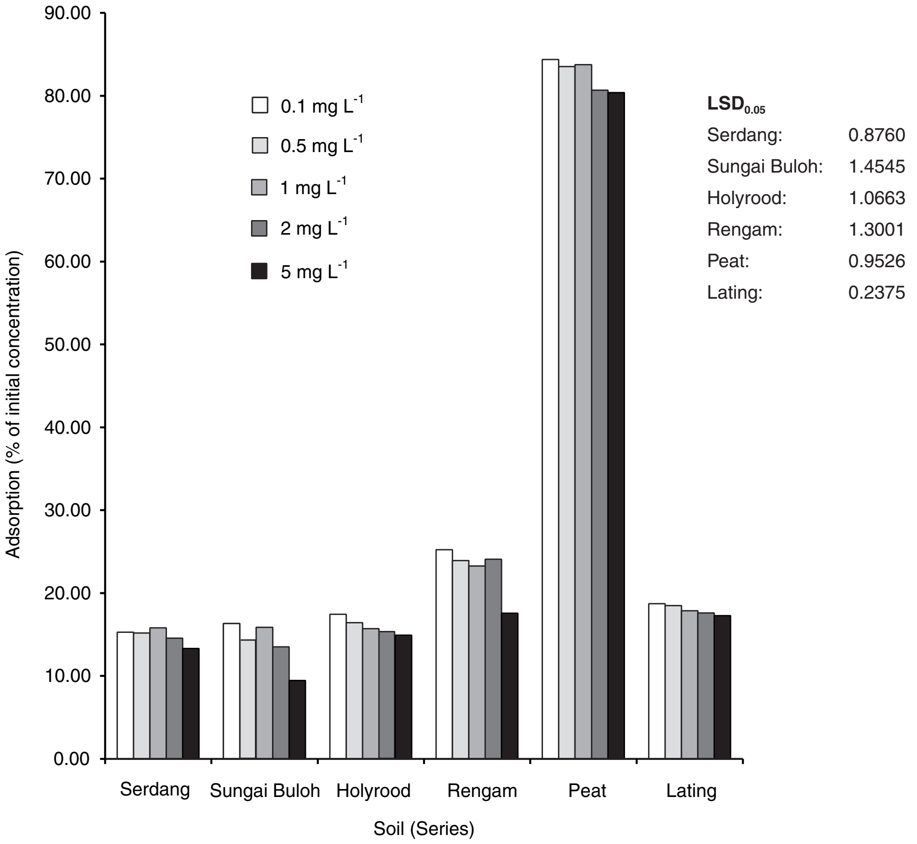

Figure 1. Percentage of metsulfuron-methyl adsorbed onto six Malaysian agricultural soils.

The columns were separated into the units indicated above, the soils from each segment were combusted using the biological oxidizer, and the carbon dioxide released was collected and radioassayed as described previously.

All experiments were conducted in three replications. Data were subjected to an analysis of variance and means were compared by the LSD test at 5% level of significance.

Results and discussion

Adsorption

The greatest amount of metsulfuron-methyl was adsorbed by the peat soil followed by soils from the Rengam Series, Lating Series, Holyrood Series, Serdang Series and the lowest percentage adsorption was observed in the Sungai Buloh Series soil. In general the percentage adsorption was lower at the higher concentrations of metsulfuron-methyl (Figure 1). For instance, in peat soil the adsorption at 0.1 mg L^{-1} metsulfuron-methyl was 85%, while it was reduced to 80.5% of the initial concentration at 5 mg L^{-1}. Similarly, at 5 mg L^{-1} of metsulfuron-methyl the reduction in the adsorption into the Rengam series soil was reduced by 10% as compared to the 0.1 mg L^{-1} concentration. This may due to the fact that most of the herbicide molecules were occupying the adsorption sites at higher concentrations.

The percentage adsorption of metsulfuron-methyl was positively correlated with organic content (r = 0.9997), but negatively correlated with clay (r = -0.23) and silt (r = - 0.26) content. Soils used in the study had a narrow range of soil pH values (from 3.62 to 4.23), therefore it is difficult to show the correlation of adsorption with soil pH. This study clearly showed that organic carbon is more important than any other soil fraction for adsorption of metsulfuron-methyl. Walker *et al.* (1989) also reported the adsorption of metsulfuron-methyl to be significantly correlated with soil organic matter. A similar pattern of absorption of other sulfonylurea herbicides in soil with higher organic matter content has been found by other researchers (Mersie and Foy 1986, Ismail and Kalithasan 1997).

