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Adsorption, Desorption, and Mobility of Metsulfuron Methyl in Malaysian Agricultural Soils

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The sulfonylurea herbicide, metsulfuron methyl (methyl 2-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]-aminosulphonyl]-benzoate) is a broad spectrum herbicide used against a wide range of broadleaf weeds as well as some grasses in Malaysia. The widespread use of this chemical has given rise to concerns over its potential to contaminate the environment. Adsorption processes in soil play a paramount role in all physical processes affecting the residue behaviour of pesticides in the agroenvironment (Scheunert 1993). By retarding the flow of pesticides, adsorption influences the rate and degree of other fate process of pesticides in soil (Sabatini 1990). The adsorption (Walker and Exposito 1998), leaching behaviour (Gunther et al. 1993; Walker and Welch 1989), biodegradation (James et al. 1995; Walker et al. 1989) and chemical degradation (Pons and Barriuso 1998; Hemmamda et al. 1994) of metsulfuron methyl have been well studied in temperate climates. Soils under tropical conditions may differ significantly in terms of physicochemical and biological properties from soil types commonly found in the temperate zone. There is little information available on the fate and behaviour of metsulfuron methyl in the tropical environment. The objective of the present study was to investigate the adsorption-desorption and leaching behaviour of metsulfuron methyl in selected Malaysian agricultural soils in order to provide data to assess the potential risk of metsulfuron methyl pollution of the environment including groundwater.

MATERIALS AND METHODS

The commercial preparation of metsulfuron methyl (Du Pont Agrochemicals, 20% a.i) was used in the present study. Analytical-grade metsulfuron methyl (Du Pont Agrochemicals, 99 % purity) was used to prepare the calibration graph used in the quantification of the chemical by HPLC. Soil from the *Segamat* series, representing plantation soil was taken from a research station of the Ministry of Agriculture Malaysia at the depth of 0-25 cm. Soil from the *Penor* series, which was used to prepare soils of varying organic matter content, was also supplied by the Ministry of Agriculture. The soils were air dried overnight and passed through 2mm sieve. Sub-samples of freshly collected soils were dried at 110°C for 24 hrs to determine initial moisture content. Particle size distribution was determined by the pipette method (Lim 1975), while organic carbon content was

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estimated using the Walkley and Black method (Lim 1975). The cationic exchange capacity (CEC) was determined using 1M ammonium acetate (Lim 1975). Soil pH was determined using a glass electrode in a 1:2.5 soil to water ratio. Removal of organic matter from the soil was performed by oxidation with hydrogen peroxide until almost all the organic matter was eliminated (Camazano and Martin 1988). The physicochemical properties of the soils are given in Table 1.

Table 1. Selected physicochemical properties of *Segamat* and *Penor* soils

Soil property	*Segamat* soil	*Penor* soil
pH	4.23	3.64
Moisture (%)	18.07	67.38
Organic matter (%)	2.77	33.80
Organic carbon (%)	1.61	19.61
CEC (cmol/kg soil)	5.68	23.57
Silt (%)	7.83	29.77
Clay (%)	79.09	37.09
Sand (%)	13.08	33.14
Texture	clay	clay loam

In addition to measuring the adsorption of metsulfuron methyl in the *Segamat* soil, mixtures of the *Segamat* and *Penor* soils were prepared at different ratios to provide sets of soil with organic matter content ranging from 33.8% to 0.09% (pH ranging from 3.63 to 4.23). The adsorption rates were determined as follows: Triplicate samples of the air-dried soils (5 g) were shaken with a solution of the herbicide in 0.02 M calcium chloride (10 mL) at concentrations of 0.05, 1, 2, 4, 6, 8 and 10.5 $\mu g\ mL^{-1}$. The samples were shaken on an orbital shaker for 24 h, allowed to stand and then centrifuged. The concentrations of the herbicide in the clear supernatant were determined by HPLC. The effect of pH on adsorption of the herbicide was determined using *Segamat* soil to which was added lime resulting in soils of different pHs, ranging from 4.3 to 7.8.

Desorption was measured on soil samples equilibrated with initial concentrations of 0.05, 4.0 and 10.5 $\mu g\ mL^{-1}$ (Reddy et al. 1995). At the end of the equilibration and centrifugation steps described above, desorption was induced by replacement of the supernatant with herbicide-free calcium chloride solution. The samples were then shaken for 9 h, centrifuged and sub-samples of the supernatant analysed for the herbicide. The procedure was repeated until the herbicide was no longer detected in the supernatant.

To assess the effect of simulated rainfall on the mobility of metsulfuron methyl, the method developed by Walker et al. (1996) was adopted. A PVC column (30 cm long x 11 cm diameter) was carefully filled with soil to a depth of 20 cm. The bottom ring of the column was filled with sand. Once the column has settled, 5 cm of soil treated with metsulfuron methyl corresponding to 75 g per hectare was introduced on top of the soil column. Five hours after adding the treated soil, 44.8 mL of distilled water, simulating 211.6 mm rainfall (average rainfall per year during the period of study) was introduced. This was repeated daily for 10 days. The moisture level of the soil was maintained at 50 % field capacity. On day 10, the distribution of metsulfuron methyl in each 5 cm soil segments was analysed. Triplicate soil samples were extracted with methanol and water (80:20 by volume) containing 0.5 % (v/v) orthophosphoric acid by shaking for one hour on a shaker. The soil was allowed to settle and the herbicide concentration in the clear supernatant was determined by HPLC.

A Gilson HPLC was used to analyse metsulfuron methyl. The column used was Jones Genesis C18 column (15 cm x 4.6 mm) and the mobile phase was acetonitrile: water: orthophosphoric acid (60: 40: 0.25 by volume) at a flow rate of 1.0 mL min^{-1}. Detection was at 242 nm. The retention time of the herbicide was 2.81 min.

RESULTS AND DISCUSSION

Solutions of metsulfuron methyl in calcium chloride subjected to the equilibration process without the soil resulted in no significant loss of the chemical. The extraction procedure of the chemical from soil was found to be efficient as indicated by the recoveries from fortified samples of soil (0.5, 4.5, 10.0 μg mL^{-1}) which were 90.2 %, 93.7% and 92.3% respectively. The corresponding standard deviations were 0.04, 0.06 and 0.06.

The preparation of mixtures of *Segamat* soil and *Penor* soil in the present study provided a range of soils of varying organic matter content. The *Penor* soil was chosen for this purpose as it has high organic matter content (Table 1). Such a practice is common among local farmers to improve soil fertility. In general the adsorption isotherms of soils with varying organic matter content corresponded to the S type (sigmoid) according to the classification of Giles et al. (1960) indicating a low herbicide-soil affinity at low herbicide concentration. The initial slope of the isotherm, which is a function of soil organic matter content, was noted to be steeper for soils with high organic matter content. The adsorption isotherms of metsulfuron methyl in all the soils fitted the Freundlich adsorption equation, $C_s = K_f C_e^{1/n}$ with r^2 values ≥0.98, where C_s is the amount of herbicide adsorbed (μg g^{-1}), C_e is the equilibrium concentration (μg mL^{-1}) and K_f and n are constants determined from the experimental values of C_s and C_e by applying the linearized form of the Freundlich equation. K_d, the distribution coefficient was also obtained. This coefficient is defined as the ratio of herbicide concentration in the soil and herbicide concentration in solution. K_d can also be expressed as K_{oc} ($K_{oc} = K_d/\%OC \times 100$). The values obtained for the constants mentioned above are given in Table 2.

The results agreed with those of Walker et al (1989) and Walker and Exposito (1998) who also observed Freundlich adsorption isotherms for metsulfuron methyl. However different K_d values were observed attributed to differences in organic matter content and pH. Hence in the study conducted by Walker et al

(1989) a K_d value of 0.132 was obtained for a soil with an organic matter content of 2.01 % and pH of 5.8. The low sorption in the latter study was thought to be more a function of soil pH rather than the differences in the organic matter content.