Metsulfuron-methyl is a weak acid with pKa of 3.3 (Beyer *et al.* 1988, Walker *et al.* 1989). This moderate affinity for OM and the relative low adsorption to clay are similar to results for other acidic pesticides (Carringer and Weber 1974). It is known that the herbicide is largely anionic in soils at high pH and are consequently only weakly adsorbed (Walker *et al.* 1989). However, the pH of all the soils studied was less than 4.23. This suggests that pH is not the major factor in differentiating the adsorption rate of the six soil types studied.

The higher K_a value observed for the peat soil suggests that a greater adsorption of metsulfuron-methyl to that soil, which is attributed mainly to the high OM (75%) of the soil. Whilst, the lower K_a observed for Sungai Buloh series is attributed to the low OM (4.69%). Sarmah *et al.* (1998) has shown that the sorption coefficient of metsulfuron-methyl in four soils with pH values greater than 5.6 were lower than our results. However, in acidic soils with pH lower than 4.23, such as in our study, the sorption coefficient was higher as expected than those reported by Sarmah *et al.* (1998). The results clearly showed that soils pH effects the sorption coefficient of metsulfuron-methyl. The sorption coefficient values generally decreased as the soil pH increased (Cranmer *et al.* 1999). However, it should be noted that the sorption of metsulfuron-methyl is strongly influenced by soil temperature, clay content, and particularly soil OM. Therefore, direct comparison with those data reported by Sarmah *et al.* (1998) are not feasible as the result might be affected by these variable factors of different locality.

The Freundlich adsorption constant, 1/n, represents the degree of non-linearity of the adsorption isotherm. The 1/n for all test soils was less than 1 indicating that the relative adsorption decreased with increasing solution concentration (Rhodes *et al*. 1970) as adsorptive sites became occupied. A similar observation was reported by Grover (1973).

Desorption

Figure 2 showed the percentage desorption of the sorbed metsulfuron-methyl in the six soils studied. The amount desorbed from the peat soil was less as compared to the other soils. In contrast, more residue was released from the sandy soil (e.g. Holyrood) when treated at 5 mg L^{-1}.

Table 2 showed the K_d of metsulfuron-methyl in the six soils. The greater K_d value for the peat soil indicated the low desorption process or in other words greater binding capacity of the soil. K_d was positively correlated to the organic content, but negatively correlated to other physico-chemical properties.

The 1/n of the Freundlich desorption equilibrium for all soils except the Rengam soil series was less than 1, which indicated that the desorption percentages were positively correlated with the total absorbed. However, as for Rengam Series, the percentage desorption of the metsulfuron-methyl was negatively correlated with the total absorbed.

The K_d desorption/adsorption ratio was 1.88 and 1.83 for Lating and peat soil, respectively. K_d desorption/adsorption ratio for metsulfuron-methyl in peat and Lating series soils proved its stronger tendency for adsorption. The higher K_d desorption/adsorption ratio for trifluralin is further evidence of its stronger tendency for adsorption, and suggests a low leaching potential (Kim and Feagley 1998). This could also explain the low level of leaching of metsulfuron-methyl in the two soils.

Mobility

Figure 3 showed the mobility of metsulfuron-methyl in the six Malaysian oil palm plantation soils. There was a clear indication that there was a reduction in the extent of leaching of the herbicide with increasing OM content. In the peat soil, a high amount of metsulfuron-methyl was detected in the top layer when applied at 0.1 mg L^{-1}. A small amount of the residue could be detected in the leachate of all the soil series. On the other hand, more metsulfuron-methyl residue was detected in the leachate of the sandy soils such as in the Serdang series soils. A similar pattern