Table 2. Percent organic matter (OM), K_{oc}, Distribution coefficient (K_d) and Freundlich constants (K_f and n) for various soil samples

Soil	%OM	K_{oc}	K_d	r^2	K_f	n	r^2
Soil a	33.8	194.79	38.18	0.99	38.73	0.99	0.99
Soil b	27.4	137.76	21.89	0.99	23.16	0.93	0.99
Soil c	16.16	169.90	15.92	0.99	16.40	0.85	0.99
Soil d	6.15	196.34	6.99	0.99	7.51	0.85	0.99
Soil e	2.77	345.34	5.56	0.98	5.36	1.16	0.98
Soil f	0.09	1200.00	0.60	0.99	0.49	1.19	0.99

(a) *Penor*, (b) *Penor: Segamat*, 2:1, (c) *Penor: Segamat*, 1:1, (d) *Penor: Segamat*, 1:10, (e) *Segamat* and (f) *Segamat* (oxidized).

Soils with high organic matter content (soils a, b and c) had high K_d and K_f values. A close relationship between K_d and K_f values was noted with n approximating 1.0. For most pesticides, organic matter is undoubtedly one of the major factors, which determine the extent of their sorption in soils (Andreux et al. 1993; Torrents et al. 1997). The results of the present study agreed with the results obtained from an investigation by Walker et al (1989), who observed significant positive correlations between organic matter content of soils with the extent of adsorption of metsulfuron methyl. Working with another sulphonylurea herbicide, chlorsulfuron, Borggaard and Streibig (1989) also reported a positive correlation between chlorsulfuron sorption and organic matter content.

Previous studies have shown that the behaviour of metsulfuron methyl, including adsorption is dependent on soil pH. Hence, as a weak acid with a pKa of 3.3, metsulfuron methyl is present in the ionic form in neutral and alkaline soil solutions. To determine the effect of soil pH on adsorption, the pH of the *Segamat* soil was adjusted by the addition of lime. As can be seen in Figure 1 increase in soil pH resulted in decreased adsorption. A negative relationship between sorption of sulfonylurea herbicides and soil pH has also been observed in previous studies (Mersie and Foy 1986; Walker et al. 1989; Walker and Welch 1989).

Table 3 shows the desorption of the adsorbed herbicide in the *Segamat* soil. The strong binding of metsulfuron methyl was indicated by the weak desorption of the herbicide. Only 18.7 % of the adsorbed metsulfuron methyl was found to have undergone desorption in the present study. This is much lower than the desorption of chlorimuron ethyl (54 to 65%) reported by Reddy et al (1995). In addition to organic matter content, the strong binding observed in the present study was attributed to the high content of clay in the *Segamat* soil as the high

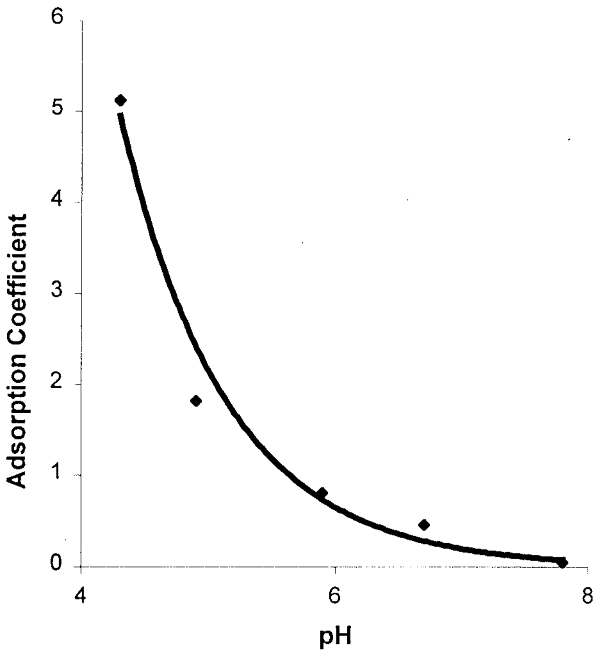

Figure 1. Influence of pH on the adsorption of metsulfuron methyl

surface area of clay particles facilitates adsorption which is essentially a surface phenomenon (Nyle, 1984).