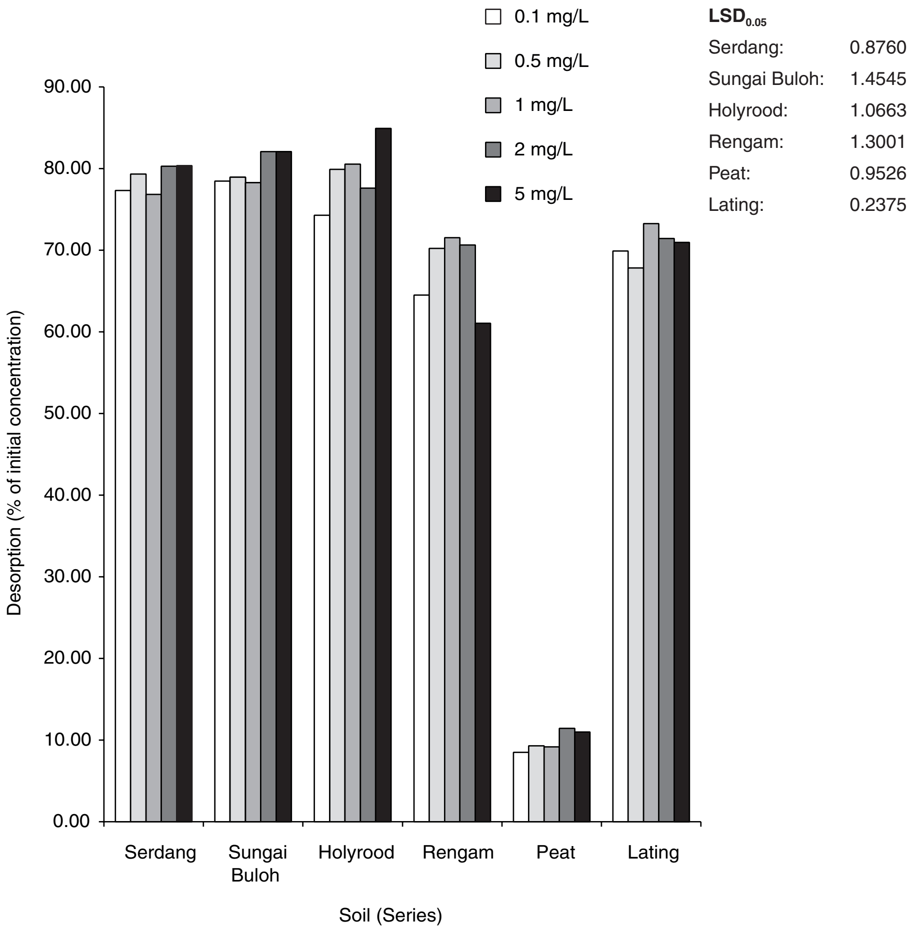

Figure 2. Percentage of metsulfuron-methyl desorbed from six Malaysian agricultural soils.

Table 2. Freundlich Adsorption (K_{ads}) and Desorption (K_{des}) Distribution Coefficients of metsulfuron-methyl in six Malaysian agricultural soils.

Parameter ($L\ kg^{-1}$)	Soil (Series)						$LSD_{0.05}$
	Serdang	Sungai Buloh	Holyrood	Rengam	Peat	Lating	
K_{ads}	0.86	0.76	0.94	1.41	20.67	1.09	0.15
$1/n_{ads}$	0.96	0.86	0.95	0.91	0.93	0.97	0.03
K_{des}	1.32	1.22	1.21	2.39	37.84	2.04	0.08
$1/_{ndes}$	0.95	0.93	0.87	1.01	0.92	0.97	0.02
K_{ads}/K_{des}	1.53	1.60	1.29	1.69	1.83	1.88	

of mobility had been observed when the soil was treated with 5 mg L^{-1}. A considerable amount of the residue was detected in the 10–20 cm layer of the Sungai Buloh series soils when soil was treated at 5 mg L^{-1} of metsulfuron-methyl. In peat soil, however, a higher percentage of metsulfuron-methyl residues was detected in the 0–10 cm zone when the soil was treated at 5 mg L^{-1}. When the soil was treated with 5 mg L^{-1}, a significant amount of metsulfuron-methyl residue was detected in the leachate of the Serdang series, Holyrood series and Rengam series soils. Low OM in these soils caused lower adsorption to the soil particles and consequently more residue moved downward.

K_{oc} values of metsulfuron-methyl in the six soils were less than 50 L kg^{-1} (unpublished) which is considered very mobile following the classification of McCall *et al*. (1980). This result is in line with the previous reports by Ismail and Kalithasan (1997) and Rahman *et al*. (1997). The weak binding of metsulfuron-methyl to soils indicated by its significant desorption from the soils contributed to the high mobility in the soil column especially in sandy soils. Therefore this could explain the existence of the residue in all of the soils studied especially when applied at higher concentrations.

The results clearly demonstrated that metsulfuron-methyl was absorbed more in soil containing high amount of OM as seen in the peat soil. The existence of the residue in the leachate could be due to weak adsorption to the soil particles in sandy soils. Acidic herbicides, such as metsulfuron-methyl are adsorbed in moderate amounts on OM and relatively low amounts on clay. Therefore, only a little amount of the residue could leach downward in the column. Further studies on the behaviour of this pesticide need to be carried out to determine its potential to contaminate underground water.

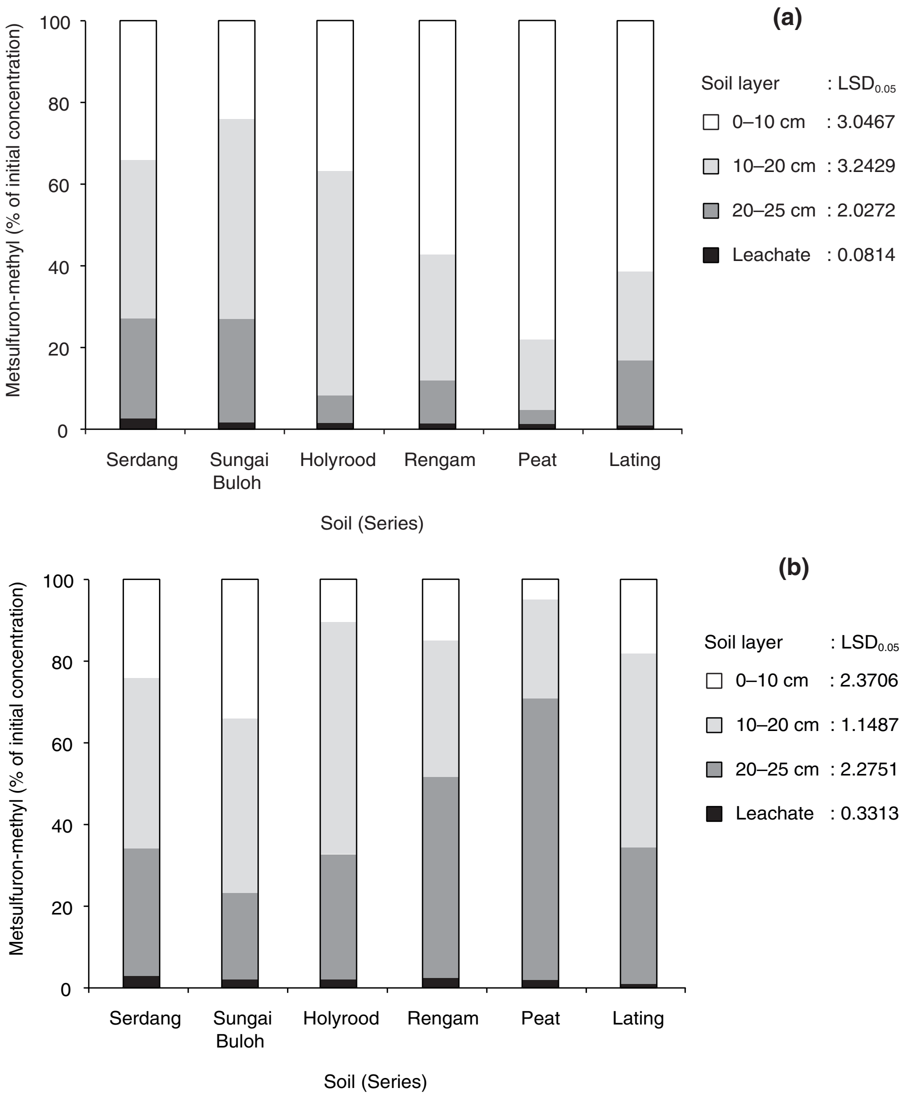

Figure 3. Mobility of metsulfuron-methyl in six Malaysian agricultural soils (a) 0.1 mg L^{-1}, (b) 0.5 mg L^{-1} metsulfuron-methyl.

Acknowledgement
This work was supported by research grant IRPA 08-02-02-0046 from the Ministry of Science, Technology and Environment of Malaysia.

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