Leaching of herbicides through the soil colummn is important to determine their efficacy as well as their potential for crop damage and environmental pollution (Mersie and Foy, 1986). Sulfonylureas are highly soluble in water, and if sorption in soil is relatively low, they are expected to exhibit considerable mobility in soils. In the present study, an exposure to a total of 211.6 mm simulated rainfall over a 10 day period following the application of metsulfuron methyl at a field application rate of 75 g/hectare in the *Segamat* soil, resulted in the leaching of the herbicide to up to 15 cm of the soil column. Much of the

Table 3. Desorption of metsulfuron methyl in *Segamat* soil

Desorption process	Amount desorbed (% of adsorbed)	K_{des}
1	7.7	11.9
2	6.1	14.1
3	3.3	24.6
4	1.6	50.3
5	not detected	-

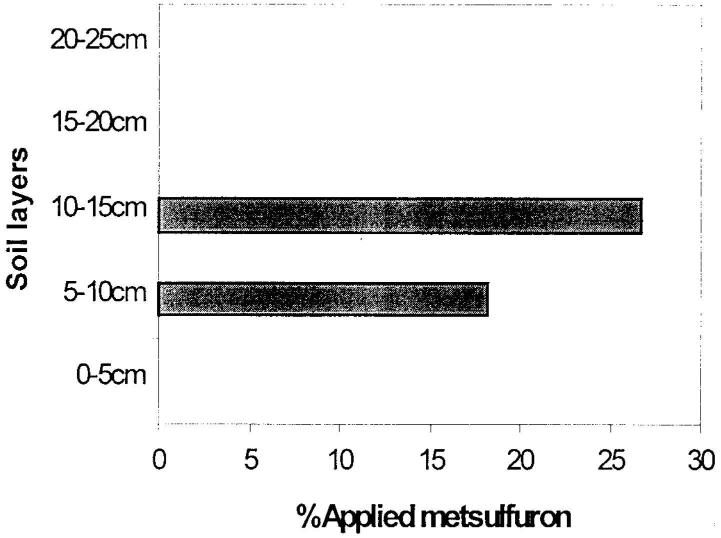

Figure 2. Leaching of metsulfuron methyl in *Segamat* soil

chemical was found in the 10-15 cm zone of the packed column (Figure 2). 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.

These results were in agreement with those observed by Ismail and Kalithasan (1997) who demonstrated the mobility of metsulfuron methyl using a bioassay technique on tropical soils with organic matter content of 3.44 % and 0.68 % respectively. Phytotoxicity was detected at 5-15 cm and 20-25 cm zone for the two soils when rainfall was simulated at 175 mm daily for 16 days. Walker et al, 1989 reported that the detection of phytotoxicity of metsulfuron methyl, as with other sulfonylurea herbicides in soil decreases with increasing soil organic matter content. Other studies also showed an inverse relationship between the bioactivity of sulfonylurea herbicide such as chlorsulfuron, and the content of organic matter in soil (Mersie and Foy 1986; Oppong and Sagar 1992).

Results obtained in the present study illustrated the influences of organic matter content and soil pH on the adsorption of metsulfuron methyl in the *Segamat* soil, a series of soil commonly found in plantations in Malaysia. It was observed that the influence of organic matter content and soil pH were consistent with reports on soils from temperate countries. It was also noted that the relatively low pH, high organic matter content and high clay content of the *Segamat* soil resulted in limited leaching of the chemical.

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